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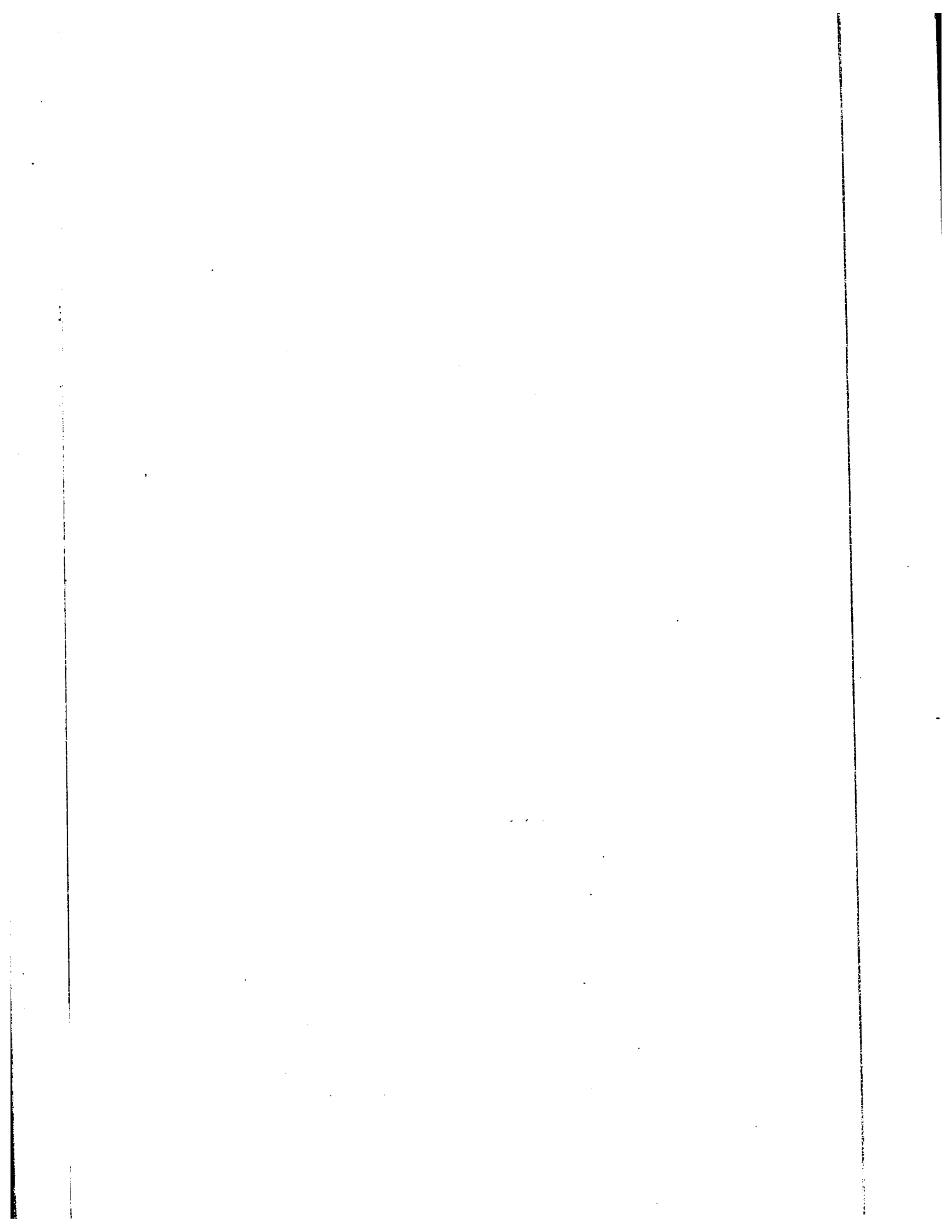
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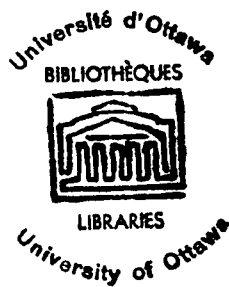
THE REACTIONS OF TRIPLET AND SINGLET METHYLENE

by

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A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy  
in the  
Department of Chemistry  
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1964



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PREFACE

This investigation was undertaken in order to compare and contrast the reactions of singlet methylene with those of triplet methylene. It was also an aim to define particular experimental conditions where the reactions actually change from those of singlet methylene to those of the triplet species. Investigations were also undertaken to shed some light on the energy transfer processes involved in these reactions. A theoretical treatment of the spin-orbit perturbation found in methylene has been included. Finally, it was hoped to establish conditions whereby the reactions of methylene could be distinguished from the (molecular) reactions of diazomethane, when these species react with olefins.

I wish to thank all those who have contributed their time, energy and encouragement to the undertaking and completion of this thesis. I would particularly like to thank the Ontario Research Foundation for their financial assistance.

This work could not have been attempted without the generous help of Professor R.F.W. Bader to whom I express my deepest thanks. His deep insight into problems encountered in this thesis was all the more remarkable in view of the unbounded enthusiasm which accompanied it.

Helpful discussions with Professor F.A.L. Anet and Dr. M. Back are deeply appreciated. A special word of gratitude is owed to Professors H.M. Frey and B.S. Rabinovitch and to Dr. D.W. Setser whose earlier works served as a framework for this thesis.

I am also grateful to Drs. F.P. Lossing and A.W. Tickner as

well as to Mr. Rudy Sander for mass spectrographic assistance.

I would like to dedicate this thesis to my parents without whose encouragement this work could not have been completed.

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ABSTRACT

The reactions of singlet and triplet methylene with butene-2 in the presence of inert gases (Ar, CF<sub>4</sub>, He, N<sub>2</sub> and Xe) have been studied. Singlet methylene (generated from the photolytic decomposition of diazomethane), upon colliding with a non-reactive gas readily undergoes a transition to the lower energy triplet methylene. At low pressures of inert gas the reactions are due to singlet, while in high pressure regions triplet methylene is the reactant. Plots of product yield vs. inert gas pressure show distinct trends in these pressure regions. Triplet methylene makes its appearance known at an inert gas-butene ratio of about 550, whereupon distinct inflections of pressure dependent curves occur. Cis-pentene-2 and 2-methylbutene-2 are formed by singlet methylene insertion in C-H bonds. 3-methylbutene-1 and trans-pentene-2 are products of the triplet reaction, but appear in the singlet region as well. Cis- and trans- 1,2-dimethylcyclopropane are unequivocally shown to be products of triplet methylene addition to the double bond, while the cis-compound (only) is directly formed by singlet methylene addition across the double bond. Direct insertion by triplet methylene does not occur, nor does triplet methylene abstract hydrogen atoms, although triplet intermediates may do so intramolecularly.

Triplet methylene reacts with molecular oxygen much more rapidly than singlet methylene does.

Attempts to directly generate triplet methylene by mercury photosensitization of diazomethane was unsuccessful owing to direct

absorption of the resonance line by diazomethane.

It has been shown conclusively that the products formed result from methylene-butene reaction and not from diazomethane-butene reaction, although the products formed in either case are the same.

The thermal reaction (225°C) of diazomethane with cis-butene-2 in the presence of inert gas was studied. The products formed are due to a butene-diazomethane adduct, and not from free methylene reaction.

A theoretical treatment of the spin-orbit perturbation reveals that the spontaneous transition from the singlet to the triplet state of methylene occurs at a rate of  $2.2 \times 10^{13} \text{ sec.}^{-1}$ . The spin-orbit perturbation found in methylene has been calculated to be 130 small calories.

### INTRODUCTION

In recent years, the study of methylene chemistry has followed two paths. On one hand, the study of methylene reactions offers an inviting jumping-off point for the study of unimolecular decompositions, since methylene addition generally leads to molecules which have excess energy and subsequently decompose. On the other hand, a study of the reactions of methylene provides verification of the various theoretical treatments of the problem of singlet-triplet transitions in this molecule.

Previous to this investigation, there was no research done which allowed one to actually follow the progression from the purely singlet reactions of methylene to the purely triplet ones. Moreover, there has been some doubt as to whether several reactions previously attributed to free methylene actually occur, or if these reactions arise by quite different mechanisms.

The present investigation, then, was undertaken to clarify these points. Once the conditions favoring the production of singlet and triplet methylene have been established, it would be possible to determine which particular products arise from each of these species and then to comment on the mechanisms involved in their reactions.

Lastly, it was hoped that through a study of the various pressure dependencies of the singlet and triplet species of methylene, some insight would be gained into the mechanisms of energy transfer processes.

Review of previous work

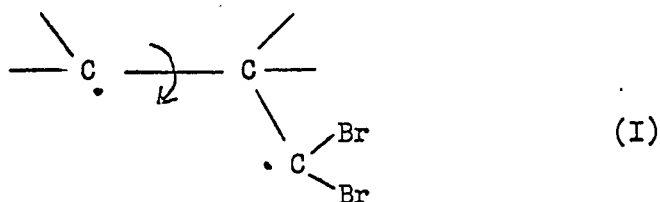
The suspected participation of carbenes (substances having divalent carbon atoms) as chemical intermediates is not new. Geuther originally suggested the possible occurrence of dichlorocarbene ( $C Cl_2$ ) in the alkaline hydrolysis of chloroform (1). Subsequently, Doering and Hoffman (2) presented the first structural evidence that dichlorocarbene was, in fact, an intermediate involved in the basic hydrolysis of chloroform. The next logical step in the study of carbene chemistry would then include research into mechanistic and stereochemical characteristics of this and related species. Doering and LaFlamme (3), investigating the mode of addition of dibromocarbene to olefins, found that cis addition occurred exclusively. In 1942, Meerwein et al (4) had photolyzed diazomethane in ether solvent, forming substituted ethers, although no unambiguous mechanism was proposed. Doering et al (5) investigated methylene insertion reactions in diazomethane-hydrocarbon solutions. The conclusion reached was that methylene must be classed as the most indiscriminate reagent known in organic chemistry<sup>1</sup> -- this statement made in view of the apparent disregard by  $CH_2$  for the type of CH bond attacked -- whether primary, secondary, tertiary, vinylic or allylic.

One of the earlier chemical indications that carbenes may involve low-lying triplets (i.e., unpaired non-bonding electrons) may be inferred from the work of Skell and Woodworth (6) in their discussion of possible intermediates in the reactions of dibromocarbene ( $CBr_2$ ) with olefinic double bonds. Subsequent work by these authors on the reactivity of diazomethane led to the conclusion that the "free" electrons in  $CH_2$

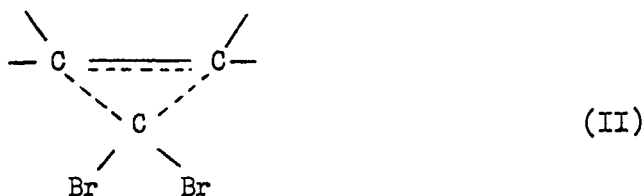
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<sup>1</sup> See however, reference (23)

were paired (i.e., in the singlet state) rather than unpaired; this conclusion followed from the stereospecific nature of the products found in the reaction between diazomethane and excess cis-butene, whether in the liquid or gas phase. On the basis of this work, Skell and Woodworth preferred the theory that dibromocarbene should also have its two electrons paired; in the case of dibromocarbene reacting with a carbon-carbon double bond, unpaired electrons would lead to an intermediate of the type



while paired "free" electrons would result in the stereospecific intermediate II



The fact that no cis-trans isomers are observed in the actual products does not preclude (I), since in order to observe geometrical isomers, the "unpaired" complex (I) should be long enough lived to allow rotation around the carbon-carbon bond. An example of a divalent carbon exhibiting free radical behavior (triplet state behavior) was introduced by Skell et al (7). Diphenylmethylene,  $(C_6H_5)_2 C$ , was one of the first compounds to yield no stereospecific products when reacted with olefins; however, in this and previous investigations, no mention is made of the possibility that the energy levels of these singlet and triplet states may be so close as to be actually interconvertible from one state to the other.

Up till this point, no mention has been made concerning the

possibility of "hot" addition products. Upon photolytically decomposing diazomethane (or ketene), one may suspect that the methylene so produced might have excess energy; reaction with an olefinic double bond would result in a complex which may have sufficient energy to undergo decomposition, or, at least, isomerization. While experiments were being conducted along lines establishing the nature of carbenes and methylene, research was being undertaken which had as its main purpose the subsequent unimolecular reactions of "hot" molecules formed by methylene or carbene reaction (8). Much of the work done up to this point involved investigations in the liquid phase or in the gas phase at high pressures. Under these conditions, cooling time for the hot intermediate may be short in comparison with the time needed for isomerization or decomposition. There are several examples in the literature wherein the isomerization of an excited adduct is competing with the collisional deactivation of this same adduct. For example, the vapor phase photolytic chlorination of methylcyclopropane occurs with the formation of many four-carbon chlorine compounds both chain and cyclic in character (9). In the liquid phase, however, only one isomer is formed. Here, it may be argued that if the complex can be quickly relieved of its excess energy (by collision with substrate, for example) it will not isomerize.

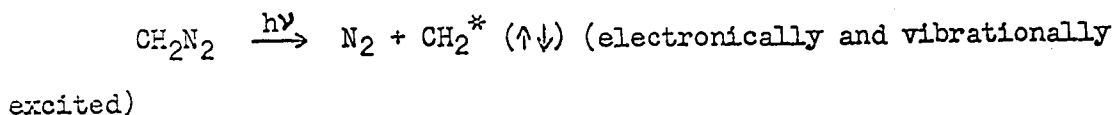
It is also noteworthy that in many of these isomerizations, along with geometrical (eg. cis-trans) isomerizations, structural isomerizations (eg. cyclic-chain) are also observed. Pyrolysis studies offer information concerning the relative rates of geometrical vs. structural isomerizations (10); these studies are a great aid in elucidating mechanisms, and reference will be made to them from time to time.

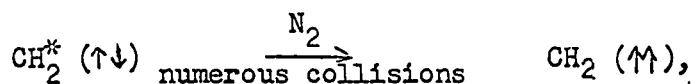
It was along lines such as these that Frey (11) investigated the reactions between methylene and olefins at lower pressures, where these isomerizations are important, thereby further developing theories of unimolecular reactions. Under the conditions followed, the primary step in the reaction of methylene with cis-butene-2 is the stereospecific formation of cis-1,2-dimethylcyclopropane (CDMC); however trans 1,2-dimethylcyclopropane (TDMC) is also found in the reaction products. This is taken as evidence that the primary step involves the formation of an excited cis 1,2-dimethylcyclopropane, CDMC\*, followed (unless deactivated) by an isomerization to the corresponding trans compound, TDMC. (This would be analogous to the case where pyrolysis of CDMC (10) results in equilibrium proportions of cis- and trans-DMC). Upon increasing the substrate pressure, these isomerizations (structural as well as geometrical) were repressed. The preponderance of CDMC (rather than equilibrium proportions of CDMC and TDMC) confirms the presence of singlet methylene rather than the triplet species.

The precursors of both singlet and triplet methylene have been ketene, diazomethane, and, more recently, diazirine (cyclo-diazomethane) (12). Methylene has been generated from these compounds by photolytic, thermal and photosensitized (13) procedures. Up until 1959, there was still much ambiguity concerning the electronic configurations (as well as the ground state) of methylene produced by these methods. Then, in an historic paper, Herzberg and Shoosmith (14) laid these doubts to rest. Under certain conditions, singlet methylene (formed by flash photolyzing diazomethane) can be induced to undergo a singlet to triplet transition, indicating that the true ground state of methylene is a

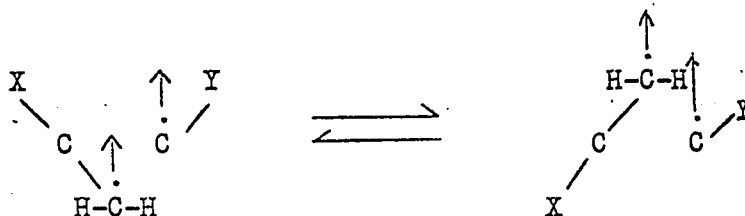
triplet, i.e., the "free" electrons are unpaired. The experimental conditions included having nitrogen present during the photolysis of undeuterated, monodeuterated and dideuterated diazomethane, the partial pressures being 2 mm nitrogen / 0.02 mm diazomethane (100:1) and higher. The spectrographic results were then correlated with various possible structures of C,H,H of C,D,H and C,D,D. Line and band assignments for the bent configuration of methylene gave results which did not correspond to those actually observed in the spectra, although the linear, symmetrical configuration ( $^3\Sigma_g^-$ )<sup>1</sup> agreed quite well. In addition, an assignment of a triplet ground state was in agreement with some of the earlier molecular orbital predictions (15).

At this stage the only evidence for a triplet ground state of CH<sub>2</sub> was the spectroscopic work of Herzberg and Shoosmith. Skell and co-workers (6,7), previous to this time, had recognized the possibility of distinguishing singlet and triplet methylene by their different reactions with olefinic double bonds, but no evidence was cited to support the existence of triplet methylene. Anet, Bader and van der Auwera (16) recognized the possibility of inducing a singlet to triplet transition and actually using the different characteristic reactions of singlet and triplet methylene as proofs of their presence. Using conditions not unlike those used by Herzberg and Shoosmith, singlet methylene, originally formed by the photolytic decomposition of diazomethane, was caused to undergo collisions with an inert gas in order to arrive at the triplet state:

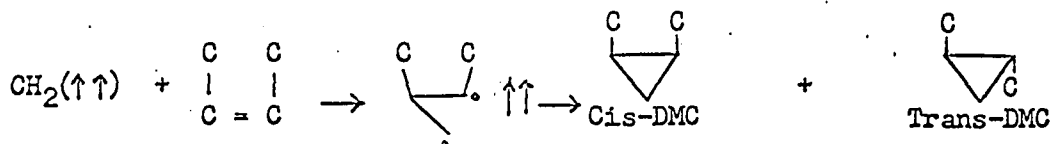
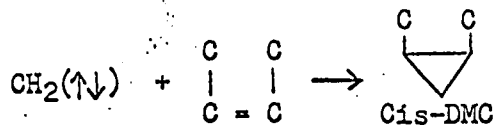




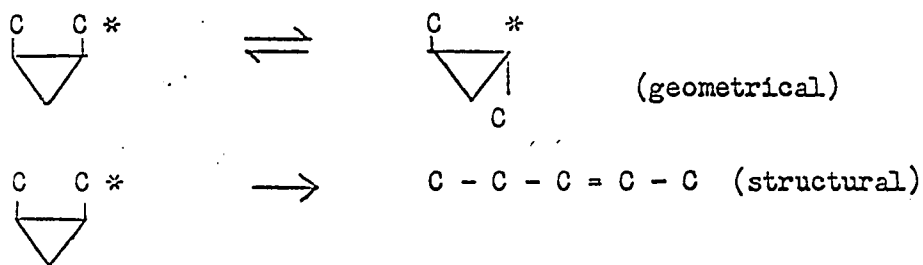
where ( $\uparrow\downarrow$ ) refers to paired and ( $\uparrow\uparrow$ ) to unpaired non-bonding electrons. Then, instead of photographing the spectrum, the methylene was reacted with cis-butene-2 and the characteristic reaction of triplet methylene was observed. This characteristic reaction is as follows: if triplet methylene adds across the double bond, the principle of spin conservation demands that the intermediate (adduct) be a triplet. This is possible only if the olefinic double bond dehybridizes into one  $\sigma$  bond and two unpaired  $p_{\Pi}$  electrons. If this is the case, a more unrestricted rotation about the carbon-carbon axis will occur:



If the substituents represented by X and Y are different (for example an H atom and a methyl group) this substance, upon reforming a double bond will exhibit geometrical (cis-trans) isomerism. This state of affairs would not occur in the case of singlet methylene, whose paired, non-bonding electrons would be expected to pair with both  $p_{\Pi}$  electrons simultaneously in the cis-butene, making geometrical isomerization improbable. Cis-butene-2 is a convenient substrate, since it is one of the simpler (gaseous) olefins which exhibits cis-trans isomerism. (Reactions of methylene with other gases have been studied (17, 18, 19, 20), but mostly in connection with unimolecular reaction theory). The difference in the reactions of the two methylene species with cis-butene-2 is summarized below:



That is, the triplet reacts non-stereospecifically to give mixtures of isomers (17, 18) while the singlet gives one (stereospecific) isomer only. In practice, however, things are not so simple. As mentioned earlier, a serious complication arises, since the dimethylcyclopropanes thus formed have excess energy, and unless collisionally de-energized will undergo geometrical isomerization (i.e., Cis-DMC isomerizes to give the trans-isomer) or structural isomerization (to pentenes or other olefinic compounds):



The original work of Anet et al has been criticized by Frey (33) on the grounds that the pressures used were not nearly high enough to eliminate the isomerizations of the initially formed dimethylcyclopropanes. Frey argued that Anet et al had not observed triplet methylene and that their observed lack of stereospecificity in the cyclopropanes was due entirely to the isomerization of the "hot" molecules.

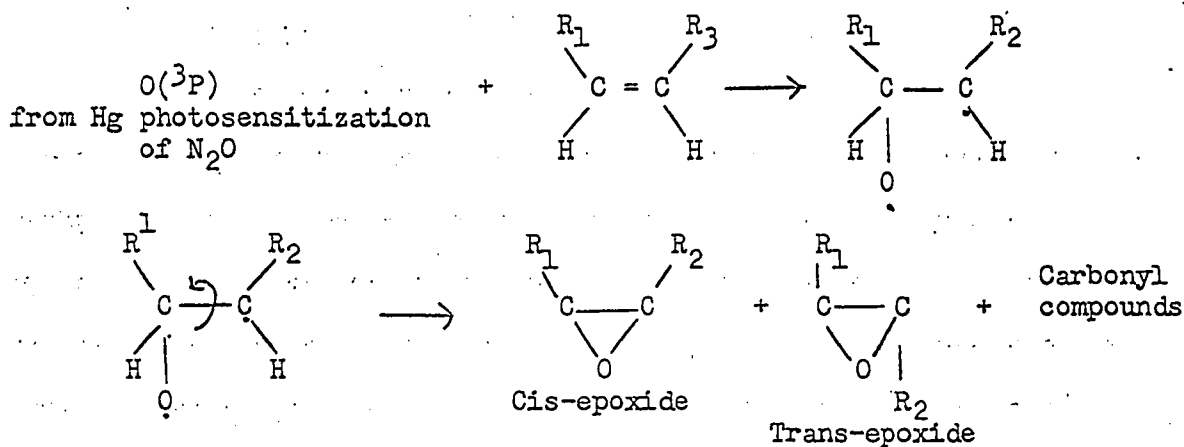
Since these isomerizations include bond breaking and rotations

of groups of atoms in excited molecules, it is easily seen why methylene reactions offer opportunities for the study of unimolecular reactions. When studying unimolecular reactions of this type it is often convenient to add inert gases and observe the changes brought about as a result. Whenever experiments are conducted along these lines, allowance must be made for the possible occurrence of both species of methylene, especially if inert bodies are present. This has not always been done in the past.

In order to unambiguously detect the presence of triplet methylene, it is important to work at high enough pressures of inert gas to avoid these types of isomerization. Alternatively, it is possible to produce triplet methylene directly by using photosensitizing reactions (13). In this case it would be possible to study the reactions of triplet methylene at low as well as high pressures.

The reactions of triplet and singlet methylene with carbon-carbon double bonds is quite analogous to the reactions of triplet and singlet oxygen atoms with the same substrate (22, 23). Whereas, with *cis*-butene-2 and triplet methylene, the reaction produces the geometrical isomers *cis*- and *trans*-1,2 dimethylcyclopropane,  $O(^3P)$  atoms react with the carbon-carbon double bond in typical diradical fashion, giving rise to geometrical isomers (*cis*- and *trans*- $\beta$ -butene oxide) as well as structural (chain) isomers, whereas with the singlet species,  $O(^1D)$ , only the *cis*-epoxide is found (i.e. stereospecific behavior). The triplet oxygen atoms may be directly prepared (precluding the need for collisions to bring about transitions from the singlet to the triplet state). In this regard these reactions closely resemble the reactions of triplet methylene prepared directly by photosensitization procedures. In addition to the reaction across the double bond, triplet oxygen atoms, when combined with *cis*-butene

also give fragmentation molecules and apparent rearrangement species in much the same way as methylene reactions do. This indicates that the adduct originally formed with butene and atomic oxygen is "hot" and will readily undergo isomerization and fragmentation. In short:



More recently, Gunning et al (24) have studied the reactions of singlet and triplet S atoms with respect to addition across olefinic double bonds, giving thiocyclopropanes. While the reactions of singlet and triplet S are akin to those of singlet and triplet O, a main difference is that adducts formed with S atoms are much less energy rich than those formed with O atoms; isomerizations with the S adducts are therefore much less prone to occur.

In addition to the study of the reactions of methylene (singlet and triplet) with olefinic double bonds, the reactions involving methylene insertion into C-H bonds are also of interest (6, 3). Triplet methylene reacts to give apparent C-H insertion products which may, however, arise through the rearrangement of an excited intermediate which does not involve a direct triplet methylene insertion into a carbon-hydrogen bond. It should be pointed out, that with sulfur atoms, direct insertion into carbon-hydrogen bonds does not appear to occur with the

triplet species,  $S(^3P)$  (25), nor is there any insertion into this bond with triplet oxygen atoms. The problem of determining if triplet  $CH_2$  directly inserts can be simplified if the researcher can choose at will the conditions under which the singlet species is present, or conditions which will bring about mainly the triplet. Moreover, working under experimental conditions where hot molecule isomerizations are repressed should aid in assigning a correct mechanism.

In this present work, various inert (non-reacting) gases were used to cool initially excited adducts (as well as to foster singlet-triplet transitions). In this respect, the addition of inert gas is typical of many studies of unimolecular reactions, the large majority of which do not involve the transfer of electronic energy. It was hoped that this aspect of the present work would offer some insight into the mode of energy transfer processes in these cooling reactions.

The reactions of methylene produced by the high temperature thermal decomposition of diazomethane are very similar to those of photo-lytically generated methylene. The thermolysis of diazomethane-olefin mixtures as done by Setser and Rabinovitch (26) offer a means of supplying varying amounts of energy to methylene molecules (by varying the temperature) thereby changing, in a known manner, the energies of the adducts formed in the primary process. Now that the heat of formation of methylene is well known (27), estimates of the energy content of "hot" cyclopropanes should be fairly accurate; activation energies and rate constants for the decomposition of the excited molecules formed, and other data can now be easily estimated.

It has been known in many cases, especially in the liquid phase (28) that diazomethane adds molecularly (not as  $CH_2$ ) to olefins,

giving nitrogen compounds having wide ranges of stability, while others decompose spontaneously to give the same compounds which would be expected from methylene addition. In view of this, further investigations were carried out with regards to the thermal reactions of diazomethane with butene-2.

Theoretical papers by Pedley (29), Walsh (15), and Jordan and Longuet-Higgins (30) all agree that methylene should be in a triplet ground-state (a near-linear configuration, with the two non-bonding electrons unpaired  $3\Sigma_g^-$ ), even though the methods used to arrive at this conclusion were quite dissimilar. Values were obtained for the heats of formation (29, 30) and are in agreement with electron impact studies (31) and ionization potential studies (32). However, no values for the rate constant involving the singlet to triplet transitions were given. More will be said along theoretical lines in a later section.

This present undertaking is an extension of the earlier work of Anet et al (16). In addition to resolving the criticisms of Frey (33) mentioned previously, it was also desired to assign relative efficiencies to the gases He, Ar, Xe, N<sub>2</sub> and CF<sub>4</sub> in effecting the singlet to triplet transition in methylene and in cooling the initially formed hot molecules. The experiment designed to answer these questions is the following: a fixed ratio of diazomethane to cis-butene-2 (about 2.5 to 1) was photolyzed in the presence of the inert gases whose pressures were varied from zero to approximately 850 torr. For any one inert gas the amount of trans-1,2-dimethylcyclopropane formed (expressed as a percentage of the total yield of dimethylcyclopropane) is plotted vs. pressure of the inert gas. This percentage yield should initially be high due to the isomerization of the hot cis- compound. As the pressure of inert gas is increased, the percent

of the trans-compound should decrease as the hot cis- 1,2-dimethylcyclopropane molecules are cooled by the inert gas before isomerizing. Eventually, at some pressure of inert gas the percent of the trans-compound will begin to increase as there will then be sufficient inert gas present to allow the methylene to reach its triplet ground state and give rise directly to the trans molecule. The graph of percent trans vs. the inert gas pressure should thus be "V"-shaped with the minimum in the curve indicating the pressure for the onset of the participation of triplet methylene in the reaction. The relative efficiencies of the various gases in bringing about the singlet to triplet transition will be reflected in the value of the pressure at the minimum of the curve and in the slope of the curve past this point. Their relative abilities in cooling the hot cis molecules will be determined by comparing the slopes of the initial decrease in the curves. Frey's criticism that pressures of approximately 2,000 mm Hg are necessary to quench the isomerization and hence detect the triplet participation can be checked immediately by noting the values of the pressure for the observed minima in the curves.

## EXPERIMENTAL

### Apparatus

The vacuum system used (Fig. 1) was capable of attaining pressures lower than  $10^{-5}$  torr. using a non-ballast rotary roughing pump (RP) in conjunction with a two-stage oil diffusion pump (DP) filled with Dow 704 silicone oil. Most runs were done in the range  $10^{-5}$  -  $10^{-4}$  torr., as measured by a Phillips-type cold cathode vacuum gauge (VG) (Consolidated Electroynamics Corporation, Rochester, N.Y.) which was calibrated for air by a MacLeod gauge on another apparatus.

The reaction vessel (RX<sub>1</sub>) was a 2 liter spherical pyrex bulb, having a condensing finger 6 cm wide and 6 cm deep.

Two Bourdon gauges (spoon type) were used for measuring the pressures of reactants and inert gases. One (B<sub>s</sub>) was an extremely sensitive (and delicate) model capable of measuring pressures of  $0.1 \pm .03$  mm Hg. The spoon envelope was connected to an air bleed of very small diameter as well as a glass backed mercury manometer (MAN 1). The pointer of this spoon gauge was drawn to an extremely fine tip and caused to travel against a very finely ruled background. The pointer was constructed so that parallax was minimal when viewed through a telescope placed 1 meter from the spoon. This sensitive spoon gauge was not used as a null instrument, but was calibrated by the following procedure. First, spoon and envelope were carefully evacuated. A minute quantity of nitrogen was next admitted to the spoon, causing deflection. The pointer reading was noted as was the corresponding pressure in the envelope (manometer). Air was slowly bled into the envelope and the manometric reading taken, with the pointer in the zero (null) position (nitrogen pressure in spoon equalling air pressure in

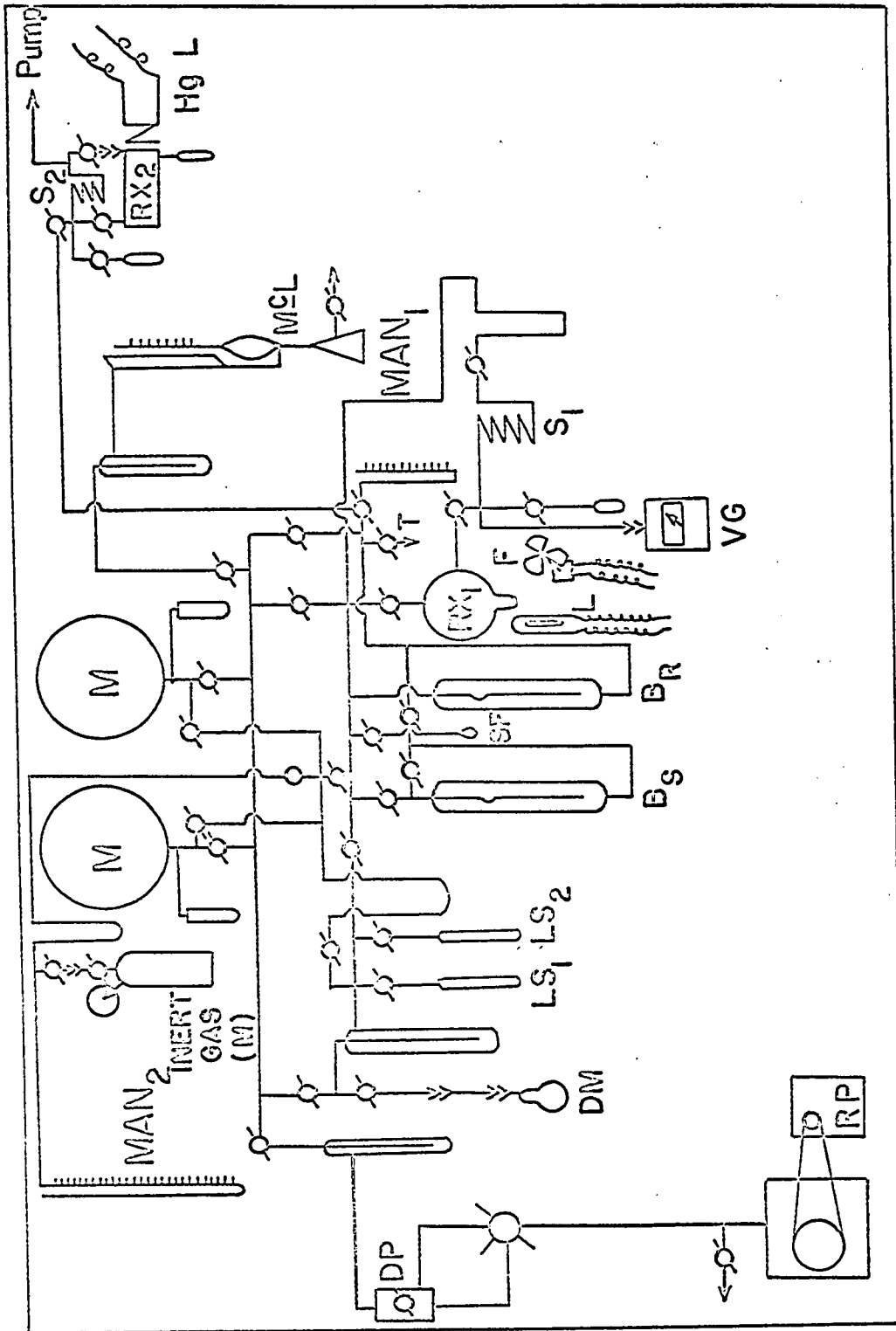


Figure 1 Schematic Diagram of Apparatus

envelope). The envelope was then pumped free of air in stages of about 0.5 mm Hg. and the pointer reading noted at each stage, together with the manometric reading. Plots of mm Hg (manometer) vs. pointer deflections were linear and highly reproducible. Three independent calibrations were done before actual reactant measurements were attempted. Sensitive spoons were re-calibrated from time to time ( $\sim 2$  month intervals) to check possible sensitivity changes brought about by ageing. These changes, if any, were negligible. Owing to the extreme delicacy of these gauges, several were inadvertently broken in the process of experiments, necessitating fabrication and calibration of new ones.

A second, much more robust, spoon ( $B_r$ ) was also incorporated into the system. This was used for measuring (high) pressures of inert gases, and was sensitive to about  $\pm 1$  mm., being used exclusively as a null point instrument (vs. air, as measured on a mercury manometer). Spoon gauges were used in order to minimize contamination of reactants with mercury vapor.

Lamp. A medium pressure mercury vapor lamp (G.E. H-4AB) was used in conjunction with a G.E. 245 volt, 2 amp autotransformer. The lamp (L) was placed 3 cm from the reaction bulb. The reaction bulb was cooled to ambient room temperature by means of a 7 inch fan (F) placed 9 cm from the reaction bulb ( $RX_1$ ). All photolytic reactions were done at room temperature which was  $25 \pm 5^\circ$  C for the vast majority of runs. Photolyses were carried out over an eight hour (automatically timed) irradiation period.

Thermal. Thermal experiments were carried out in a 3 liter spherical pyrex flask of shape similar to the vessel used in photolysis.

This vessel was well blackened on the outside to exclude stray light. It was attached (for filling with reactants) by means of a standard taper (T). In order to accommodate a reaction vessel of this size, a large oil bath of 20 liter capacity was used. This bath was well insulated and was wound with resistance wire; with 10 l of oil (Esstic 23, Esso) the temperature was kept constant at  $220 \pm 5^{\circ} \text{C}$  as measured by a thermometer. Due to the buoyancy exerted by the hot oil and the large volume of the reaction vessel, a metal jig was fabricated to support the vessel; jig and reaction vessel were then lowered into the bath and the insulated top affixed. While temperatures greater than  $220^{\circ} \text{C}$  could be reached, it was felt that this would be quite dangerous because of the nearness to the flashpoint of the oil. Heating of the reaction mixtures (butene-2, diazomethane and  $\text{N}_2$ ) lasted about  $4\frac{1}{2}$  hours.

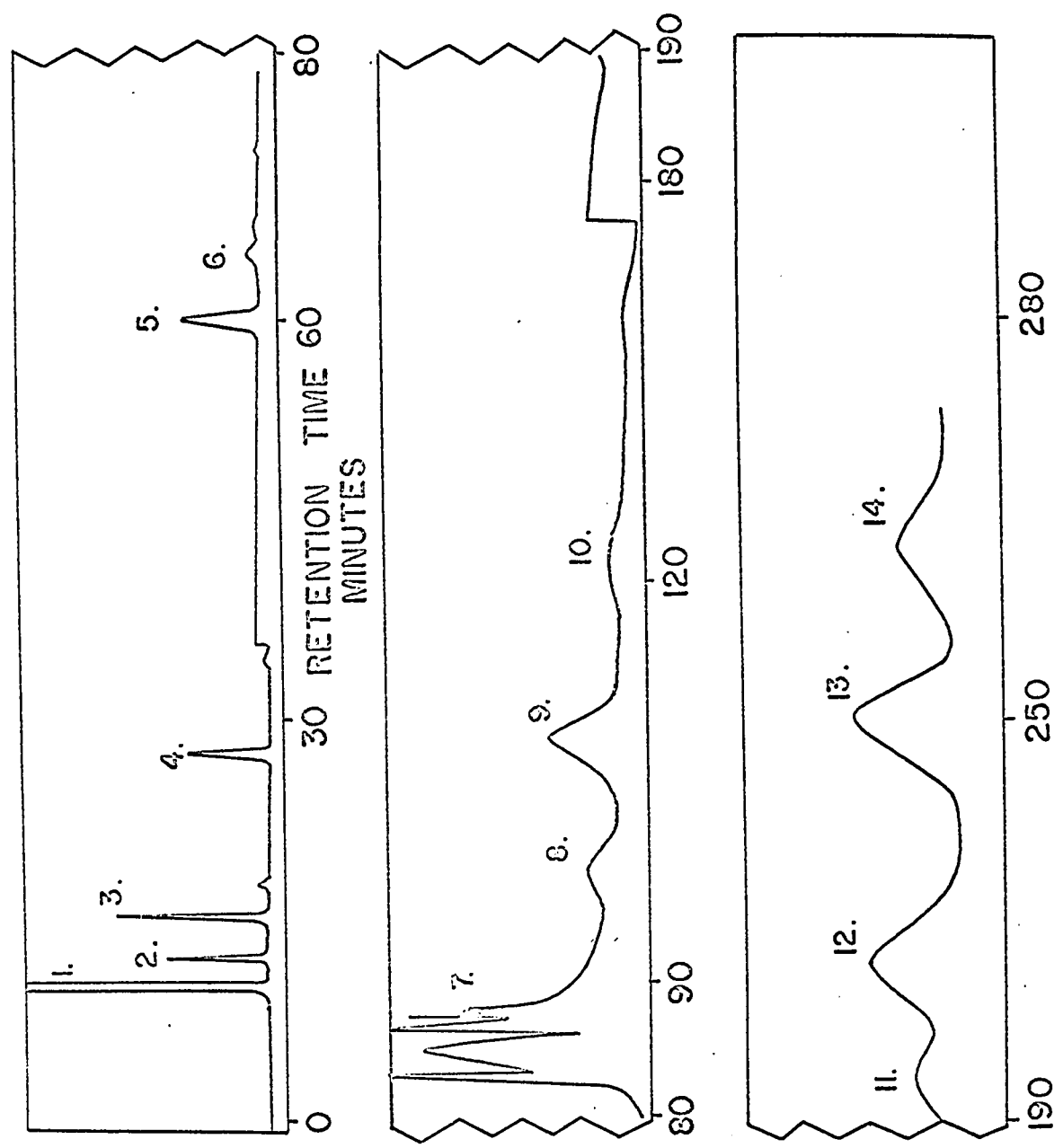
Analyses. Analyses of products were performed by gas-liquid phase chromatography (GLC) using thermistors for thermal conductivity measurements. The chromatographic instrument was a home-made model using a large number of parts from a Perkin-Elmer Model 154-C instrument. Columns used were 23% by weight 2, 5 hexanedione (acetyl-acetone) on 30-60 mesh Columnpax (Fisher Scientific) of 8 meter length and 0.83 cm inner diameter. This coiled column was kept in an ice bath, the temperature of which was about  $+3^{\circ} \text{C}$ . In series with this column was a Perkin-Elmer HX column (2 m x 0.83 cm i.d.) composed of a silver nitrate-propylene glycol solution supported on diatomaceous earth. This column (HX) was kept at room temperature. Helium (Linde Ltd.) was used as a carrier gas after being passed through a tube containing ascarite. The flow rate was maintained at 22 cc per min. at 12 psi inlet pressure. A gas sampling device was fitted to the apparatus which could accept the

reaction products in aliquots or in their entirety. Impulses from the detector were recorded on a Leeds and Northrup (0 - 1 mv / 0 - 5 mv) recorder, without automatic integration; chart speed was 1.28 cm/min. An example of a GLC obtained under the conditions outlined is shown in Fig. 2.

### Materials

Diazomethane. Diazomethane was prepared after the method of Arndt<sup>1</sup> and Amende (34) which involved dissolving 2.5 grams of N-nitrosomethylurea in an ice-cold mixture of 15 ml of decalin and 10 ml of water made basic with 10 grams of potassium hydroxide<sup>2</sup>, the reaction mixture stirred magnetically in an ice bath. After a five minute reaction time, the mixture was placed in an ungreased separatory funnel (moistened with decalin), allowed to stand (about 3 minutes) after which the water layer (lower portion) was discarded. The remaining liquid (clear, deep yellow), a solution of diazomethane in decalin, was allowed to drop slowly over potassium hydroxide pellets in a small (50 ml) erlenmeyer flask, after which the solution was allowed to stand (cork stoppered) in the dark at -10° C for two hours. After this drying period the decalin-diazomethane solution was poured into a 50 ml round bottom flask with a standard taper and attached to the vacuum line (DM). The solution thus prepared was stored at -196° C.

- 
1. Modified slightly by using decalin rather than diethyl ether.
  2. If sodium hydroxide is used instead of potassium hydroxide, the reaction mixture invariably froths, and in the majority of cases, explodes.



- 1. Air
- 2. Ethylene
- 3. Propylene
- 4. Unknown
- 5. Trans-Butene-2
- 6. Isobutene
- 7. Cis-Butene-2
- 8. 3-Methylbutene-1
- 9. Trans-1,2-dimethyl-cyclopropane
- 10. Methylchloride
- 11. Trans-Pentene-2
- 12. Cis-1,2-dimethyl-cyclopropane
- 13. Cis-Pentene-2
- 14. 2-Methylbutene-2

Figure 2 GLC Recorder Tracing of an Experimental Run.  
Flow Rate 22 cc per min. (He) at 12 psi Inlet Pressure

Cis-butene-2. Cis-butene-2 was obtained as a cylinder gas in lecture bottle lots from Matheson (Canada) Ltd., Whitby, Ontario. After degassing by alternately freezing (in liquid nitrogen) and warming (to room temperature), the cis-butene-2 was subjected to several trap to trap distillations at dry ice - acetone temperatures. This treatment resulted in cis-butene-2 having less than 0.4% trans-butene-2 and 0.1% isobutene impurities as shown by GLC.

Trans-butene-2. Trans-butene-2 was obtained from the same source and was given similar treatment. GLC analysis showed less than 0.6% cis and less than 0.2% isobutene impurities. Both butenes (cis and trans) were stored as liquids (LS<sub>1</sub>, LS<sub>2</sub>) at dry ice - acetone temperature.

Nitrogen. The nitrogen used was Matheson pre-purified grade specified to have less than 7 ppm oxygen impurity. Lecture bottles were used in conjunction with (specified) needle valves which were tested for air leakage previous to use. Nitrogen from Linde Ltd. specified not to contain more than 10 ppm oxygen as impurity was also used after the following precautions were taken to remove the oxygen--the nitrogen, after being obtained from the cylinder, was passed through a powdered copper-kieselguhr column (7 x 50 cm) capable of being heated to 400° C by means of a nichrome winding the length of the column. The column was attached to the vacuum line by means of a glass spiral (1 m length, when extended) which was immersed in liquid nitrogen when the column was in use. Reactions between diazomethane and butene-2 in the presence of nitrogen purified in this manner showed no detectable difference from the same reaction performed with the prepurified grade nitrogen used without purification. Hence, because of the simplicity of lecture bottle use, the

The prepurified nitrogen was used for all experiments.

Argon. Argon was obtained in lecture bottles from Matheson. Purity was stated to be 99.99% and the argon so obtained was used without further purification.

Helium. Helium of 99.99% purity was obtained from the same source. It, too, was used without further purification.

Xenon. Research Grade Xenon was obtained in a lecture bottle (0.8 atm.) from Air Reduction Co. (Airco), Rare Gas Division, New Jersey, and was not subjected to further purifying treatment.

Carbon Tetrafluoride. Carbon tetrafluoride ( $\text{CF}_4$ ) was obtained in lecture bottles from Matheson Ltd., being not less than 95% pure. This  $\text{CF}_4$  was pumped through a spiral of 1 meter length (uncoiled) cooled in liquid nitrogen. This was repeated several times to remove non-condensibles, especially oxygen, if any. The  $\text{CF}_4$  was next passed through the same spiral cooled by a pentane-liquid nitrogen mixture at  $-140^\circ \text{C}$  to free any condensibles of relatively high vapor pressure. Finally, the  $\text{CF}_4$  was pumped through a large U-tube 35 x 1.5 cm filled with silica gel (20 mesh) and kept at  $-135^\circ \text{C}$  to remove any remaining hydrocarbons. GLC analysis showed no hydrocarbon impurity. All inert gases were stored in two 5-l storage flasks attached to the vacuum line. These bulbs were fitted with vacuum-backed stopcocks rather than mercury float valves to insure against mercury contamination.

Oxygen. Oxygen of 99.99% purity was obtained from Matheson Ltd. and was used without further purification.

Owing to the high expense of Research Grade Xenon, it was purified for re-use by the following technique: after completion of a

reaction, the contents of the reaction bulb were passed through a spiral cooled to  $-140^{\circ}$  C. This treatment trapped the bulk of the  $C_4$  and all the  $C_5$  hydrocarbons, although the lower boiling components (ethylene, ethane, etc.) were partially pumped away with the Xenon. After passing through this spiral, the remaining solution (Xenon, light hydrocarbons) was then pumped through a U-tube of 40 cm length and 2 cm width cooled in liquid nitrogen. The gases were then passed through the cooled ( $-135^{\circ}$  C) silica gel U-tube twice to rid it of any remaining hydrocarbons. GLC analysis showed no hydrocarbon impurity after this treatment. The purified Xenon was then frozen in liquid nitrogen and subjected to extended pumping at liquid nitrogen temperature to free it of any oxygen which may have possibly been entrained in the purifying process. Xenon, like all the third bodies used, was stored in two (taped) five-liter storage flasks (M).

Commercial samples of cis- and trans- 1, 2 dimethylcyclopropane (Columbia Organic Chemicals Co., Inc., Columbia, South Carolina), 2-methylbutene-2, 2- and 3-methylbutene-1, cis- and trans-pentene-2 and pentene-1 (all obtained from Matheson, Coleman and Bell, East Rutherford, N.J.) were used for GLC standards.

#### Procedure

The photolytic reaction vessel was conditioned by photolyzing mixtures of diazomethane and cis-butene-2 for several hours and discarding each run. The results obtained from the unseasoned vessel were characterized by the failure to notice any  $C_5$  hydrocarbon products, presumably because the diazomethane reacted very quickly with the "rough" walls of the reaction vessel.

The products of the reaction were identified by collection of

each component (as eluted from the GLC) in a "U" tube filled with CS<sub>2</sub> and cooled in a dry ice - acetone slush. After all peaks were thus collected (in separate "U" tubes) the contents of each were examined by infra-red spectrophotometry (Perkin-Elmer "Infracord") using 1 mm cavity cells, and comparing the spectra with those of known compounds (35). Since the products found in this work would be the same as those found by Frey (11), spectral interpretations were made much simpler. As a further check, retention times of the products found in typical reactions were matched with the retention times of the chemical samples kept for this purpose. One, usually minor, peak appeared occasionally, which, by its retention time seemed to be a C<sub>5</sub> compound; mass spectrometric analysis revealed, however, that it was methyl chloride, a by-product from the preparation of diazomethane. This accounted for no more than 0.5% impurity in the diazomethane. Although it probably could have been removed by repeated distillations, the risk of diazomethane explosion precluded this step. As a final check on the assignment of retention times (as well as a test of the general procedure) a few of Frey's (11, 36) runs were duplicated, using cis-, trans-, and isobutene. All peaks could be accounted for (with the exception of methyl chloride) and the results (as determined by percent areas) matched to within a few percent, even though, presumably, the geometry and conditioning of the reaction bulbs were dissimilar.

As more and more experiments were performed, a thin layer of polythene (presumably) was deposited on the inner surface of the reaction bulb. Since, conceivably, this film could selectively absorb light of certain wavelengths and allow others to pass, runs were repeated near the

termination of this work to confirm previous results. Any variations in results created by this possible opaqueness were not distinguishable from experimental error.

Experiments were performed in the following manner. The vacuum line was pumped down to a suitable low pressure. Cis-butene was then distilled from its storage vessel directly into the finger (cooled in liquid nitrogen) of the reaction flask, allowed to warm to room temperature, and the pressure (as indicated by the sensitive spoon gauge) noted; butene was added or removed according to the pressure desired. When the correct pressure was reached, the entire contents of the reaction vessel (and both spoon gauges) were frozen into a "standby" finger (SF). Immediately prior to use, diazomethane, stored at  $-196^{\circ}\text{C}$ , was allowed to warm to room temperature, refrozen to  $-196^{\circ}\text{C}$  and pumped. This procedure was repeated at least three times, to remove non-condensibles. The storage bulb (DM) containing diazomethane (in decalin) was next immersed in a n-propanol - liquid nitrogen mixture at  $-125^{\circ}\text{C}$  and subjected to pumping for at least  $\frac{1}{2}$  hour in order to remove ethylene formed by diazomethane decomposition. After this treatment, the mixture was warmed to  $-70^{\circ}\text{C}$  and distilled into the reaction vessel. When a more than sufficient amount was condensed in the vessel, the storage vessel was isolated. The reaction vessel was then opened to pumping and the liquid nitrogen trap removed from the vessel finger. Any ethylene which was present in the reaction vessel was pumped off while the diazomethane was still a solid. Excess diazomethane was pumped away (into a pumping fore-trap) until the desired pressure was reached, as shown by the Bourdon gauge. Both Bourdon gauges were isolated, then the diazomethane and

butene (frozen in the "standby" finger) were recondensed into the reaction bulb using liquid nitrogen. With the liquid nitrogen surrounding the reaction bulb finger and the robust spoon gauge in operation, the inert gas was very slowly admitted; air was simultaneously admitted by the air bleed in order to keep, as nearly as possible, both the inside and outside pressures of the spoon equal. After the desired amount of the inert gas had been admitted, the inert gas reservoirs were isolated and the reaction bulb was allowed to warm to room temperature and the final pressure noted. Due to the fact that three different gases were used in each run, the possibility of imperfect mixing was explored. Experiments done at high pressures of inert gas were allowed to stand (in the dark) for at least 2 hours. As test cases, a few high pressure runs were allowed to stand for as much as 6 hours prior to irradiation. No differences were noticed in the overall percentages of products. After 8 hours irradiation, the products and unreacted gases were pumped through a spiral ( $S_1$ ) of 2 meter (uncoiled) length immersed in a suitable cooling bath. (When the inert gases used were nitrogen, helium and argon, this cooling bath was liquid nitrogen; when the inert gases were xenon and  $CF_4$ , the spiral was immersed in a liquid nitrogen - n-pentane mixture kept at about  $-140^\circ C.$ ) After at least one hour's pumping time the products trapped in the spiral were recondensed (using liquid nitrogen) in a sampling finger with a standard taper to mate with that of the gas sampling device. The gas sampling device was fitted with its own pumping system as well as a cooling trap which could be used to condense all the products for analysis. A few runs were done with nitrogen-oxygen solutions as the "inert gas". Oxygen was mixed with nitrogen in the gas

storage bulbs (M) until oxygen was at the desired percentage of the overall solution; pressures were measured by means of a manometer (MAN<sub>2</sub>) equipped with a "U" tube which could be cooled to prevent admixture of mercury vapor with the inert gases. When adding the oxygen-nitrogen solution, the cold finger on the reaction bulb was cooled to -140° C to guard against possible condensation of oxygen in the finger. Irradiation and recovery were carried out as previously described.

Thermal runs. The well-blackened bulb for the thermal reactions was attached to the vacuum line by means of standard tapers, the vessel being eased into place by means of a lab jack (T). Reaction samples were prepared in a manner similar to those above, nitrogen being used as the inert gas in all thermolyses. After filling, the bulb was removed from the vacuum line and clamped in its metal jig. The bulb itself had a long, thin neck in the middle of which the stopcock was placed; whereas the entire bulb was immersed in the bath, the thin neck (and stopcock) were not--however, the dead space was less than 1%. After 4½ hours immersion, the bulb and contents were allowed to cool. The reaction bulb was then re-affixed to the vacuum line and the products recovered exactly as before.

Mercury Photosensitization. A few experiments were done involving diazomethane - trans-butene and diazomethane - cis-butene as reactants. The irradiation vessel was cylindrically shaped, having a capacity of about 220 cc with flat quartz windows at both ends and a finger for condensing reactants (or products) at one end (RX<sub>2</sub>, Fig. 1). Mercury vapor was admitted by means of a stopcock that opened into the vessel from a mercury reservoir (R). The mercury lamp itself was a flat, coiled one of the same diameter as the windows of the cell. Owing to its

flat design it could be placed in direct contact with the windows. The lamp was water cooled and fitted with a transformer but no ammeter. Experiments were done without mercury vapor in the cell (after thorough cleansing with hot chromic acid solution) as well as with mercury vapor present. It was hoped that "blank" results could be obtained (no Hg vapor present) enabling one to compare these results with those obtained with mercury vapor present.

RESULTS

Raw data for GLC peak areas are given in the following tables. The areas have been calculated after the method of Bartlett and Smith (38); spot checking the areas with a planimeter showed agreement within 2% for relative areas.

Table 1

Relative Areas (arbitrary units) of C<sub>5</sub> Hydrocarbon  
Peaks Obtained in the Photolytic Reactions Between  
Cis-Butene-2 (0.3<sub>g</sub> torr) and Diazomethane (0.8<sub>g</sub> torr)  
in the Presence of Inert Gas

<u>N<sub>2</sub>,</u> <u>torr</u>	<u>3MeBu-1</u> <sup>1</sup>	<u>TDMC</u>	<u>TPe-2</u>	<u>CDMC</u>	<u>CPe-2</u>	<u>2MeBu-2</u>
14	588	1996	1828	1420	3301	1599
59	492	1099	994	1433	2236	838
174	1663	1625	1915	4032	6118	1581
195	1145	976	2449	2798	2924	738
258	1152	1003	1848	3381	3290	816
345	229	226	488	452	162	319
653	2482	2980	2570	2964	3310	917
673	173	206	293	265	351	Tr <sup>2</sup>
752	462	500	566	571	721	165

1 3MeBu-1, 3-methylbutene-1; TDMC, trans-1,2-dimethylcyclopropane;  
 TPe-2, trans-pentene 2; CDMC; cis-1,2-dimethylcyclopropane; CPe-2;  
 cis-pentene-2

2 Trace amount

Table 2

Relative Areas etc.

<u>Argon,</u> <u>torr</u>	<u>3MeBu-1</u>	<u>TDMC</u>	<u>TPe-2</u>	<u>CDMC</u>	<u>CPe-2</u>	<u>2MeBu-2</u>
36	390	1600	1189	1480	2673	1522
39	427	1552	1364	1633	3124	1210
55	263	262	416	466	625	245
123	374	768	559	1114	1745	209
189	865	1265	1200	1990	3405	1234
191	302	574	711	1305	1872	712
231	275	340	312	660	1359	219
268	265	497	457	730	1327	249
283	203	279	217	714	750	212
386	231	283	440	583	693	167
390	3710	410	2800	450	2100	520
466	422	450	701	1090	1359	204
663	248	316	496	583	594	182
686	506	617	598	943	1013	Tr

Table 3

Relative Areas etc.

<u>Helium,</u> <u>torr</u>	<u>3MeBu-1</u>	<u>TDMC</u>	<u>TPe-2</u>	<u>CDMC</u>	<u>CPe-2</u>	<u>2MeBu-2</u>
40	285	2002	1094	1704	3435	1715
96	243	820	634	1198	1869	835
120	255	911	878	1994	2463	1243
128	193	658	511	1290	4476	853
142	195	601	254	1212	2408	439
187	120	410	455	1100	1187	535
191	215	594	682	1546	675	537
338	120	181	411	577	666	273
551	287	322	560	1291	1467	553
569	284	222	278	727	875	395
654	212	217	409	725	901	154
716	250	305	304	785	1286	349

Table 4

Relative Areas etc.

<u>CF<sub>4</sub></u> <u>torr</u>	<u>3MeBu-1</u>	<u>TDMC</u>	<u>TPe-2</u>	<u>CDMC</u>	<u>CPe-2</u>	<u>2MeBu-2</u>
0	361	183	364	367	587	452
8.3	1413	3532	3648	3204	6698	367
26.3	474	149	142	222	378	196
58	1564	842	2184	3497	6679	2582
62	1781	1004	1800	3404	4731	3062
148	2315	704	1648	3192	4132	1781
213	1862	1030	1517	2591	3009	1119
244	2352	878	1602	2213	2092	88 <sup>1</sup>
258	1412	1148	1596	1403	2480	974
398	293	108	246	238	263	133
459	5190	4343	6080	7500	3352	585
480	740	652	682	988	933	184
516	2139	1238	1276	1692	1369	323
568	1963	1184	1190	1870	1440	159
666	3160	1195	1515	1951	1896	2.3
857 <sup>1</sup>	4290	2880	2490	2841	2974	989

1 estimated

Table 5

Relative Areas etc.

<u>Xenon,</u> <u>torr</u>	<u>3MeBu-1</u>	<u>TDMC</u>	<u>TPe-2</u>	<u>CDMC</u>	<u>CPe-2</u>	<u>2MeBu-2</u>
11.2	724	155	265	795	375	233
12.2	875	1683	2393	1184	3701	1748
50	2178	1352	1274	1104	1700	505
209	1102	409	1540	1224	1074	946
352	564	497	1110	1114	743	394
387	377	655	1421	1337	867	1193
462	3423	3427	3148	3595	3000	980
573	630	540	442	1040	808	707
581	859	725	1181	1037	1240	448
585	706	471	1248	776	1920	1459
770	565	1202	2331	2089	1225	784
780	1007	515	517	534	-	146
780	1366	416	441	331	412	237

Table 6

Relative Areas, etc.<sup>1</sup>

<u>N<sub>2</sub>,</u> <u>torr</u>	<u>3MeBu-1</u>	<u>TDMC</u>	<u>TPe-2</u>	<u>CDMC</u>	<u>CPe-2</u>	<u>2MeBu-2</u>
201	214	216	355	598	719	260
262	172	147	244	347	447	DNM
554	552	663	832	1390	1620	277
688	959	1114	1021	2215	2519	422

Table 7

Relative Areas, etc.<sup>2</sup>

Cis-Butene (0.35 torr); Diazomethane (0.88 torr)

<u>(N<sub>2</sub>+O<sub>2</sub>)<sup>2</sup>,</u> <u>torr</u>	<u>3MeBu-1</u>	<u>TDMC</u>	<u>TPe-2</u>	<u>CDMC</u>	<u>CPe-2</u>	<u>2MeBu-2</u>
32.3	Tr	405	584	468	811	316
107	Tr	165	368	376	585	95
510 <sup>3</sup>	Tr	381	319	2932	1939	1271
515	Tr	210	501	4425	3297	1280
517	Tr	40	Tr	1297	514	101

- 1 1.9 torr cis-butene-2 and 0.5 torr diazomethane
- 2 Oxygen pressure is 10% of overall (N<sub>2</sub>+O<sub>2</sub>) pressure
- 3 Oxygen pressure is 3% of overall (N<sub>2</sub>+O<sub>2</sub>) pressure

Table 8

Relative Areas (arbitrary units) of C<sub>5</sub> Hydrocarbon

Peaks Obtained in the Photolytic Reactions

Between Cis-Butene-2 and Diazomethane<sup>1</sup>;

No Inert Gas Present

<u>Butene,</u> <u>torr</u>	<u>3MeBu-1</u>	<u>TDMC</u>	<u>TPe-2</u>	<u>CDMC</u>	<u>CPe-2</u>	<u>2MeBu-2</u>
27	DNM	863	72	1598	2532	989
231	DNM	399	160	2105	2035	775
571	DNM	161	88	1857	1465	504
762	DNM	202	137	1632	473	428

1 4 torr

Table 9

Relative Areas (arbitrary units) of C<sub>5</sub> Hydrocarbon

Peaks Obtained in the Thermal Reactions Between

Cis-Butene-2 (0.7 torr) and Diazomethane (0.9 torr)

in the Presence of Nitrogen, 225°C ±5

<u>N<sub>2</sub></u> <u>torr</u>	<u>3MeBu-1</u>	<u>TDMC</u>	<u>TPe-2</u>	<u>CDMC</u>	<u>CPe-2</u>	<u>2MeBu-2</u>
0	Tr	388	1178	1214	2923	3067
124	Tr	260	3123	2012	2146	1503
220	242	174	1817	1811	2946	3020
702	159	483	4914	7689	9721	5402





and unsaturated. The initiating process is



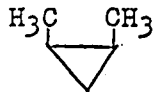
whereupon this product reacts with methylene to form the next higher homolog and so on. In agreement with Frey (33), the olefins formed in highest yields are ethylene (highest), propylene, and butene-1 (lowest).

The principal products, as noted in the scheme, generated by the unfiltered photolysis of diazomethane in the presence of cis-butene-2 and inert gas are cis- and trans- 1,2-dimethylcyclopropane (called CDMC and TDMC, respectively), cis- and trans-pentene-2, 3-methylbutene-1 and 2-methylbutene-2. 2-methylbutene-1 has been reported to occur in very small amounts (11, 26, 13), but due to the long GLC retention time and the small percentage of the total yield for this product, accurate measurements were not possible. Moreover, in the research most closely allied to this present work (33), no mention at all is made of this compound. Setser and Rabinovitch (26), in their discussion of the thermal reaction of methylene with butene, prefer to discuss 2-methylbutene-1 together with 3-methylbutene-1 (i.e. discussion of methylbutene-1 only). This was not done in the present work owing to the possibility that these two compounds may arise by two quite different mechanisms.

The formation and pressure dependence of each of the C<sub>5</sub> hydrocarbons will now be discussed. Different inert gases (N<sub>2</sub>, Ar, He, CF<sub>4</sub> and Xe) were used in conjunction with methylene photolysis in order to bring about the singlet to triplet transition as well as to cool the various excited products. In the figures presented in this thesis, the gases showing the greatest and least efficiencies in this respect (usually CF<sub>4</sub> and He, respectively) are plotted. Exceptional and anomalous behavior is

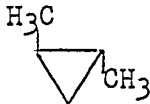
noted in the text. The partial pressures of reactants used were cis-butene-2, 0.35 torr and diazomethane 0.8g torr, unless otherwise noted.

Cis-1,2-dimethylcyclopropane, CDMC



The dependence of the yield of CDMC (expressed as a percentage of the total yield of C<sub>5</sub> hydrocarbons) on the pressure of inert gas is shown in Fig. 3. At low pressures of inert gas (below 150 torr), there is an increase in the yield of this compound with increases in inert gas pressure. This means that the CDMC originally formed from the energy rich methylene addition isomerizes. As the pressure of inert gas is increased, these isomerizations are repressed (in favor of collisional deactivation). Thus, an increase in pressure should reveal an increase in the yield of CDMC until the high pressure limit is reached. If one were dealing with only singlet methylene, the high pressure limit reached would represent the rate with which CH<sub>2</sub> added across the double bond relative to the sum of the rates for all the other reactions. (For instance, if this limit occurs at a yield percent of 25, one may say that for every 100 reacting encounters of CH<sub>2</sub> with butene, 25 of these result in CDMC). This low pressure behavior is identical with that reported by other workers (26, 11). Comments concerned with the triplet behavior of methylene will be made subsequently.

Trans-1,2-dimethylcyclopropane, TDMC



As mentioned earlier, the best diagnostic chemical test for the occurrence of triplet methylene is the appearance of trans-1,2-dimethylcyclopropane (TDMC) when methylene is reacted with cis-butene-2. In practice, this is not so, since the initially formed CDMC which may arise by the singlet addition of methylene to cis-butene-2 contains

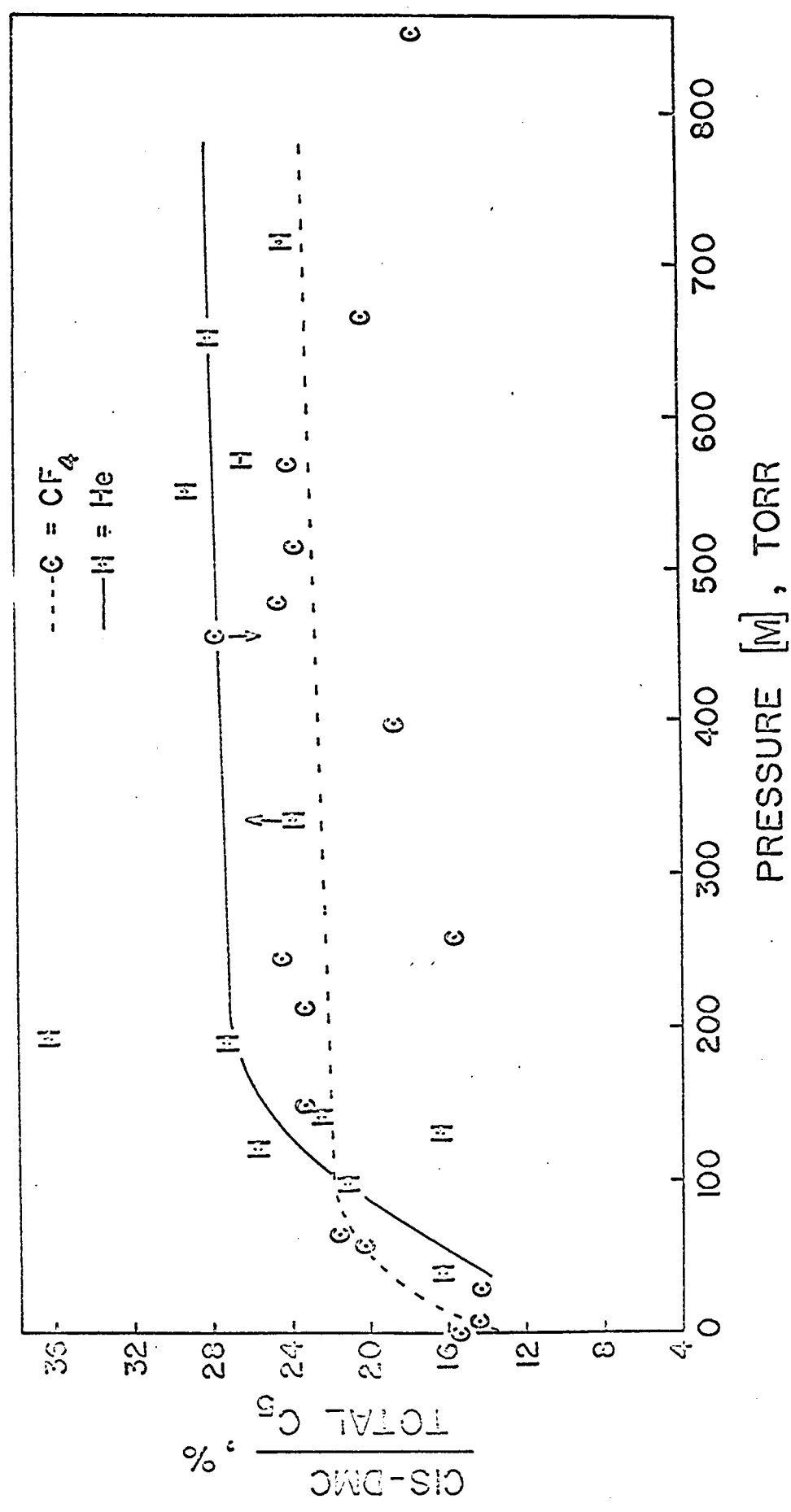


Figure 3 Cis-1,2-dimethylcyclopropane Yield vs Inert Gas Pressure

sufficient energy to undergo geometrical isomerization (to the trans compound) as well as the structural isomers mentioned in the scheme. The yield of TDMC as a function of inert gas pressure is illustrated in Fig. 4. This behavior can readily be explained in the following manner: originally, singlet methylene reacts stereospecifically to form excited CDMC, which quickly isomerizes to TDMC. As the pressure of the inert gas is increased, the CDMC\* originally formed undergoes collisional deactivation resulting in lower yields of TDMC. This behavior, too, is analogous to the purely singlet methylene behavior reported by other researchers. A certain pressure is reached, however, where this trend is abruptly reversed, and more TDMC is formed with increases in pressure. To explain this behavior one may invoke equation 4; triplet methylene reacts to give trans- and cis-DMC directly. The trans compound (like the cis) is excited and will isomerize. As the pressure is increased further, first of all, the isomerizations of excited TDMC are repressed; also, more triplet methylene is formed--both processes lead to increased yields of TDMC.

An instructive way of summarizing the behavior of these compounds (cis- and trans-DMC) with pressure is to consider the percent TDMC of the total yield of cyclopropane only (i.e. TDMC/total DMC). This behavior is shown in Figs. 5 and 6. At zero pressure of inert gas, the singlet addition of CH<sub>2</sub> to cis-butene-2 results in the stereospecific product CDMC\* which immediately isomerizes to the trans compound. As the pressure is increased, less trans DMC is produced because CDMC\* is being collisionally stabilized before isomerizing to the trans compound. Up till this point, the behavior is similar to that observed in pyrolysis

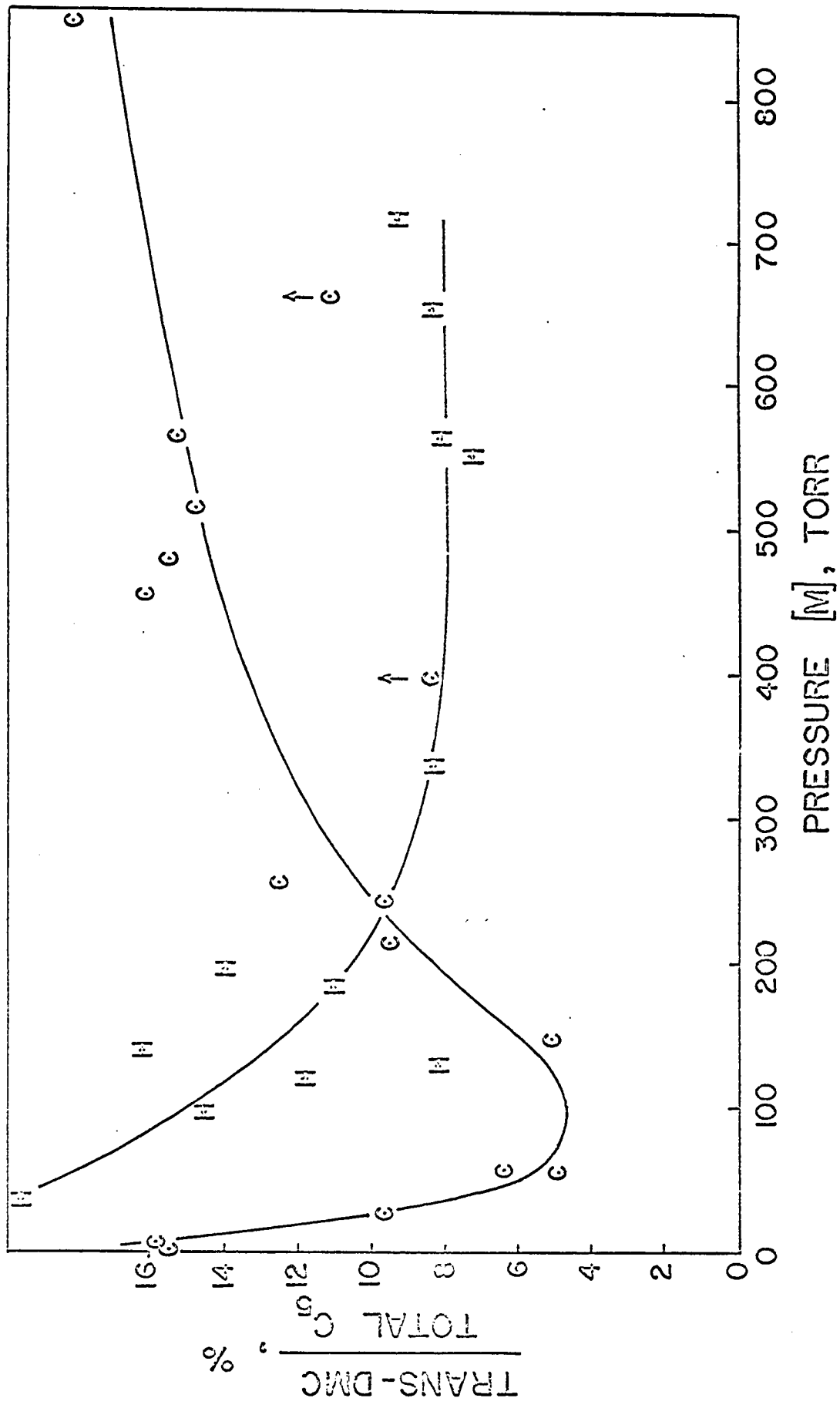


Figure 4 Trans-1,2-dimethylcyclopropane Yield vs Inert Gas Pressure

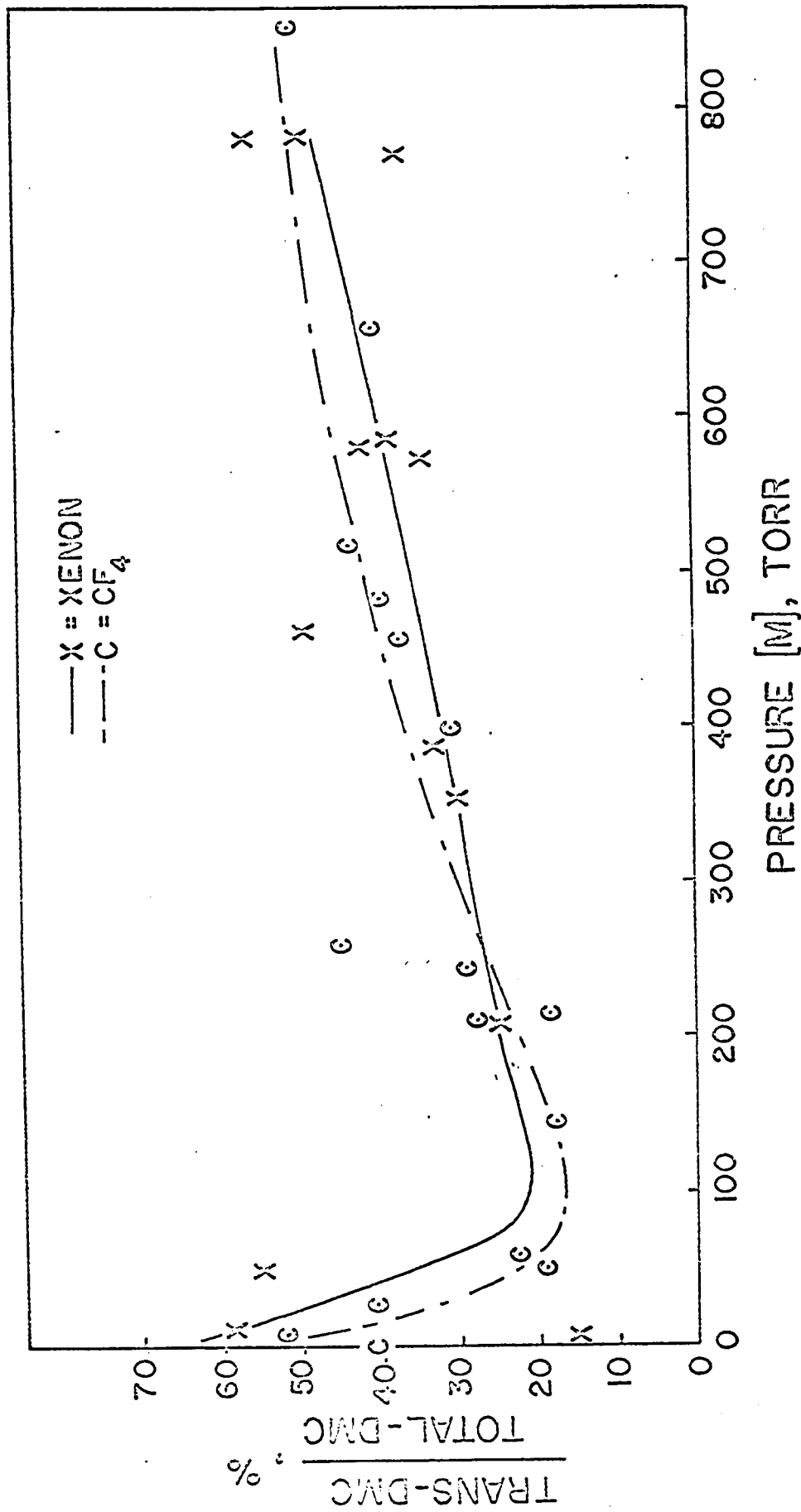


Figure 5 Trans-1,2-dimethylcyclopropane as a Percent of Total Dimethylcyclopropane Yield vs Inert Gas Pressure

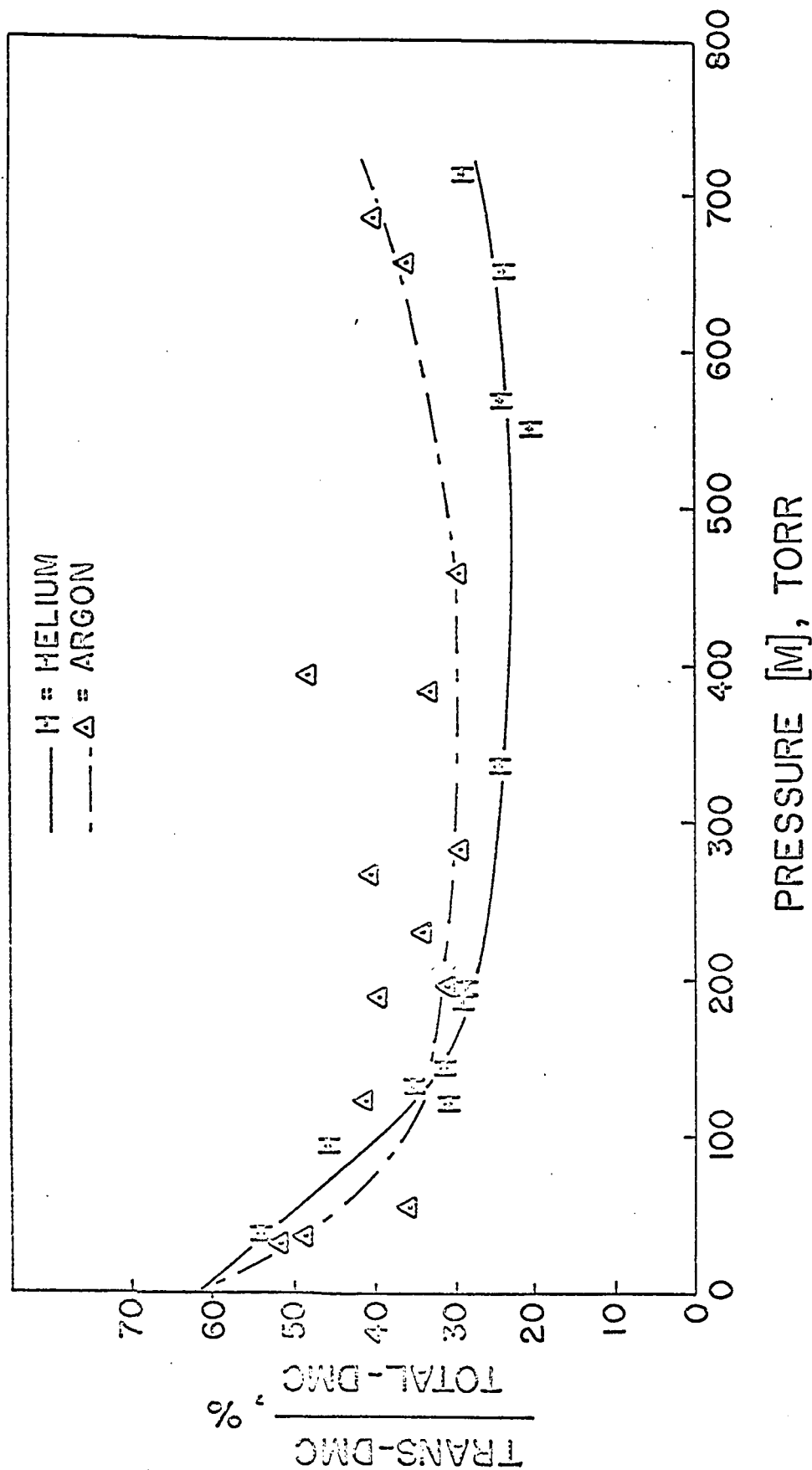


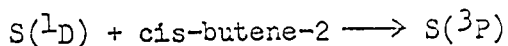
Figure 6 Trans-1,2-dimethylcyclopropane as a Percent of Total Dimethylcyclopropane Yield vs Inert Gas Pressure

studies of CDMC, performed by Flowers and Frey (10). According to those authors, if CDMC is strongly heated it undergoes isomerization to the trans isomer. At the lowest pressures, the CDMC\* isomerizes to TDMC. As the pressure is raised, the excited CDMC is collisionally deactivated before it isomerizes, resulting in less TDMC, this trend continuing throughout the entire pressure range. In this present work however, a point is reached (about 150 mm of inert gas) where this trend is reversed, and more TDMC is formed. This cannot be due to the isomerizations mentioned, since at these pressures collisional deactivation is more rapid than isomerization. Thus, one is able to separate the behavior of methylene into two classes corresponding to two different pressure regions--the first being largely singlet behavior (below 150 torr) and the second being (increasing) triplet behavior at pressures higher than 150 torr (although even at pressures as high as 850 torr, purely triplet behavior is not observed, as seen from the failure to reach a high pressure limit at this point).

If cis-butene-2 were used as both a reactant and cooling molecule, rather than fostering the change in multiplicity, a reaction would occur, effectively removing singlet methylene from the system before it could undergo the transition to the triplet state. In a situation like this, only singlet behavior would be observed. (This is not to say that it is impossible for butene to convert singlet methylene to the triplet without reacting, but rather that reaction is more probable than this conversion<sup>1</sup>. In view of the foregoing comments, performing experi-

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1 According to Gunning et al (24, 25), reactions of cis-butene with singlet sulfur atoms may result in a triplet sulfur rather than a reaction (to form a cyclic mercaptan):



ments with higher and higher partial pressures of butene should result in less and less triplet behavior for the simple reason that singlet methylene has increasing opportunities to react with butene rather than undergoing conversion to the triplet state. This is seen in Fig. 7, where, as the partial pressure of butene is raised, the triplet nature of the reaction is retarded; this is shown by the less dramatic increase in the percent TDMC of the total DMC at pressures of inert gas greater than 200 torr. If this experimental variation is continued (i.e. increasing the partial pressure of butene), the increase in the percent TDMC will be less noticeable, ultimately reaching the state where no triplet behavior is in evidence. Worthy of note from an experimental standpoint is the lack of point scatter as the partial pressure of butene is raised. That this should be the case is obvious from two considerations; first, more accurate metering of reactants is possible and second, larger amounts of products results in easier quantitative determinations of products.

One of the main objects of the present work was the investigation of the effects of different inert gases on the singlet to triplet transition. This has a high degree of theoretical significance (as will be explained in greater detail in a later section); a study of the various effects of these different gases answers questions concerning the nature of the singlet to triplet transition.

One would not expect to find large differences in the effects of different inert bodies (on the singlet to triplet transition) if the partial pressure of butene is high (compared to that of the third body). In this case, singlet reactions would be important (and detrimental as well), since the singlet effects would first have to be accounted for

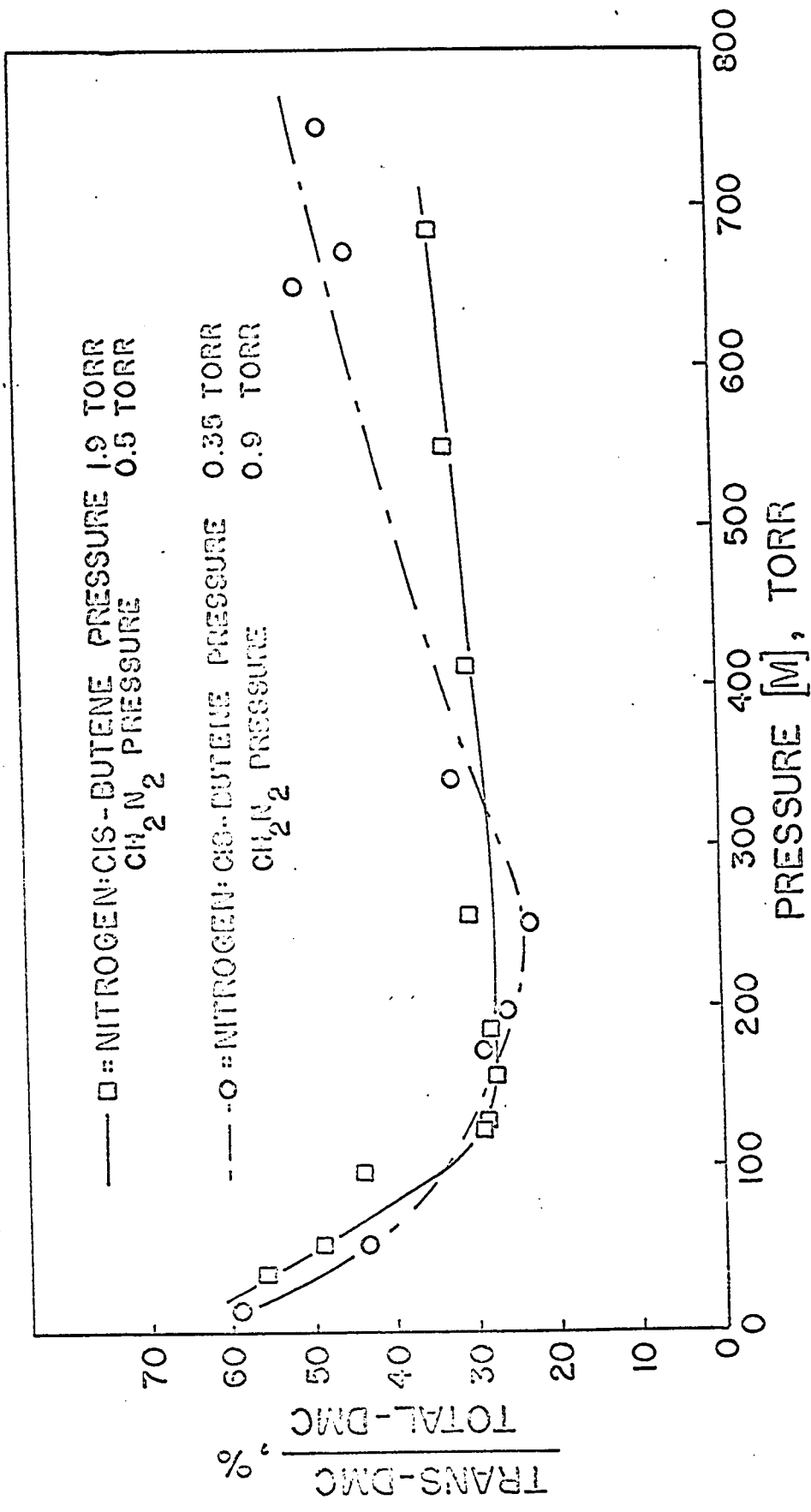


Figure 7 Trans- 1,2-dimethylcyclopropane as a Percent of Total Dimethylcyclopropane Yield vs Inert Gas Pressure, Showing Effect of Raising Partial Pressure of Cis-Butene-2

before any conclusions concerning the relative efficiencies (in the singlet to triplet transition) of the different inert gases could be drawn. The alternative is to work at extremely small partial pressures of butene. As mentioned previously, low absolute amounts of reactants give small amounts of products; the use of a fairly large (2 l) reaction vessel, while permitting low partial pressures of butene, resulted in reasonable (but by no means oversufficient) amounts of products to analyze. The conditions finally chosen were done only after much preliminary experimentation and seemed to be the best compromise between product point scatter with low partial pressures of butene on the one hand, and the inability to notice any differences (with different inert gases) at high partial pressures of butene on the other.

The differing abilities of the third bodies in bringing about differing ratios of TDMC/Total DMC is taken in this work as a measure of the ability of each inert gas to bring about the singlet to triplet transition (at high pressures). From a comparison of Figs. 5, 6, and 7, it is evident that helium is the worst<sup>1</sup>. Argon, while being noticeably better than helium is notably poorer than  $CF_4$ ,  $N_2$  and Xe. These latter three are remarkably alike in their abilities to bring about the singlet-triplet transition in methylene even though the structures of these three vary exceedingly. Again, working at still lower partial pressures of butene would resolve this apparent similarity, although the experimental details would have to be changed; still the experimental conditions chosen in this

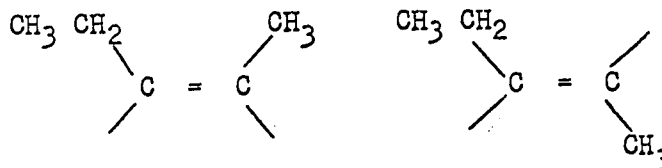
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1 Helium does cause the formation of some triplet  $CH_2$  as will be discussed in a later section.

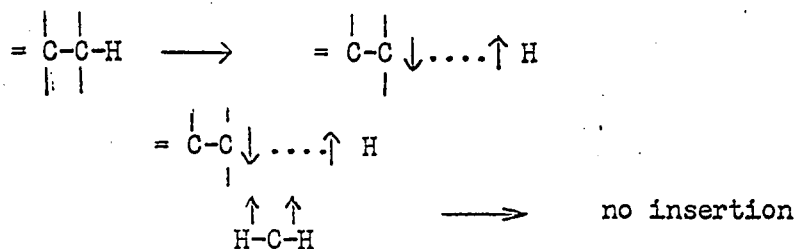
present work allowed a ratio of pressures of inert gas/butene higher than ever used before. Having results obtained from such dissimilar third bodies permits some insight into the nature of the perturbations bringing about the singlet-triplet transition. This aspect will be considered after the formation of the other C<sub>5</sub> products has been discussed.

Formation of structural isomers

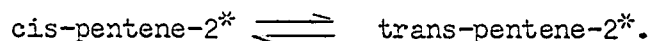
cis- and trans-pentene-2



Methylene may insert between carbon-hydrogen bonds as well as undergo additions to the carbon-carbon double bond (37). In this present work, it appears on the basis of experimental results, now to be discussed, that the singlet species is the one responsible for these insertions. That this should be so can readily be seen from theory: when a C-H bond separates in order to accommodate an incoming CH<sub>2</sub> molecule, there is no reason to believe that one of the electrons (formerly involved in a carbon-hydrogen bond) should reverse its spin, unless the methylene carries enough energy to excite this bond to such an energetic state. (This case is different from the situation involving a carbon-carbon double bond where there are comparatively low-lying triplet states). As triplet methylene approaches this separating C-H bond, one of its electrons will pair with one having an opposite spin and a bond will be formed; the remaining electrons, since they have identical spins, may not pair up under the energy conditions involved. This case is shown schematically as follows:



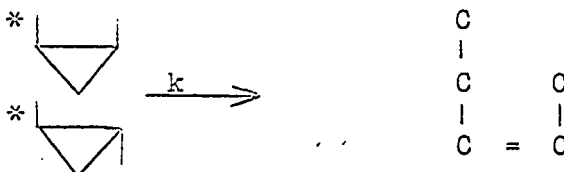
whereas with singlet methylene all four electrons accommodate themselves very easily. This is not to say that if triplet methylene is present, C-H insertions will not be evidenced. Apparent triplet insertions may come about by quite another mechanism; for instance, triplet methylene may react with butene-2 to give a "hot" adduct which may isomerize structurally--this product formed through isomerization may appear to have been formed directly by triplet methylene. For example, cis-pentene-2 may be formed directly by singlet insertion into a carbon-hydrogen bond in cis-butene-2. Since singlet methylene carries with it a certain excess energy (estimated by Setser and Rabinovitch (26) to be about 110 kcal) the cis-pentene-2 will be vibrationally energized, and will, unless collisionally deactivated, isomerize to its geometrical isomer trans-pentene-2, i.e.,



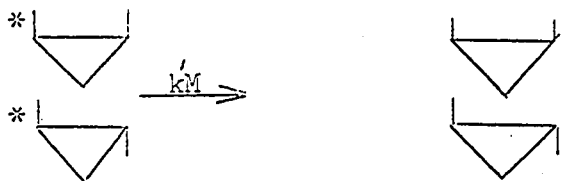
In addition, structural isomerization of DMC\* (formed entirely by triplet addition to a carbon-carbon double bond) may give rise to compounds which would appear to have been formed by direct insertion of triplet methylene into a carbon-hydrogen bond. Since the dependencies of singlet and triplet methylene on pressure are now known (from the study of cis- and trans-DMC) the appearance or disappearance of the chain isomers under similar conditions enables one to say whether these isomers arise through

the intervention of triplet methylene or not.

The percentage yield of cis-pentene-2 (percent composition of the total yield of C<sub>5</sub> hydrocarbons) is shown in Fig. 8 as a function of pressure. Cis-pentene-2 is seen to undergo an initial rise in percent yield as the pressure is increased; at zero pressure of inert gas, for instance, the percent cis-pentene is low; this is probably due to the isomerization to the corresponding trans compound, as indicated previously. As the pressure of the third body increases, this isomerization is retarded, the main process now being collisional deactivation; this results in more "cool" cis-pentene-2 and the observed rise in percent yield of cis-pentene as the pressure is increased. Also, at the very low pressures of inert gas, DMC\* is not being deactivated to any large extent, and this, too, contributes to the appearance of cis-pentene. A pressure region is reached, however, where DMC\* is rapidly cooled, and no longer undergoes structural isomerization, i.e. the following reactions



are repressed in favor of the reactions



Thus, the more inefficient deactivators such as He should produce more of the structural isomers of DMC than an efficient collision partner (CF<sub>4</sub>) would; that is, if collisional deactivation is competing with structural isomerization, CF<sub>4</sub> should be producing less cis-pentene (at a given

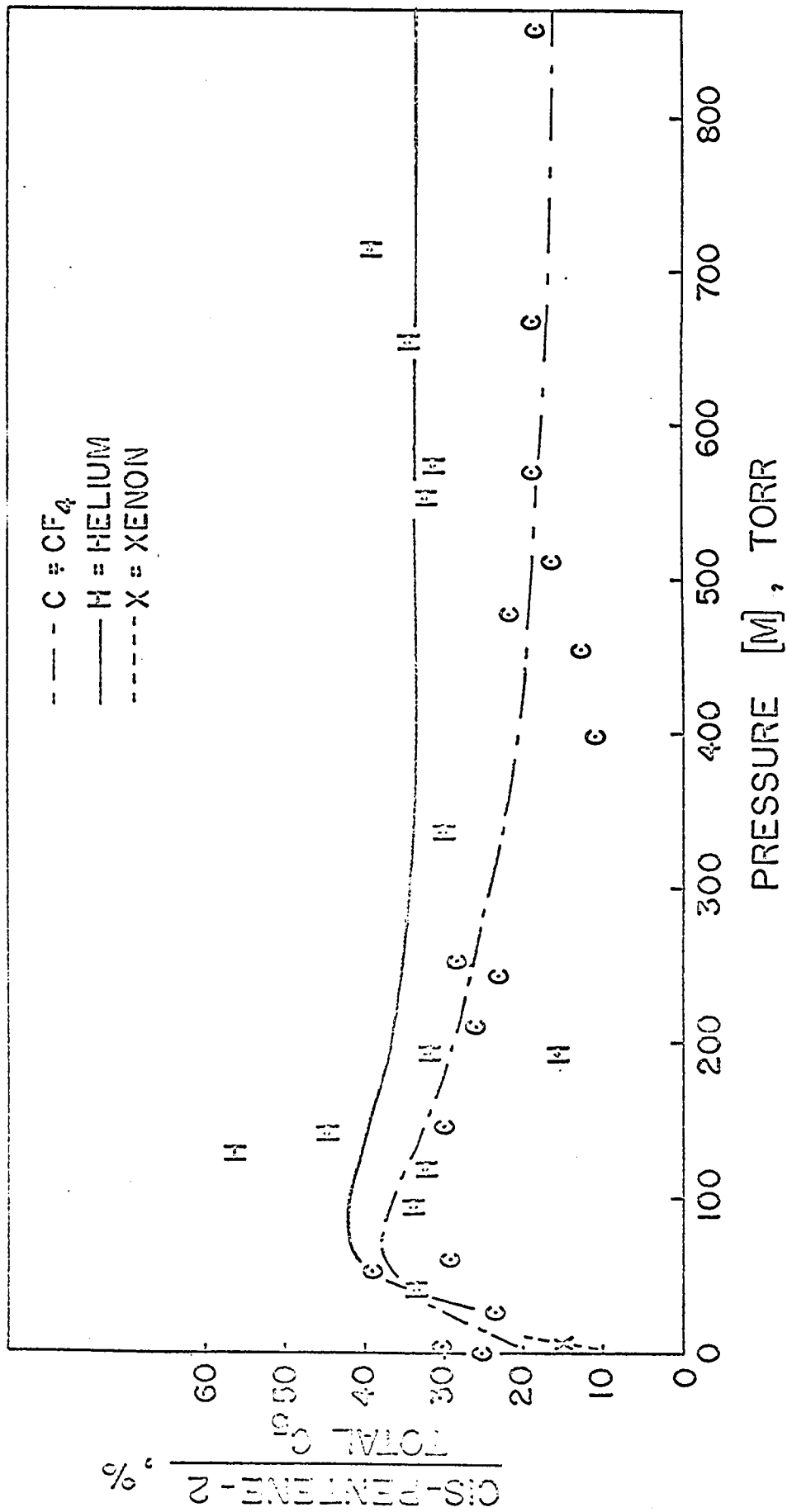


Figure 8 Cis-Pentene-2 Yield vs Inert Gas Pressure

pressure) than He does. This is difficult to assess, since too few runs were performed at low pressures; moreover, the rapid production of triplet methylene by  $\text{CF}_4$  clouds the interpretations along these lines. With the increased production of triplet methylene, one would expect the percentage of cis-pentene-2 to fall, keeping in mind what was said earlier concerning the inability of triplet methylene to react. Since the other sources of cis-pentene-2 (i.e. isomerizations) have been repressed by collisional deactivation, and since triplet methylene cannot insert into the carbon-hydrogen bond, one would predict a decrease in the percentage yield of cis-pentene-2 as more triplet is formed (or, as the pressure of inert gas is increased). Since triplet methylene is formed less rapidly by He than by  $\text{CF}_4$ , one would expect more cis-pentene to be formed by He than by  $\text{CF}_4$ , especially at higher pressures; this is again borne out by the figure.

The behavior of trans-pentene with pressure is seen in Fig. 9. Bearing in mind the comments made concerning cis-pentene-2, the low pressure behavior of trans-pentene-2 is expected; that is, the insertion of singlet methylene into a C-H bond of cis-butene-2 initially gives cis-pentene-2, which, being highly energized, readily isomerizes to the trans compound. As more and more collisions with M gas occur, the hot cis-pentene-2 is collisionally deactivated before undergoing geometrical isomerization, and the amount of the trans-compound should decrease with initial increases of inert gas. Likewise, if the excited dimethylcyclopropanes give rise to trans-pentene-2 through structural isomerization, an increase in third body collisions should deactivate these hot species, thereby decreasing the yield of trans-pentene-2. This is readily seen from the figure. At higher

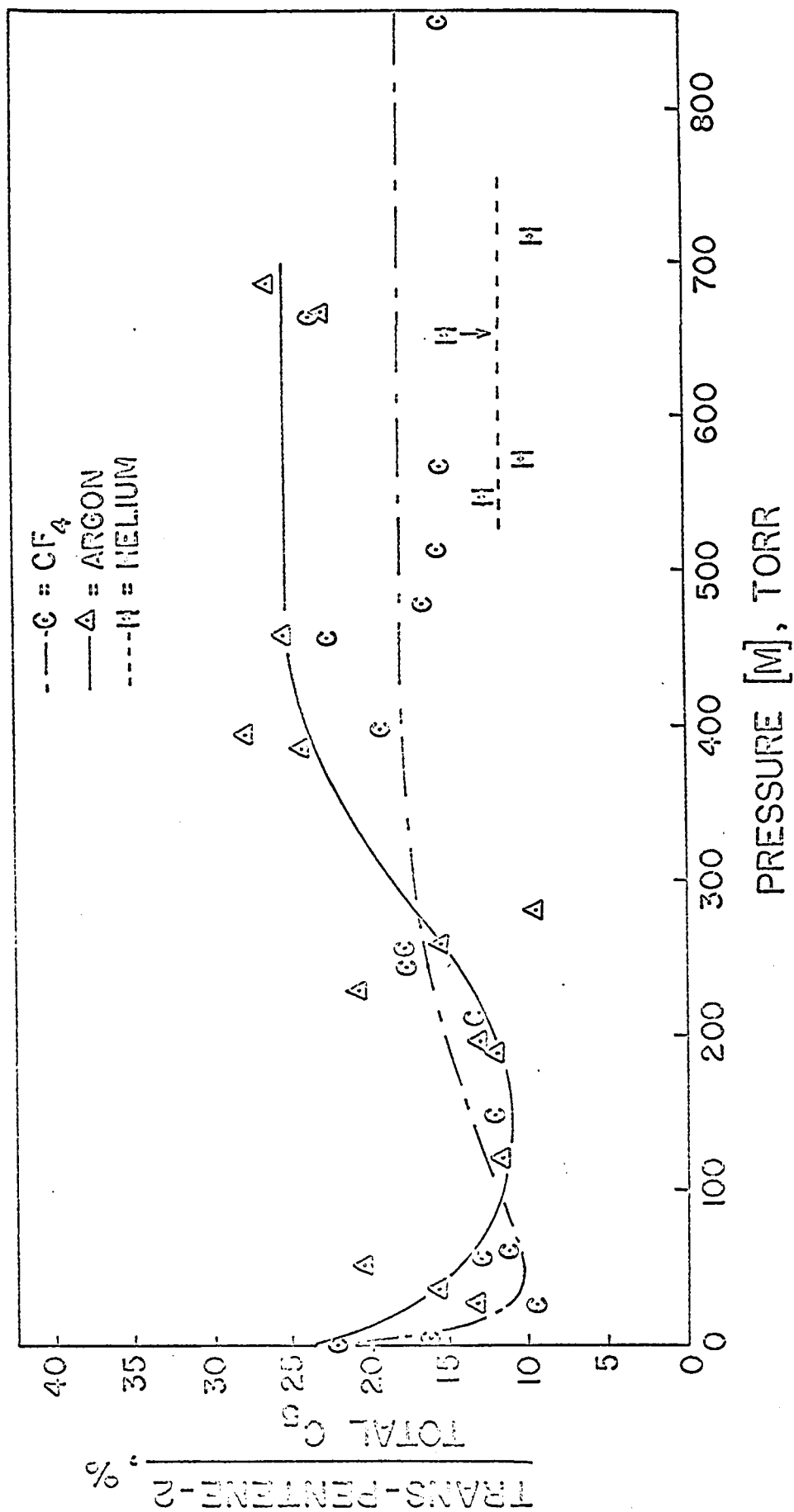
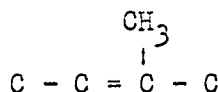


Figure 9 Trans-Pentene-2 Yield vs Inert Gas Pressure

pressures, the behavior of trans-pentene-2 is difficult to explain. There is no known reason why the percentage yield of this compound should rise with increasing pressure as shown by the experimental results. One may invoke a triplet abstraction scheme (see subsequent discussion), but it is not plausible to use this explanation in describing the appearance of trans-pentene-2 and not cis-pentene-2. Relatively large yields of trans-pentene-2 have been found with triplet methylene both by Duncan and Cvetanović (13) and Frey (11). Another anomaly appears when considering the results of the individual inert gases. If a triplet abstraction scheme were operative, the inert gas which brings about the highest yield of triplet methylene would result in the highest yield of trans-pentene-2. The behavior of argon in this respect is most odd. Since  $CF_4$  is more effective in producing triplet methylene, it would be expected (if the triplet abstraction scheme were in operation) that it would produce more trans-pentene-2 than argon. This is not the experimental case.

2-methylbutene-2



The pressure dependency of the yield of 2-methylbutene-2 is shown in Fig. 10. The appearance of this compound may be explained most readily as a case of methylene insertion into a vinylic C-H bond. At very low pressures of inert gas, the percent yield of this compound is very high and drops to a few percent at higher pressures of inert gas. Besides direct insertion of methylene into a carbon-hydrogen bond, 2-methylbutene-2 may arise through the structural isomerizations of  $DMC^*$ ; this would be expected to be important at lower pressures of inert gas, where  $DMC^*$  has ample time to isomerize before being deactivated by colliding with inert gas. As the pressure is increased these isomerizations

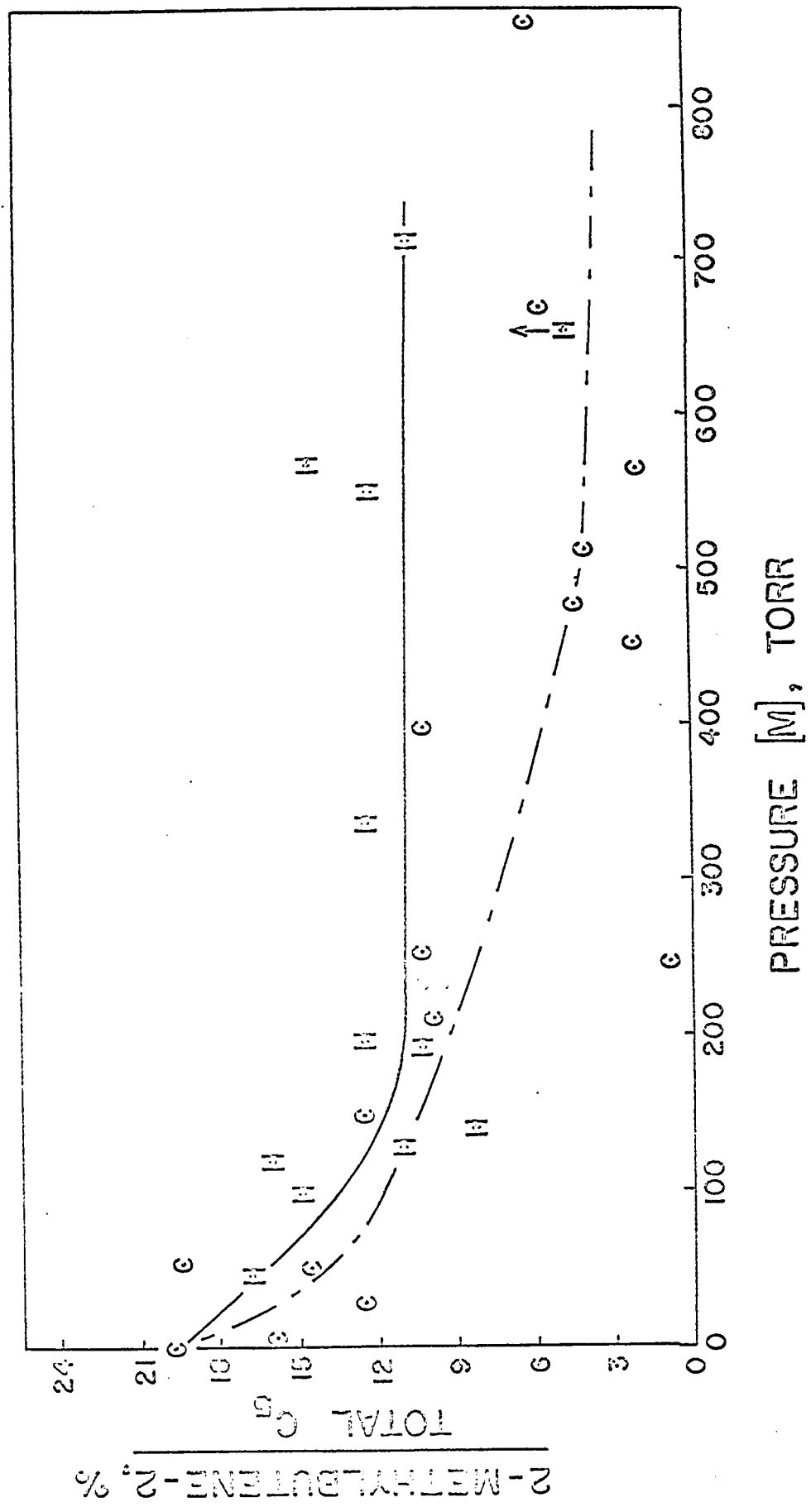
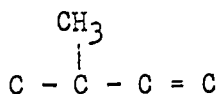


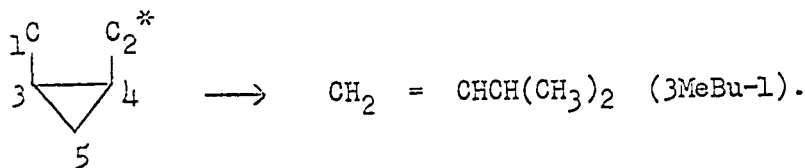
Figure 10 2-Methylbutene-2 Yield vs Inert Gas Pressure

play a less important role--so, too, does singlet methylene, as now it is being converted to the triplet state. As seen in the figure, triplet methylene clearly does not lead to the formation of 2-methylbutene-2; the enhanced ability of helium in bringing about this compound is further evidence for the non-reactivity of triplet methylene in this regard--the fewer the number of triplet molecules brought about (i.e. the larger the percentage of singlet molecules left) the greater will be the percentage yield of this compound.

3-methylbutene-1



The characteristic plot of 3-methylbutene-1 as a function of pressure is shown in Figs. 11 and 12. There have been many mechanisms put forth to explain the appearance of this compound; as seen from its structure, it cannot be explained by methylene insertion either in a carbon-hydrogen single bond or across a carbon-carbon double bond. Before touching on these points, it should be pointed out that Frey (11) does not mention 3-methylbutene-1 as a product of the reaction of singlet methylene with cis-butene-2, but in a later work (33) he does. Setser and Rabinovitch (26) also report this compound. Experimental results show an extremely rapid decrease in the percentage yield of 3-methylbutene-1 with only slight (initial) increases in pressure. As far as devising a mechanism for the behavior with singlet methylene, Setser and Rabinovitch invoke an excited dimethylcyclopropane mechanism as well as a singlet methylene abstraction one. By the former mechanism,



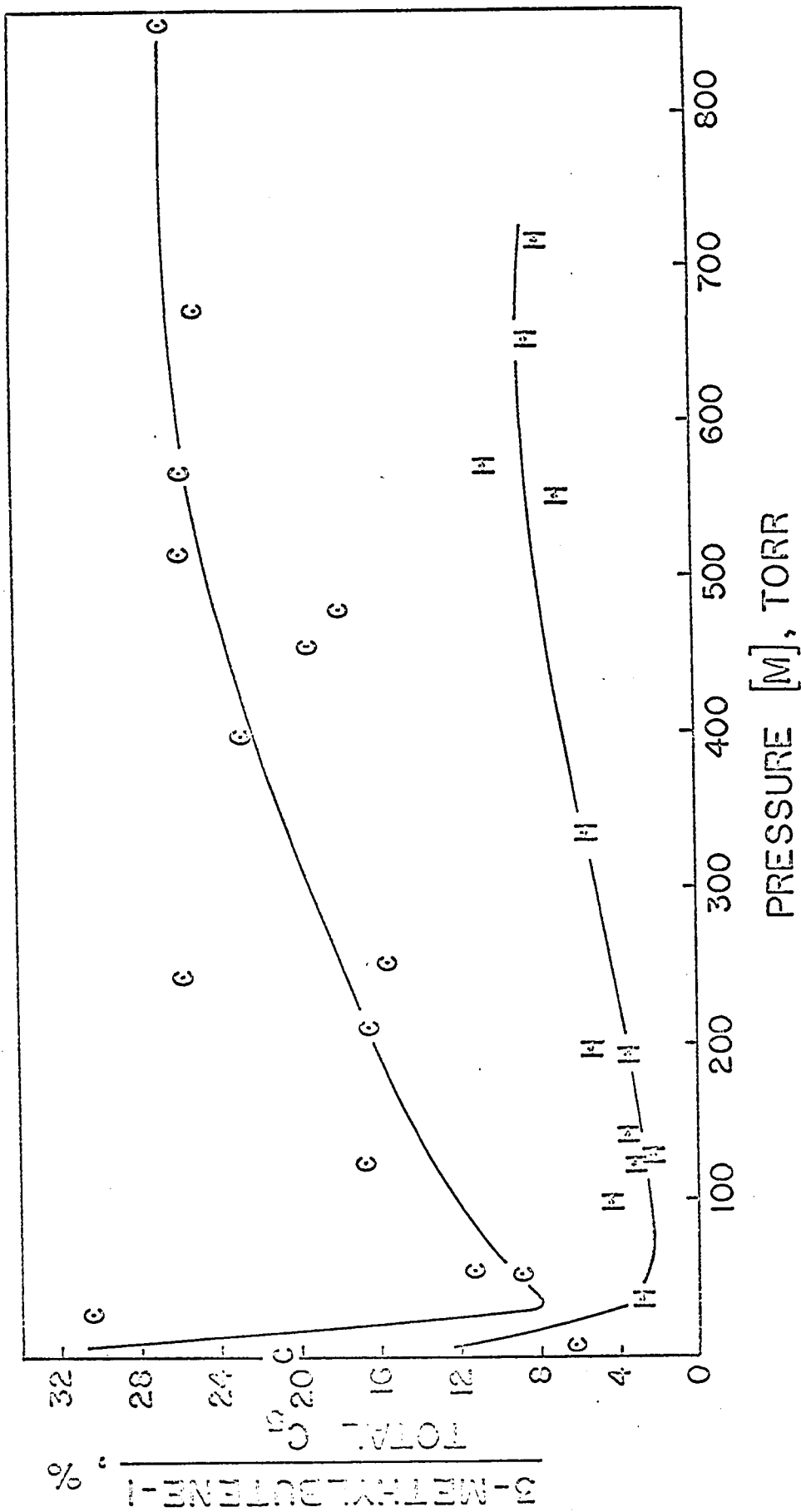


Figure 11 3-Methylbutene-1 Yield vs Inert Gas Pressure

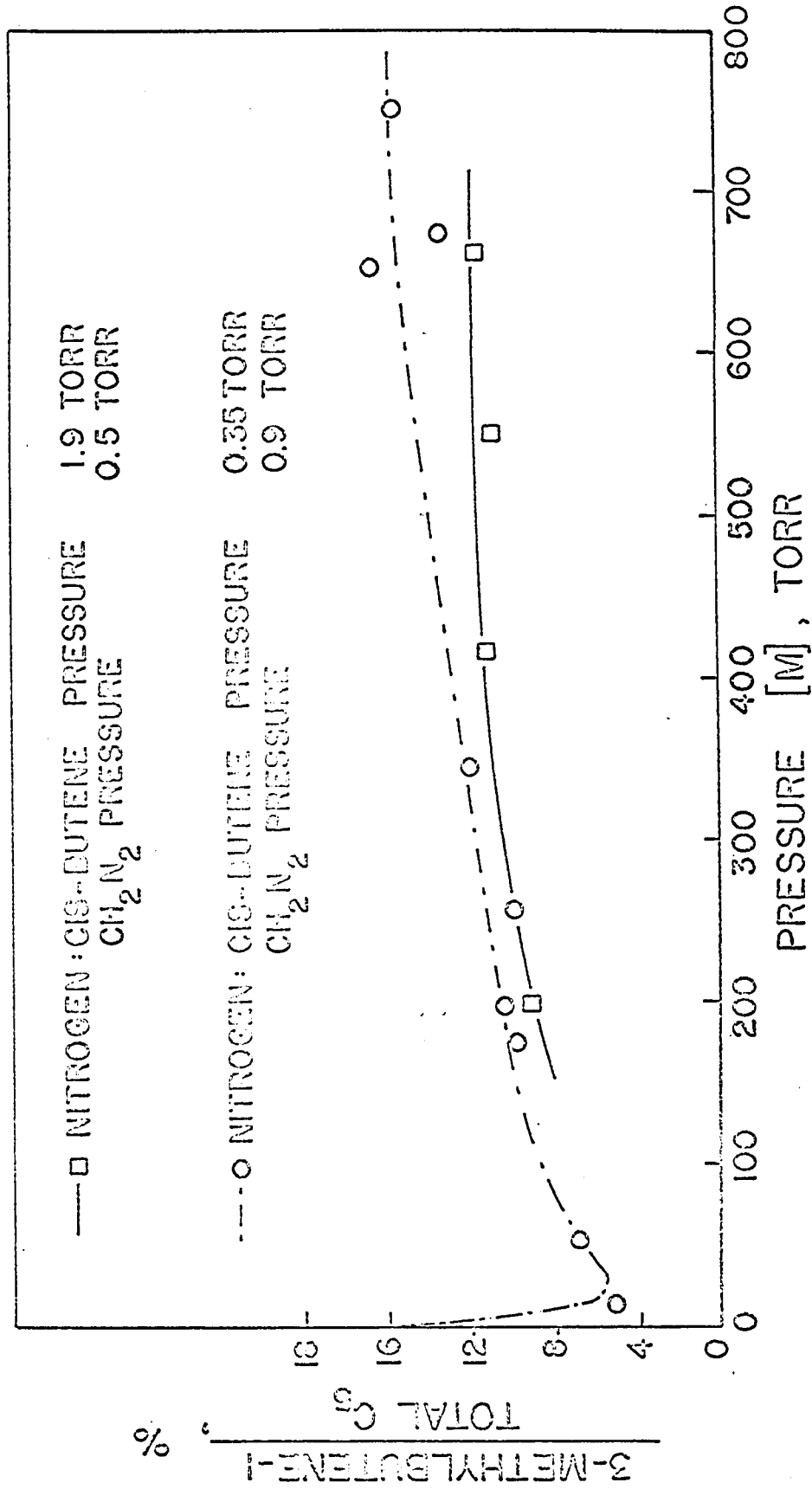
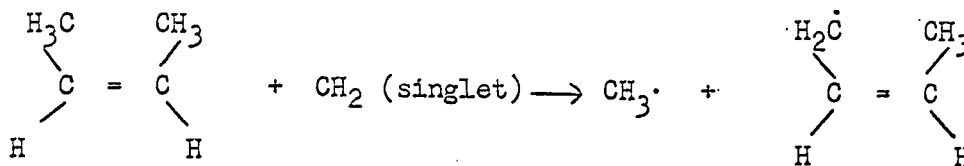


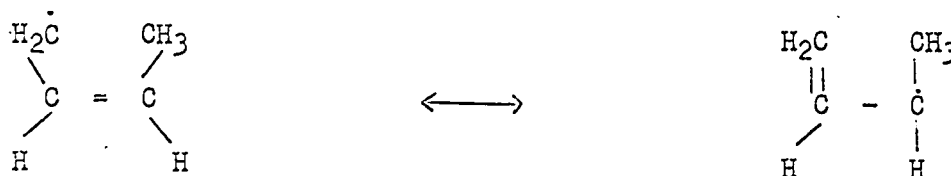
Figure 12 3-Methylbutene-1 Yield vs Inert Gas Pressure, Showing Effect of Raising Partial Pressure of Cis-Butene-2

For this reaction to occur requires a hydrogen migration from carbon (1) or (2) to carbon (5) with subsequent or simultaneous breaking of a carbon (4) - carbon (5) bond (or, indistinguishably, a rupture of a carbon (3) - carbon (5) bond). Alternatively, methyl group migration between (3) and (4) would give the same results.

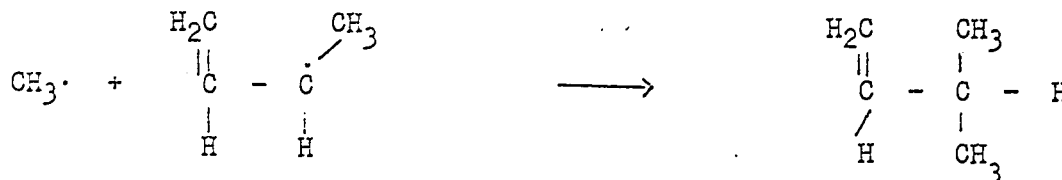
An alternative mechanism involves singlet methylene abstraction of hydrogen from cis-butene-2 to give methyl and cis-butenyl radicals:



Then,



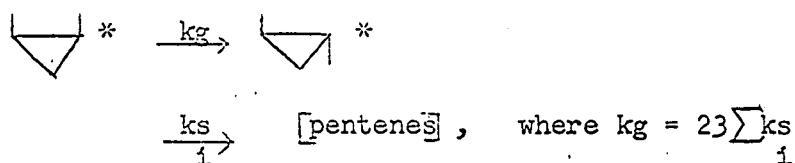
followed by recombination,



An abstraction scheme would be expected to be only slightly sensitive to pressure changes, inasmuch as the scheme does not include "hot" (vibrationally excited) molecules. Clearly, then, a singlet abstraction mechanism is non-operative here. An interesting aspect of this problem now arises. In an experiment performed with cis-1,2 dimethylcyclopropane (10), this compound was isomerized and decomposed by thermal methods. The

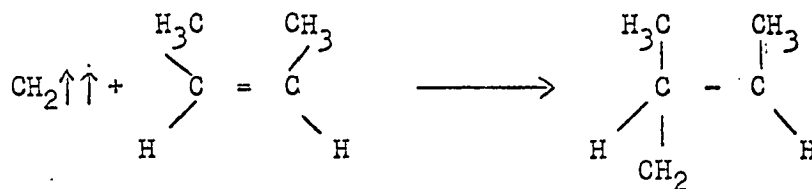
usual geometrical isomerization was found (i.e. cis- isomerizes to trans DMC). In addition, the usual structural isomerization products (cis- and trans-pentene-2, 2-methylbutene-1 and 2-methylbutene-2) were found; however, only minor amounts of 3-methylbutene-1 were found, even at the lowest pressures of cis-DMC studied (6.5 mm Hg). Investigation of this isomerization at pressures lower than this pressure may reveal increases in the percent yield of 3-methylbutene-1, in view of the findings in this thesis. In this present work, for instance, if no experiments were performed at pressures of inert gas below about 25 mm Hg, the sharp decrease in the yield of this compound with slight increases in the pressure of inert gas would have gone unnoticed. Since dimethylcyclopropane bath molecules (Flowers and Frey) may be more efficient as cooling third bodies than  $\text{CF}_4$  (this present work), the failure to work at pressures lower than 6.5 mm Hg may be the reason why no 3-methylbutene-1 is observed. In this regard, Setser and Rabinovitch observe a sharp decrease in the combined percent yields of 3-methylbutene-1 and 2-methylbutene-1 with initial small increases in pressure of bath molecules (cis-butene-2); at "zero" pressure, the combined yields are about 20 percent of the total, but by the time 5 mm Hg of reactants is reached, the yield of the methylbutenes-1 has dropped to about 5 percent of the total. If this is the combined yield of both 3-methyl- and 2-methylbutene-1, the separate yield of 3-methylbutene-1 cannot but be less than 5 percent. At any rate, until proven otherwise, the conclusion drawn in that work (Flowers and Frey) still stands, namely that in the thermal isomerization of dimethylcyclopropane, 3-methylbutene-1 is not formed. If this is the case, the isomerization of DMC as done thermally should proceed by a different mechanism than the isomerization of the hot DMC produced chemically (by singlet  $\text{CH}_2$  addition to cis-butene-2).

This does not seem plausible; perhaps the difference observed is simply a matter of the dimethylcyclopropanes formed by two different methods having different amounts of energy. Some indication of the reaction mechanism can be gleaned from the present work. Flowers and Frey (10) have shown that the geometrical isomerization of DMC\* proceeds at a faster rate than the structural isomerization, i.e.



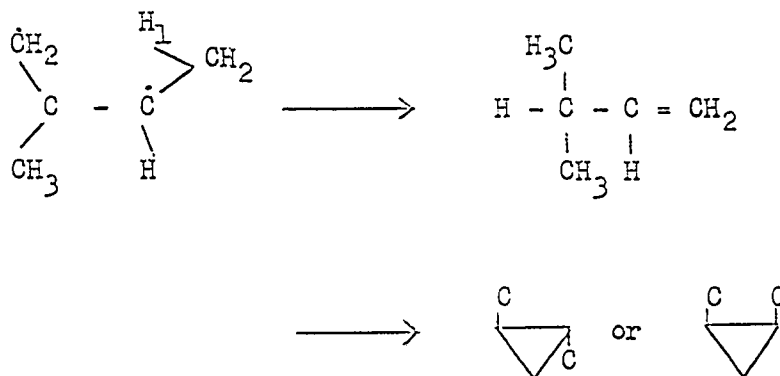
Clearly, there is a difference in activation energy between geometrical and structural isomerization. If this excess energy may be removed by collision with a third body, the reaction path requiring the highest amount of energy will be the most affected. According to the present work, there is, as pointed out earlier, a sharp decline in the percent yield of 3-methylbutene-1 with initial increase in pressure. There is, then, the possibility that relatively few collisions are needed to remove the amount of energy over and above that needed for this structural isomerization.

As seen from the figure, 3-methylbutene-1 yields increase with increasing concentration of triplet methylene. That 3-methylbutene-1 is produced by the reaction of triplet methylene has been pointed out by Frey (33) and Duncan and Cvetanović (13). A mechanism proposed involves a triplet addition complex followed by the appropriate migrations to produce 3-methylbutene-1:



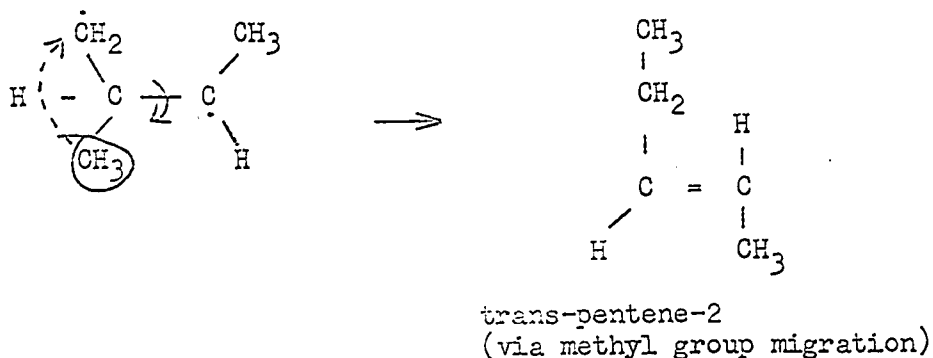
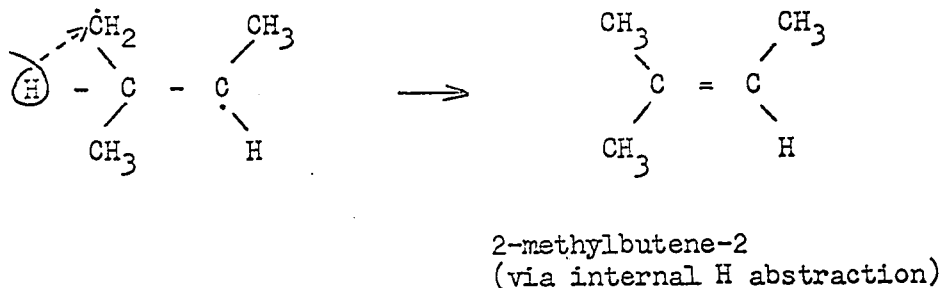
Several reaction paths are now available for this intermediate:

- a) the (cis) addition product may close immediately to give cis-1,2 dimethylcyclopropane.
- b) the cis addition product may rotate around the uncoupled double bond to give the analogous trans- addition product, which then closes to give trans-1,2 dimethylcyclopropane.
- c) the methylenic carbon may internally abstract  $\text{H}_\perp$  in a typical three-center type manner to give 3-methylbutene-1, as follows:



Theoretically, similar steps may account for the other pentene products, although not as straightforward as internal abstractions and requiring hydrogen and methyl group migrations. For instance, if 2-methylbutene-2 appears by this mechanism, the presence of increasing amounts of triplet methylene would result in the formation of greater yields as the pressure increases; this does not occur. This type of mechanism may be invoked to explain the occurrence of trans-pentene-2--this would involve a methyl group migration between vicinal carbon atoms. If one puts forth this

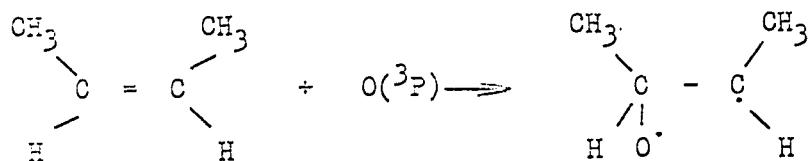
argument, there is no reason why there should not be a hydrogen migration between these same vicinal carbon atoms--that there is none is evidenced by the lack of 2-methylbutene-2 in this pressure region. The mechanism is:



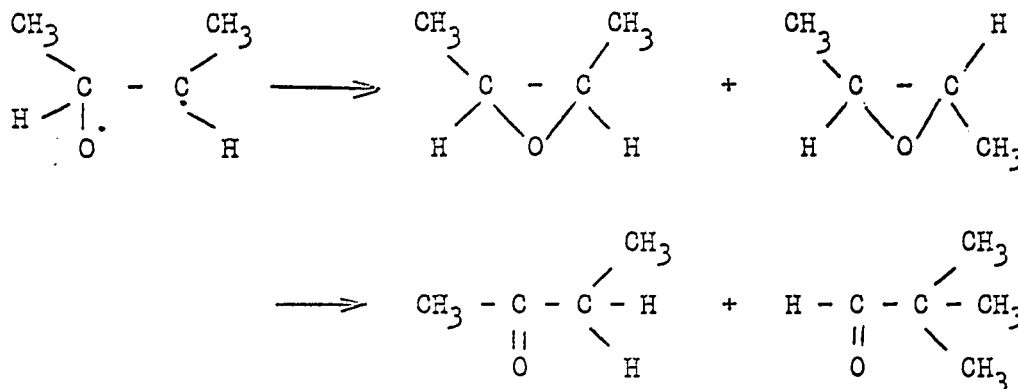
As indicated by Anet et al (16), the addition complex formed by the reaction of cis-butene-2 would be expected to be in the triplet state, if the law of spin conservation is obeyed. In order to re-form carbon-carbon bonds, this complex must undergo a triplet to singlet transition. Alternatively, according to Frey (33), the complex may isomerize (before the transition to singlet) to the triplet state of the pentene in question which then undergoes the triplet to singlet transition. If this were the case, one would expect nearly equal percentage yields of cis- and trans-pentene-2 at high pressures of inert gas; this assumes, however, that the time needed for rotation around a carbon-carbon bond is short compared

with the time needed for the collision-induced transition from the triplet to the singlet state. There can be little doubt that this triplet to singlet transition of the complex is quickened by the presence of inert gas, in much the same way that singlet methylene is converted to its ground state triplet; with the complex, however, the ground state would probably be a singlet.

As mentioned previously, the formation of 3-methylbutene-1 may be explained by various migration mechanisms. Theories involving methyl group and hydrogen migrations are not new, being quite common in organic rearrangements; in fact some examples of this phenomenon show marked resemblance to the methylene - cis-butene-2 experiments. Cvetanović, (22, 23) using photosensitizing procedures, has prepared oxygen atoms in their ground electronic states  $O(^3P)$  and then subsequently caused these atoms to react with olefinic double bonds. The expected ring compounds (epoxides), analogous to the cyclopropanes (formed when methylene adds across an olefinic double bond) were found along with certain carbonyl compounds; the appearance of these compounds can be most easily explained by invoking various migration mechanisms as well as radical splits and recombinations:



According to Cvetanović, this triplet addition product may cyclize (before or after carbon-carbon bond rotation) to give compounds analogous to 3- and 2-methylbutene-1.

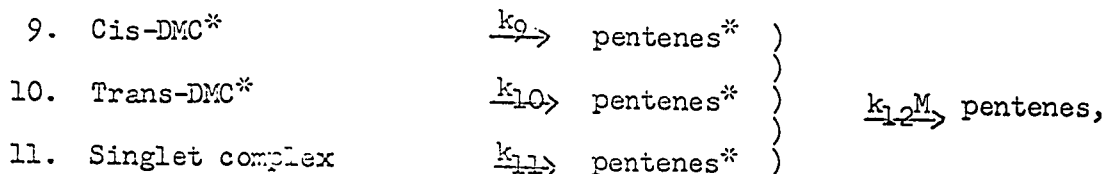


A major difference between the oxy-butene radical and the methylene-butene diradical appears to be their respective lifetimes; more will be said concerning this behavior when the experiments performed with added amounts of molecular oxygen are discussed.

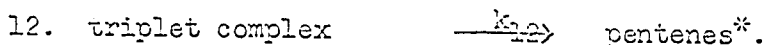
The steady-state treatment

The steady state scheme is reproduced below. It is essentially the same scheme reported earlier in this work, but is reprinted here for convenience. The scheme is:

1.  $\text{CH}_2$  (triplet) + cis-butene-2  $\xrightarrow{k_1}$  Triplet complex
2.  $\text{CH}_2$  (singlet) + cis-butene-2  $\xrightarrow{k_2}$  Singlet complex
3. Triplet complex  $\xrightleftharpoons[k_{-3}]{k_3}$  cis-DMC\*
4. Singlet complex  $\xrightleftharpoons[k_{-4}]{k_4}$  cis-DMC\*
5. Triplet complex  $\xrightleftharpoons[k_{-5}]{k_5}$  trans-DMC\*
6. Cis-DMC\*  $\xrightleftharpoons[k_{-6}]{k_6}$  trans-DMC\*
7. Cis-DMC\*  $\xrightarrow{k_7 M}$  cis-DMC
8. Trans-DMC\*  $\xrightarrow{k_8 M}$  trans-DMC



where "triplet complex" and "singlet complex" refer to the complexes formed by triplet methylene with butene and singlet methylene with butene--these complexes would be expected to have different structures. "Pentenes" refers to all C<sub>5</sub> hydrocarbons with the exceptions of cis- and trans- 1,2-dimethylcyclopropanes. An asterisk represents an excited molecule which may isomerize or be collisionally deactivated. An objection may be raised when "pentenes" is used rather than making reference to each individual pentene--cis-DMC\*, trans-DMC\* and the singlet complex all may not give the same pentenes. Inclusion of each pentene would have greatly complicated the steady state solution for the above scheme. In addition, a step involving the decomposition of the triplet complex to "pentenes" was neglected, i.e. no provision was made for



This is not too serious in view of the fact that direct triplet intervention accounts only for 3-methylbutene-1 and trans-pentene-2; as before, separation of "pentenes" into each olefin would greatly complicate the steady-state derivation. Still a further simplifying factor has been assumed--namely, that the presence of either complex is not directly pressure dependent. While it may be said with a reasonable amount of certainty that the complexes involved are of a radical nature, it is almost as certain that they are "hot" in the sense that they are vibrationally excited as well. Collisions will deactivate these species but may have little effect on their behavior as radicals. Since it is not

known whether the vibrational character or the radical nature of the complexes is the deciding factor in their reactions, the simpler case, where it is assumed that the complex shows no direct pressure dependency was chosen. Invoking the steady-state assumptions for the reactive species (the complexes and the asterisked compounds) results in the following relationship:

$$\frac{[M][\text{PENTENES}]}{[\text{Cis-DMC}]} = k + k' M, \quad (\text{A})$$

where M is the pressure of inert gas, "pentenes" is the total percent of five-carbon olefins formed in a run performed at pressure M, and "cis-DMC" is the percent yield of this compound, also at pressure M. The k and k' terms<sup>1</sup> represent combinations of the rate constants encountered in the foregoing scheme. A plot, then of the left hand side of equation (A) vs. the right, should result in a straight line of slope k' and intercept k (which must equal zero). This plot is shown in Fig. 13. From this plot it is seen that the equation is valid in the triplet as well as the singlet range. It should also be noticed that there is a difference in slope for He and CF<sub>4</sub>. That this is so would be expected from steps 7, 8, and 12 in the foregoing scheme. A similar solution to the scheme involving trans-

$$1 \quad k' = \frac{(k_9 + k_{10} / K_6 + k_{11}k_4)}{k_5k_3 + k_6}$$

$$k = \frac{(k_{10} + k_{-5} + k_{-6}) (k_9 + k_{10} / K_6 + k_{11} K_4)}{k_8 (k_5K_3 + k_6)}$$

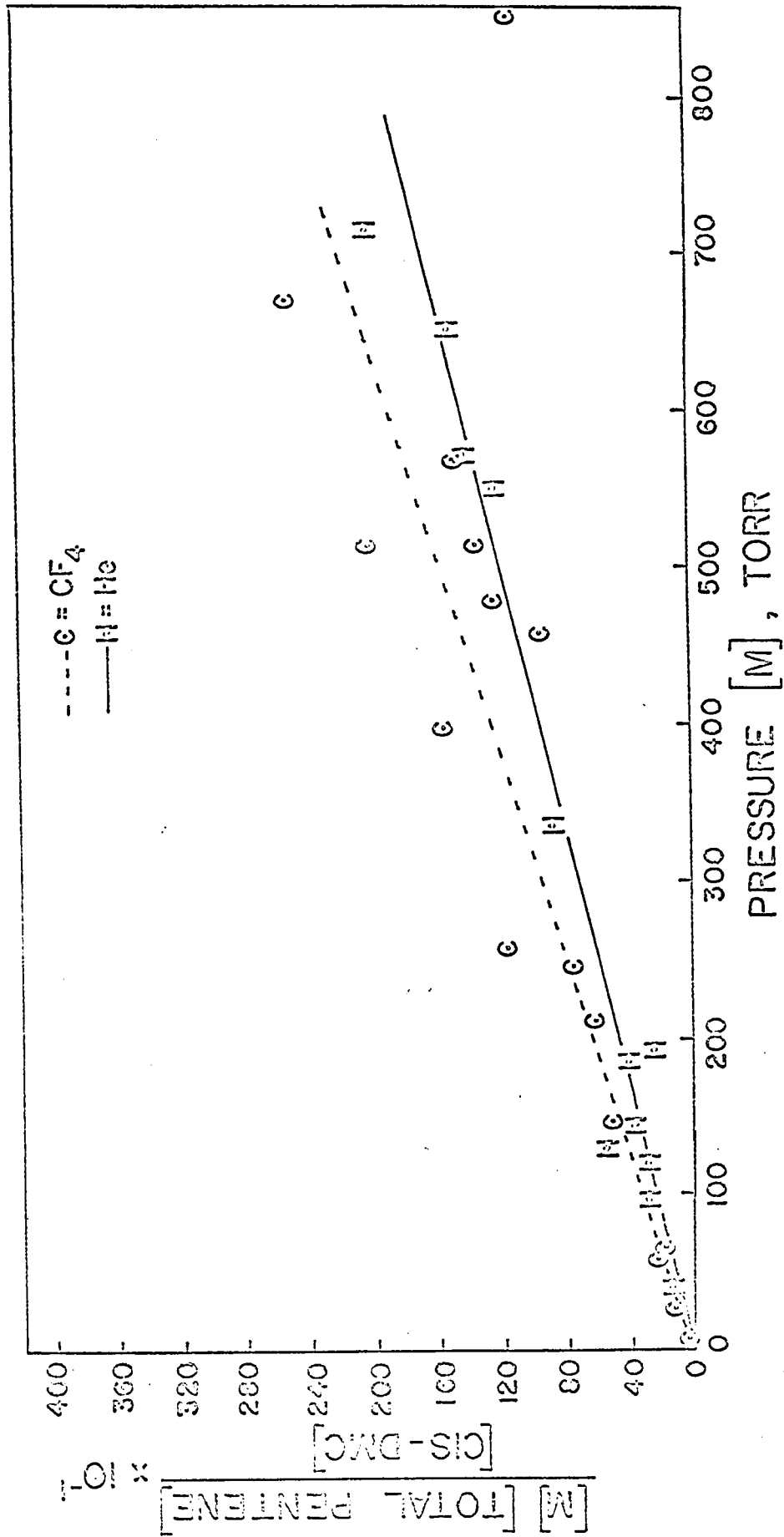


Figure 13 Steady-State Plot for Cis-Butene - Diazomethane Photolysis in the Presence of Inert Gas

DMC (rather than cis-DMC) may also be derived. Owing to the complex nature of  $k$  and  $k'$ , and the assumptions inherent in the overall scheme, no attempt was made to arrive at the analytical solution for the individual rate constants.

The reactions with molecular oxygen

Conceivably, molecular oxygen, in the  $^3\Sigma_g^-$  ground state may react directly with methylene and/or with the complex formed in the reaction of methylene with cis-butene-2. The question arises over the relative rates of reactions between oxygen in its ground state and methylene in its ground ( $^3\Sigma_g^-$ ) and excited states (as well as between ground state oxygen and the radical complexes, which may be in a ground or excited state).

In this regard, the derivation developed by Eyring (39) (along the lines of absolute rate theory) reveals that the specific rate of a chemical reaction is dependent on a "transmission coefficient" which represents the fact that in any chemical reaction not all species which possess the necessary energy to cross the potential energy barrier do this; some, even though they reach the top of this barrier return to the original state. This transmission coefficient,  $t$ , then, is actually the probability that a reaction which has arrived at the activated state will proceed to the product state. Hirschfelder and Wigner (40) have shown that for reactions concerning molecules in their ground states,  $t$  is close to unity; however, in reactions involving electronically excited species it is very often less than unity (41). Thus, the reaction between oxygen and triplet methylene would be expected to proceed at a faster rate (other things equal) than the reaction of oxygen with singlet ( $^1A_1$ ) methylene, since the former reaction involves only ground states. Another way of

looking at this situation involves the realization that before the two unpaired electrons on the oxygen atom may bond with those on singlet methylene, these latter electrons must receive energy in order to undergo unpairing before they may be involved in bonding<sup>1</sup>; this leads to an energy of activation above that required for the triplet-triplet reaction, and on these grounds one would expect the triplet-triplet reaction to occur more readily. Assuming that methylene reacts with butene before reacting with O<sub>2</sub>, either a triplet complex or a singlet one would result, depending on whether the reaction is with triplet or singlet methylene. Again, for the reasons just mentioned, one would expect the reaction of O<sub>2</sub> with the triplet complex to be more rapid than the one with the singlet complex.

This state of affairs has experimental verification, as seen in Fig. 14. It is noted that the triplet behavior of methylene (which would be evident in increased percent yield of trans-DMC) is sharply reduced by the admixture of 3% (total pressure) O<sub>2</sub>. This behavior in the high pressure region is, in fact, evidence for believing that numerous inert gas collisions are necessary for effecting the singlet to triplet transition in methylene, since if this were not so, the addition of small amounts of "scavenger" should have only little effect. In contrast, molecular oxygen appears to react very rapidly with the triplet states involved here. Since there is no evidence as to the ratio of lifetimes of triplet methylene to the triplet complex, little may be said as to whether O<sub>2</sub> reacts mainly with methylene itself or mostly with the triplet

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1 or, the two paired electrons of (<sup>1</sup>A<sub>1</sub>) methylene may be involved in the unpairing.

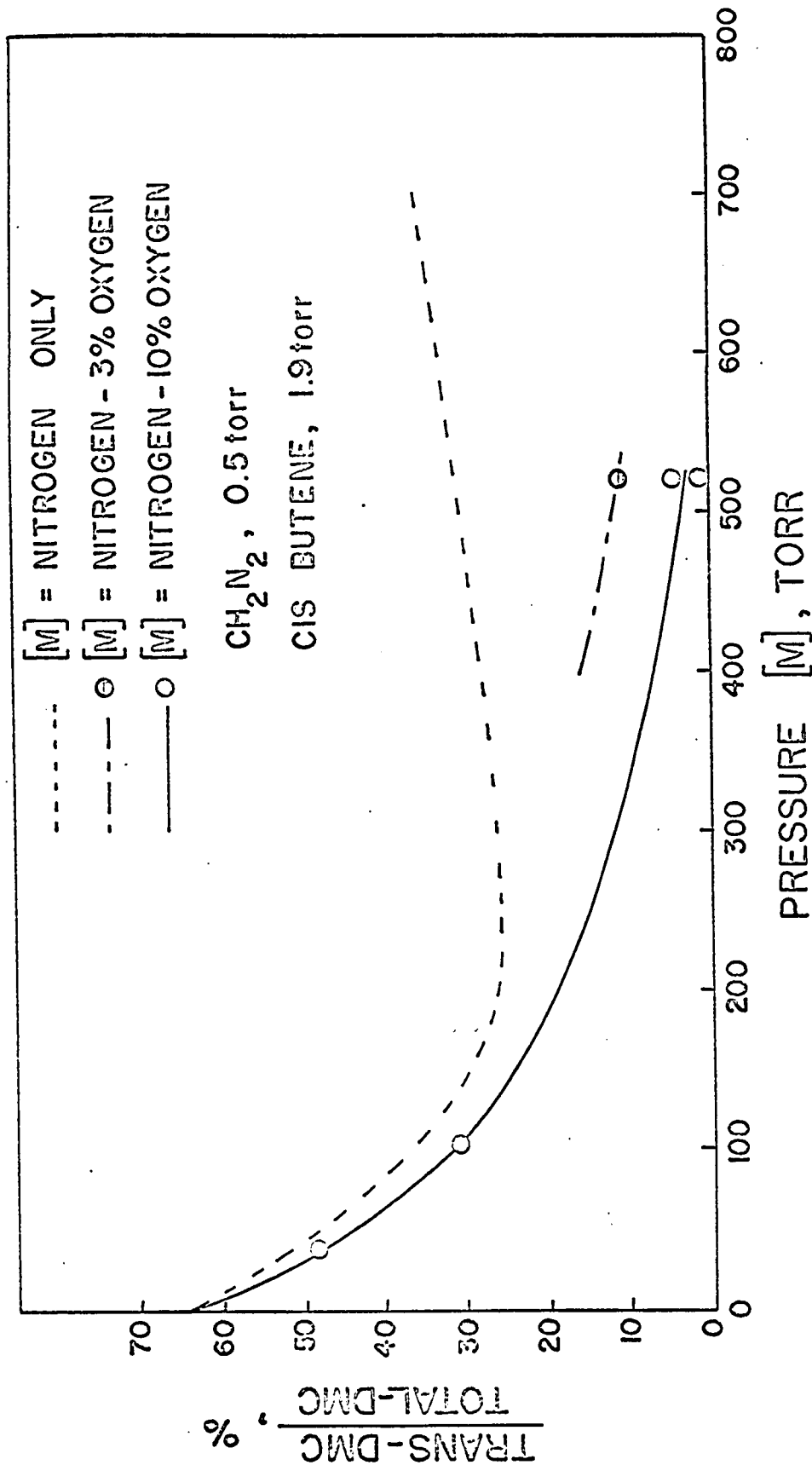


Figure 14 Effect of Adding Molecular Oxygen on Percent Trans-1,2-dimethylcyclopropane of the Total Dimethylcyclopropane Yield

intermediate. In this regard, it is advantageous to compare the results found in this present work with those found by Cvetanović (23). In that work, molecular oxygen was added to systems containing cis-butene-2 and  $O(^3P)$  (analogous to the present work involving additions of molecular oxygen to systems containing cis-butene-2 and  $(^3\Sigma)$  methylene). The formation of epoxides (analogous to the dimethylcyclopropanes) was unaffected by added molecular oxygen (but the compounds formed by group migration were). In contrast with the methylene case, it would appear that in the epoxide situation either the reaction of  $O_2(^3\Sigma)$  with  $O(^3P)$  is less rapid than the reaction of  $O_2(^3\Sigma)$  with  $CH_2(^3\Sigma)$ , or the reaction of  $O_2(^3\Sigma)$  with the butene-oxygen atom diradical is slower than the reaction of  $O_2(^3\Sigma)$  with the butene-methylene radical, or both. The latter possibility may be due to a shorter lifetime of the butene-oxygen diradical when compared with its methylene counterpart. It is interesting to note that in the singlet region (low pressure of M) the effects of adding small amounts of molecular oxygen (10% of the total pressure) are less drastic than they are in the triplet region. True, in the low pressure region there is only a relatively small number of  $O_2$  molecules (compared to the number in the high pressure region). An objection might be that at high pressure the effect should be more marked for the simple reason that there are more  $O_2$  molecules present at these pressures than at lower ones. This argument is not valid since the same relative collision frequency (of  $CH_2$  with  $O_2$ ) should occur at all pressures. Moreover, an experiment was done at high pressure where the number of  $O_2$  molecules was the same as a low pressure experiment; this involved performing a run at 525 torr (of which 3% was  $O_2$ ). This resulted in the same number of  $O_2$  molecules as appeared

at 150 torr containing 10% O<sub>2</sub>. The same conclusion as before may be drawn--the effect of added oxygen is much more pronounced in the high pressure region than in the low pressure one. This is an added indication that there are two distinct species of methylene present--singlet at low pressures of inert gas and triplet at higher pressures.

Too few runs were performed with added amounts of O<sub>2</sub> to warrant individual plots of the behavior of all products as a function of pressure. The results are given rather, in table 10. From these results it will be noticed that the percentage yields of 3-methylbutene-1, trans-pentene-2 and trans-DMC are most affected by the addition of molecular oxygen. Cis-DMC, cis-pentene-2 and 2-methylbutene-2 are not; these results confirm the statement made earlier concerning these three--that these compounds are formed in the high pressure region through the intervention of triplet methylene.

Table 10

Relative Areas Obtained in GLC Analysis of the  
Photolysis of Diazomethane (0.5 torr) in the Presence of  
Cis-Butene-2 (1.9 torr) and Nitrogen (containing 10% O<sub>2</sub>)

Percent Yields Are Given in Parentheses

<u>N<sub>2</sub>+O<sub>2</sub>, torr</u>	<u>3MeBu-1</u> <sup>1</sup>	<u>TDMC</u>	<u>TPe-2</u>	<u>CDMC</u>	<u>CPe-2</u>	<u>2MeBu-2</u>
32	Tr <sup>2</sup> (0)	405(15.7)	584(22.6)	468(18.1)	811(31.4)	316(12.2)
107	Tr (0)	165(10.4)	368(23.1)	376(23.7)	585(36.8)	95 (6.0)
515	Tr (0)	21 (2.2)	50 (5.1)	443(45.6)	330(33.9)	128(13.2)
517	Tr (0)	Tr (0)	Tr (0)	1297(67.9)	514(26.8)	101 (5.2)
515 <sup>3</sup>	Tr (0)	38 (5.6)	32 (4.7)	293(42.3)	194(28.3)	127(18.6)

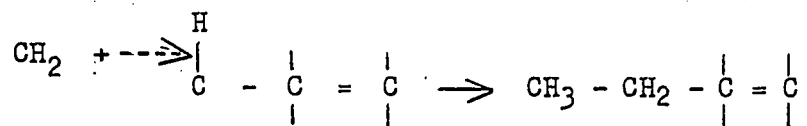
1 3MeBu-1, 3-methylbutene-1; TDMC, trans-1,2-dimethylcyclopropane;  
TPe-2, trans-pentene-2; CDMC, cis-1,2-dimethylcyclopropane; CPe-2,  
cis-pentene-2; 2MeBu-2, 2 methylbutene-2

2 Trace

3 With 3% molecular oxygen

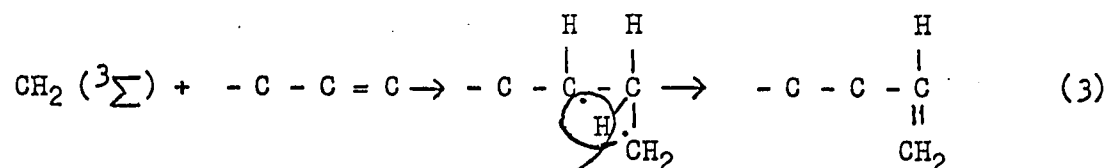
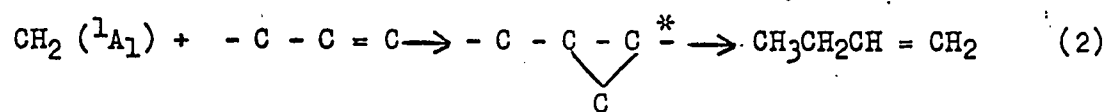
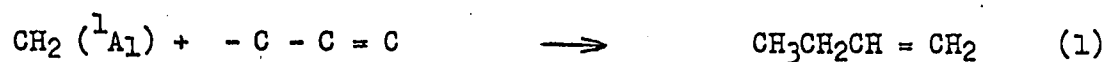
The reactions of methylene with simple olefins

As was mentioned in earlier investigations (11, 26, 37) (and verified in this present work), the decomposition of diazomethane (alone) results in the formation of simple olefins--ethylene, propylene and butene-1 being the ones produced in highest yields. If one were to follow the yield of one of these with inert gas pressure, for example, butene-1, information could be obtained which would support the conclusions reached earlier in this work regarding singlet vs. triplet insertion, etc. Apparently (intramolecular rearrangements aside), the higher homolog is formed by the insertion of methylene into the carbon-hydrogen bond vicinal to the carbon-carbon double bond (i.e. the allylic carbon-hydrogen bond) of the lower homolog. Thus, in the formation of butene-1 the scheme would appear to be:



The corresponding cyclic compound, methylcyclopropane, if produced at all, was not identified (in the GLC analyses there were some unidentified peaks of relatively small area compared with the peak area of butene-1). Previous experience would predict that if appreciable amounts of propylene were present, the cyclic product should be found. Besides direct insertion of methylene into a carbon-hydrogen bond, a reaction involving a direct CH<sub>2</sub> addition to the double bond resulting in a vibrationally excited species which isomerizes to butene-1 is plausible. This is not unlike the situation found in the formation of 3-methylbutene-1 from the

reaction of methylene with cis-butene-2. In order to explain the formation of butene-1, an internal hydrogen abstraction mechanism (akin to the one proposed in reference to 3-methylbutene-1) may be proposed as well as one involving the isomerization of "hot" methylcyclopropane. Conceivably, as in the case of 3-methylbutene-1, butene-1 may be found in both singlet and triplet regions. Since triplet methylene does not insert in carbon-hydrogen bonds, no butene-1 should be found in the triplet region, if this type of mechanism is the only one operative. If an abstraction type mechanism is involved, butene-1 should appear in the triplet as well as the singlet regions. The mechanisms then, are:



As mentioned earlier, these three mechanisms would account for the appearance of butene-1 throughout the entire pressure range of inert gas. This expectation was verified experimentally. (Since the GLC analyses were not performed under conditions of constant sensitivity, absolute yields of butene-1 were not measured--rather, the GLC peak area of this compound was compared to the peak area of unreacted cis-butene-2 which was always about 10 to 20 fold larger than that for butene-1. Since the same amount of cis-butene-2 was used as substrate throughout all photolysis, this was taken as a standard with which to compare the yields of

butene-1. An objection would be that the amounts of cis-butene-2 left unreacted would depend on the nature of the methylene attacking it; eg., singlet methylene may react more readily with cis-butene-2 than triplet methylene does, thereby leaving a smaller amount unreacted. This is only a minor fault, since in all cases reaction was carried out to only a few percent completion (less than 10%)--in other words, the amounts of unused cis-butene-2 are large compared with the amount reacted, making errors based on the unused portion very small. The relative percents of butene-1 measured in this manner are shown in table 11). The results of the thermal reaction of diazomethane with cis-butene-2 are given in this table for later reference. In this table, the results of experiments performed with He and  $CF_4$  are compared;

Table 11a

Yield of Butene-1 as a Percent of Unreacted Cis-Butene-2  
in the Photolysis of Diazomethane (0.8g torr) - Cis-Butene-2  
(0.3g torr) Mixtures in the Presence of Third Body

<u>He Pressure,</u> <u>torr</u>	<u>Butene-1 %</u> <u>Cis-Butene-2</u>	<u>CF<sub>4</sub> Pressure,</u> <u>torr</u>	<u>Butene-1 %</u> <u>Cis-Butene-2</u>
96	5	8	5
142	6	398	2
171	5	459	1
187	5	516	5
191	4	568	4
338	6	666	5
654	5	667	5
716	6	857 <sup>1</sup>	2

Table 11a (cont'd)

<u>(N<sub>2</sub> + 10% O<sub>2</sub>) Pressure,</u> <u>torr</u>	<u>Butene-1 , %</u> <u>Cis-butene-2</u>
32	1.1
107	0.8
517 <sup>2</sup>	0.6
550	Trace

Table 11b

Yield of Butene-1 as a Percent of Unreacted Cis-Butene-2  
in the Thermolysis<sup>3</sup> of Diazomethane (0.8g torr) - Cis-Butene-2  
(0.6g torr) Mixtures in the Presence of Nitrogen

<u>N<sub>2</sub> Pressure,</u> <u>torr</u>	<u>Butene-1 , %</u> <u>Cis-Butene-2</u>
0	0.13
124	0.06
220	0.2
570	Trace
702	0.2

- 1 Estimated
- 2 3% added O<sub>2</sub>
- 3 220<sup>±</sup> 5°C

within experimental error they appear identical. Worthy of note, however, is the appearance of butene-1 at pressures of inert gas where large amounts of triplet methylene are present. Clearly, then a free radical intermediate is in keeping with this behavior (rather than singlet insertion). The results obtained with small added amounts of molecular oxygen (as before, 10% of the total pressure) indicate that the production of butene-1 is sharply curtailed--this is in keeping with a (triplet) diradical nature of the intermediate. Too few runs were done at low pressures of inert gas to warrant comment on the effect of adding O<sub>2</sub> in the singlet region; one would expect the formation of butene-1 in this region not to be drastically different from the results obtained without added oxygen. This should be so due to singlet insertions and/or isomerizations of excited cyclic compounds.

The Mercury Photosensitized Reaction: Diazomethane and Cis-Butene-2

If the laws concerning spin conservation in chemical reactions are valid, then the reaction between mercury excited to the <sup>3</sup>P<sub>1</sub> state and diazomethane (presumably in singlet ground state) should result in the formation of triplet methylene directly (without the intervention of inert gas), the production of CH<sub>2</sub> (<sup>1</sup>A<sub>1</sub>) being strictly forbidden. The advantages of this situation are such that the behavior of triplet methylene (and its addition products with cis-butene-2) may be followed at very low substrate pressures (where isomerizations, decompositions etc. are important), as well as high pressures (where these secondary reactions are not as important). There would be no need, then, to interpret results in the light of possible reactions of singlet methylene. Experiments along these lines suffer from the severe handicap that diazomethane would be expected to

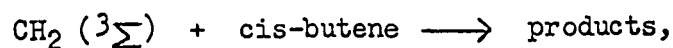
absorb the mercury resonance line, since it has been shown that  $\text{CH}_2\text{N}_2$  exhibits a strong absorption region in the neighborhood of this line (42, 43); experiments done with diazomethane verified these earlier works. Still, even though diazomethane competes favorably with  $\text{Hg} (^1\text{S}_0)$  as far as absorption of the resonance line is concerned, it was thought that at least some triplet mercury might react with diazomethane to form triplet methylene; it would remain, then, only to separate the results obtained from experiments performed with mercury vapor present from the results of experiments performed under exactly similar conditions except that mercury vapor would be excluded (i.e. running "blanks"). Differences, then, in the two sets of experiments could be attributed to the intervention of triplet methylene.

While, in theory, this might be possible, under actual experimental conditions the problems were insurmountable. In the first place, exposing diazomethane to the mercury resonance line resulted in the deposition on the quartz windows of the reaction vessel of a film of what appeared to be polythene; this was extremely opaque to the radiation employed, which made exact duplication of the blank runs virtually impossible. Even under conditions as adverse as these, it was apparent that the results of experiments performed with mercury vapor could not be distinguished from the results of experiments performed without the presence of mercury vapor. Thus, the "mercury photosensitized" reactions of diazomethane with both cis- and trans-butene-2 as performed in this work were no different from the results obtained from the "straight" photolyses done by Frey (11).

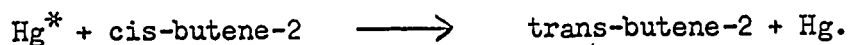
Since further investigations along these lines would not have

been worth the strenuous effort involved, experimentation was halted; moreover, photosensitization experiments involving ketene ( $\text{CH}_2\text{CO}$ ) which does not strongly absorb the mercury resonance line, were reported by Duncan and Cvetanović (13) about this time. Further investigations along these lines would be most fruitful.

In closing, it should be pointed out that the mercury photosensitized isomerizations of cis- to trans-butene-2 (and vice-versa) which had earlier been reported by Cundall and Palmer (14) were also observed in this present work; this, in fact, is another complicating factor in the quantitative interpretation of the results involving photosensitization. Experiments would have to be performed on the relative efficiencies of the reaction with diazomethane —



when compared to the photosensitized isomerization:



### The Nature of the Collisional Process

The whole question of the relative abilities of different inert gases in bringing about singlet to triplet transitions involves a study of energy transfer processes, a topic about which a great deal of knowledge is lacking.

Basically, the problem is this: the change in multiplicity of methylene involves a loss of electronic energy; since there is little known concerning the nature of the most highly excited electronic states, little can be said about the nature of the transitions involved. One of the things that is known is that in the two lowest states electronic transitions are inseparable from vibrational ones. This is shown in Fig. 18, page 114, where for these states the multiplicity is shown as a function of bond angle (or bending vibration). It would seem that knowledge of the relative probabilities (or rates) of energy transfer between various levels (electronic, vibrational, rotational and translational), both intramolecularly and intermolecularly, would go far in explaining the results obtained in this present work. Actually, since very little quantitative information concerning the intramolecular processes is available, it is hoped that the results obtained in this present work will add a little to this knowledge.

Electronic-electronic, vibrational-vibrational, etc. transitions in molecules have been well characterized through studies on molecular spectra. Only recently, and through refined experimental techniques, have intermolecular transitions (as they occur in collisional processes) been receiving the study they deserve as fundamentals in chemical processes. The aforementioned "refined techniques" conveniently fall into three cate-

gories. Dispersion methods, as used, for example, in measuring relaxation<sup>1</sup> times in shock tube studies, give useful information on intermolecular transitions concerning excited states having relatively little energy over the ground state; transitions usually dealt with are vibration-translation ones for polyatomic systems and vibration-vibration transitions in simpler (e.g. diatomic) collisions (45). Chemical excitation can be used in the study of vibration-vibration transitions and in higher energy vibration-translation studies, since one may, in theory, energize a system to high, but known, vibrational levels of the ground electronic state. An example of chemical activation involves the addition of H atoms to cis-butene to form highly excited (vibrationally) sec-butyl radicals presumably in the ground electronic state which are then collisionally deactivated by collisions with atoms (46) or molecules (47). The third technique involves fluorescence methods. Although not new, recent developments utilizing sharp emission lines and sensitive detectors (48) allow excitation to known electronic, vibrational and rotational levels. The course of subsequent de-energizations by third bodies allows insight into the exchange processes involved. Although methylene does not fluoresce, knowledge gained from transfer processes in fluorescing systems may go a long way in explaining reaction paths in methylene systems.

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1 "Relaxation" refers to a time lag involving internal energy (vibration, rotation, electronic) redistributions in excited species. When a molecule undergoes any process involving very rapid energy change the internal energy equilibrium lags ("relaxes") behind the translational energy equilibrium, so that the electronic/vibrational/rotational temperature of the molecule is not the same as the translational temperature. The term "relaxation" is applied in general to energy transfer processes, since these processes require finite time.

On the question of methylene transitions, one is faced with energy transfer problems which are very complex. Unlike species studied by dispersion methods, methylene carries a large amount of excess energy when prepared; unlike fluorescence problems, the exact state of the methylene is not known and unlike certain chemical activation researches, the methylene formed is not merely in an excited vibrational mode of the ground electronic state.

Theories have been devised by Zener (49) and Landau and Teller (50) to predict the probability of vibrational-translational energy transfer for diatomic molecules (this theory was later extended by Schwartz, Slawsky and Herzfeld, SSH) (51). Experimental information on energy transfer involving excited states of diatomics indicates that these theories are inadequate when higher energies are involved. In addition, transition probabilities for polyatomics (even those involving low energy transfers) are not as well established as they are for diatomic molecules. Very little information on energy transfers in excited polyatomic molecules is available, even with relatively simple collision partners such as helium. Certain facts, though, have emerged through study of these processes. Applying the SSH equation to large polyatomic molecules involving multi-quantum transitions, it is predicted that only small amounts of energy (of the order of magnitude 30 cal) may be transferred per collision (52). Available experimental information indicates, however, that up to several kcal/mole may be exchanged. In this regard, recent studies (53) on cyclopropane and dimethylcyclopropane indicate that energy  $\sim 15$  kcal/mole may be efficiently removed. Thus, presumably, for systems involving small changes in vibrational quanta (this situation corresponds to vibrational energies approaching the dissociation energy; in this vicinity levels are

closely packed), vibration-translation transitions are not necessarily required for efficient energy transfer, whereas for the case of high energy vibrations (and, therefore, widely spaced), transfer of quanta to translational degrees of freedom is necessary.

The inability to transfer large amounts of energy to very simple molecules is readily seen when studying photosensitized reactions. Consider the following array (54):

<u>Quenching Cross Section</u>			
<u>Quencher</u>	<u>Na(<sup>2</sup>P)</u>	<u>Cd(<sup>3</sup>P)</u>	<u>Hg(<sup>3</sup>P)</u>
He	0	0	0
N <sub>2</sub>	14.5	0.02	0.19
CO	28.0	0.14	4.07

The energies involved in these transitions are Na(<sup>2</sup>P-<sup>2</sup>S), 48 kcal; Cd(<sup>3</sup>P-<sup>1</sup>S), 87 kcal; Hg(<sup>3</sup>P-<sup>1</sup>S), 112 kcal. First of all, one notices the complete inability of helium to quench these excited states. This behavior is in strict agreement with SSH theory. Secondly, it would appear that since Cd\* and Hg\* require the loss of much energy, cooling of Na\* (which requires less) should occur at a greater rate. Even though this is, in fact, experimentally so, the argument is at once false, since the Na(<sup>2</sup>P-<sup>2</sup>S) transition proceeds with spin conservation, whereas cadmium and mercury transitions do not (and, on these grounds, quenching should be small). Since Cd(<sup>3</sup>P-<sup>1</sup>S) requires a loss of 87 kcal and Hg(<sup>3</sup>P-<sup>1</sup>S) requires 112, it would appear that quenching of Cd(<sup>3</sup>P) should be more favorable than quenching of Hg(<sup>3</sup>P). The fact that it is not probably indicates that the vibrational frequencies of the collision partners

are playing important roles. It would seem that an experimental study of quenching to the metastable states of mercury and cadmium would be of some use. The transitions  $\text{Cd}(^3\text{P}_1-^3\text{P}_0)$  and  $\text{Hg}(^3\text{P}_1-^3\text{P}_0)$  require less deactivation than  $\text{Na}(^2\text{P}-^2\text{S})$ ; moreover, spin is conserved in all three. Quenching with a large inert gas (eg. Xe) would be an excellent test of theory.

As mentioned earlier, energy transfer seems to be enhanced if the energy lost (or gained) in the collision process corresponds to a resonant or near resonant vibration frequency. Herzfeld and Litovitz (55) have dramatically demonstrated this fact by noting that vibrationally excited  $\text{O}_2$  ( $\nu = 1580 \text{ cm}^{-1}$ ) is very rapidly cooled with small additions of  $\text{H}_2\text{O}$  ( $\nu = 1595 \text{ cm}^{-1}$ ) while the cooling was decidedly more ineffective with  $\text{D}_2\text{O}$  ( $\nu = 1178 \text{ cm}^{-1}$ ).

In reviewing the case of methylene, several factors are in need of clarification. First of all, the noble gases are not all alike in their behavior towards cooling the singlet to the less energetic triplet state. An objection may be raised in connection with plotting pressure--rather than some figure related to a collision number--as abscissa. Since the collision number depends on the average collision diameter and the reduced mass of the partners, this objection has some merit, due to the small size and small mass of the methylene molecule. According to collision theory, the number of collisions/ $\text{cm}^3/\text{sec}$  between unlike particles is given as (56):

$$Z_{\text{CM}} = \pi N_{\text{C}} N_{\text{M}} d_{\text{CM}}^2 \times \sqrt{\frac{8kT}{\pi \mu}}$$

where  $N$  = number of molecules/ $\text{cm}^3$   
 $d$  = mean molecular diameter

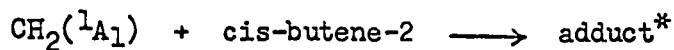
k = Boltzmann constant

$\mu$  = reduced mass.

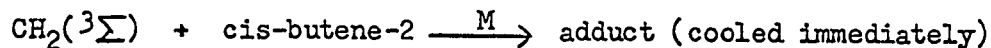
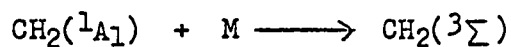
Subscript "C" refers to methylene while "M" refers to inert gas. It is not necessary to know the exact values for N, since at the same pressure (but different M gas)  $N_M$ 's will be equal, and likewise the  $N_C$ 's, assuming that the pressure of diazomethane is the same in each case. The molecular diameter of  $CH_2$  is also assumed constant. One may assume numbers for these figures and plot Z rather than pressure. Alternatively, one may calculate relative collision numbers since the only values which do not cancel upon taking ratios are  $d^2$  and  $\mu$ , eg. -

$$\frac{Z_{CH_2-He}}{Z_{CH_2-Ar}} = \frac{d^2_{CH_2-He} \sqrt{\frac{1}{\mu_{CH_2-He}}}}{d^2_{CH-Ar} \sqrt{\frac{1}{\mu_{CH_2-Ar}}}}$$

The values used for the molecular and atomic collision diameters (in Angstroms) were taken from the literature (57,58,59): He, 2.2; Ar, 2.9;  $N_2$ , 3.2; Xe, 3.5;  $CF_4$ , 4.9. The molecular diameter of  $CH_2$  in the bent configuration was estimated to be 3.0 (compare  $H_2O$ , 2.8). Values calculated in either manner lead to the following relative results, taking  $N_2$  as 1:  $Z_{Rel}$  (dimensionless):  $N_2$ , 1; Ar, 0.87; Xe, 0.99;  $CF_4$ , 1.46; He, 1.22. In other words, "torr x  $Z_{Rel}$ " is plotted as abscissa rather than "torr" only. It should be pointed out that this is done only in the "triplet region". In the "singlet region", below, say, 250 torr, the main reaction is no longer between  $CH_2$  and M, but rather between  $CH_2$  and butene, followed by isomerization. For example, at zero pressure of M, the reaction sequence is



whereas at high pressures of inert gas the scheme is



The percent TDMC/TotalDMC vs. Torr.  $Z_{\text{Rel}}$  for all M gases is shown in Fig. 15. It is readily seen that on a collision basis, the effect on the singlet-triplet conversion for methylene is the same for all third bodies (within experimental scatter) with the exception of He. Owing to the assumptions used in calculating collision numbers, comments made in this work have dealt mainly with observed pressure rather than corrected pressure. Only in the case of argon does any serious objection arise; in the experimental pressure plots, argon falls about midway between He and the other M gases, while in the corrected pressure case argon is indistinguishable from the other M gases in effecting the singlet to triplet conversion.

The very fact that helium does bring about (some) triplet methylene<sup>1</sup> certainly indicates that only a minimum amount of energy must be transferred to bring about the transition of singlet to triplet. If, as in the situation with Na(<sup>2</sup>P), a relatively large amount of energy has to be accommodated, He would hardly have any effect at all. There

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1 This may be seen by comparing Fig. 6 with Fig. 14. The results obtained with oxygen indicate the behavior to be expected when triplet methylene is absent. Contrasting these results with those obtained with helium, Fig. 6, shows a (high pressure) discrepancy which is attributable to triplet methylene.

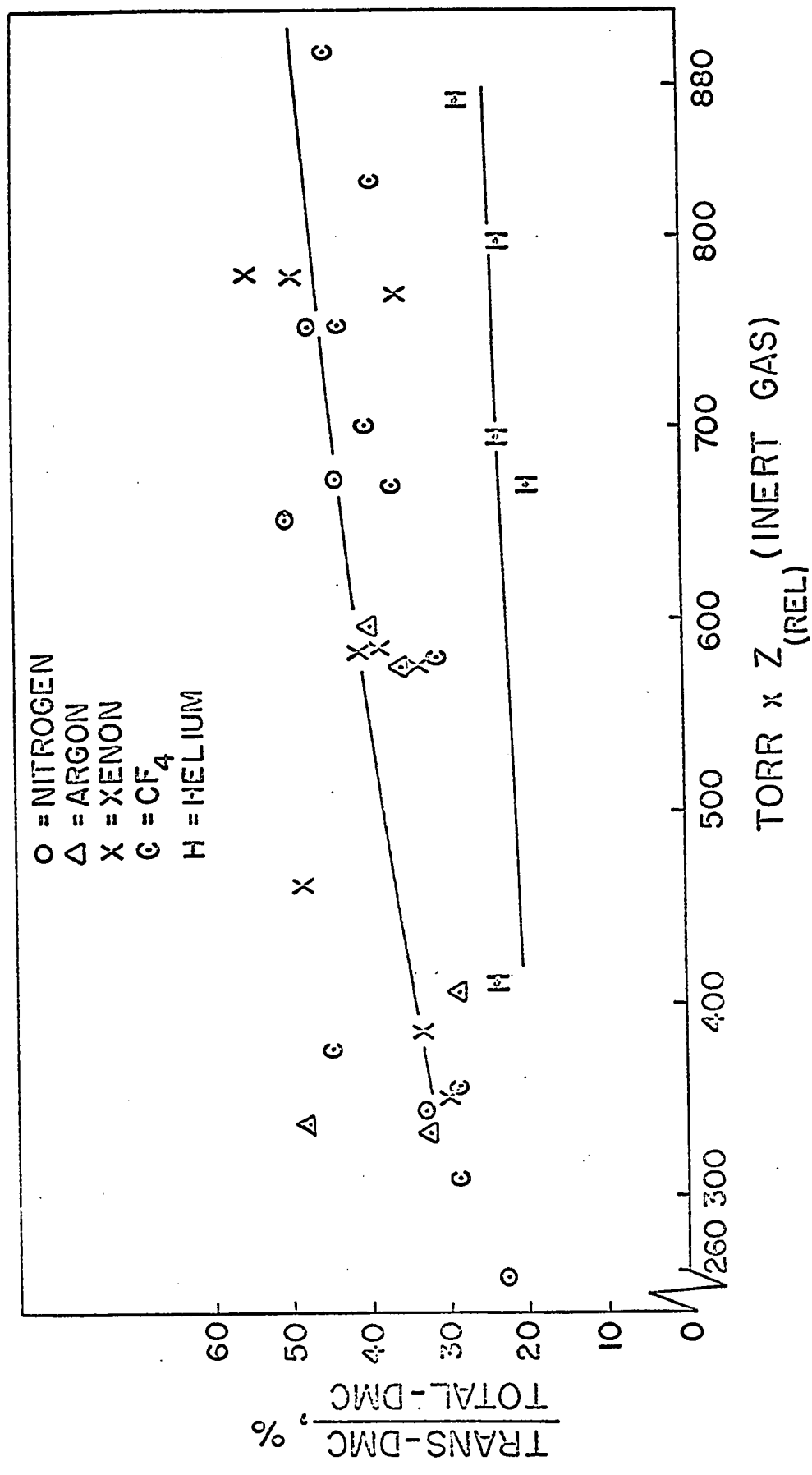


Figure 15 Trans- 1,2-dimethylcyclopropane as a Percent of Total Dimethylcyclopropane vs Relative Collision Number

can be little doubt that when  $\text{CH}_2$  is originally formed from diazomethane it is in a singlet state which is not necessarily the ground state singlet. How the molecule reaches the ground state singlet is another question--whether a single jump is involved or whether the transition involves extremely rapid jumps from the highest level to the next lowest, and so on down, until the lowest state of the same multiplicity is reached (cascading process). Strictly on the basis of the present experimental evidence, spin is conserved; i.e., there is little spontaneous, unperturbed transitions from singlet to triplet levels--if there were, triplet behavior would be observed even in the absence of inert gas. Calculations performed in a later section reveal that the crossing of the ground state singlet and the ground state triplet involves a spin-orbit resonance<sup>1</sup> energy of around 130 (small) calories. An amount as small as this should be quite amenable with regards to transferring energy even to a quencher such as helium. The situation may not be as simple as pictured, however. It is also possible that excited singlet and excited triplet levels may cross, and not only the lowest singlet and triplet ones. These (excited) levels may be fairly widely separated--so wide, in fact, that helium would be hard pressed in causing their crossing. The other M gases may effect this crossing with varying degrees of ease.

The behavior of nitrogen may be regarded as strange. That it is better than argon in quenching from singlet to triplet may be an argument in favor of near resonant frequencies being capable of quickly removing energy. Clearly, this would not apply to the ground state crossing, as the frequency would have to be impossibly low--it might be

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<sup>1</sup> See subsequent discussion

true in the more highly excited singlet and triplet states. The same might be said for  $\text{CF}_4$ . The frequencies of  $\text{CF}_4$  may be in resonance with transitions with different energies than those involved in the case of the nitrogen induced transition. Another possible explanation is that perhaps  $\text{N}_2$  is not a very good quencher, but rather  $\text{CF}_4$  (the only other vibrator) is a poor one. Such may be the case if  $\text{CF}_4$  is very efficient in causing the transition from an excited singlet to the ground state singlet while at the same time removing enough vibrational energy so that the "cooled" (both electronically and vibrationally) methylene does not have enough vibrational energy to approach the crossing point--thus staying in a potential well until enough energy is gained to overcome a (small) barrier.

So far, little has been said concerning the lifetimes of methylene in the excited singlet states. If methylene has a relatively long lifetime (relative to the time needed for successive deactivating collisions), it would be quite possible that it may lose much of its excess energy in very small quanta. This would perhaps explain why helium and argon show different quenching abilities from the other inert gases; the lifetime of methylene is such that small differences in quenching ability will appear--if the lifetime<sup>1</sup> were extremely short, spontaneous transitions would be occurring at a faster rate than collision-induced transitions.

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1 In reactions of olefins with singlet methylene (no inert gas present) the lifetime of (singlet) methylene is of longer duration than the time required for singlet methylene-olefin reaction, even at relatively high concentrations of olefin (1 atm.). For triplet methylene, Herzberg and Shoosmith (8) calculate the lifetime of triplet methylene to be about 15 microsec.--about the same time as the time between collisions of  $\text{CH}_2$  with diazomethane (0.02 mm diazomethane with 2 mm inert gas).

The question of resonant frequencies does not explain the relative ease of Xe (equally effective as  $N_2$  and  $CF_4$ ) in inducing the spin change observed in methylene. Being more electronically complex than He and Ar, one might expect that it would be more efficient than either of its sister gases insofar as electronic-electronic relaxation is concerned. In this regard, xenon would be more likely to undergo so-called "sticky collisions" than either of the other two, which would more closely approximate the hard spheres of collision theory. The distinct possibility arises, then, if the collision occurs over a period of time (momentary complex formation) there is more rapid interchange of electronic, translational, rotational and vibrational energy (even though xenon does not vibrate, the xenon-methylene complex would, and, when the complex decomposes, the xenon "fragment" may carry with it a large portion of the energy formerly associated with the complex).

An interesting comparison may be made between energy transfer in the case of excited NO molecules--inert gases and the case of methylene-inert gases energy transfer. Broida and Carrington (48) find that as far as the transfer of rotational energy is concerned (comparatively small energy differences in rotational levels), He, Ar,  $N_2$ , and  $CO_2$  are all equally as efficient in removing excess rotational energy. Concerning the transfer of vibrational and electronic energy from the electronically excited NO molecules to the ground electronic state, there is the expected low efficiency for monatomic gases, with nitrogen being intermediate between these gases and the more strongly interacting  $CO_2$  and (unexcited) NO molecules. If one were to compare the efficiencies of vibrational deactivation in the electronically excited ( $^2\Sigma$ ) state of NO, with vibrational deactivation (by the same gas) in the ground elec-

tronic state ( $^2\Pi$ ), he would find that  $\text{CO}_2$  deactivates (vibrationally) 100 times more easily in the excited state than it does in the ground state; with  $\text{N}_2$  as deactivator, this figure is  $10^4$ . (In other words, vibrational relaxation in the excited ( $^2\Sigma$ ) electronic state is  $10^4$  times more probable than it is in the ground electronic state, with the same collision partner in each case). In the case of methylene, arguing along similar lines could show that some particular collision partners are very efficient in connection with relaxation in high energy states rather than in the lower ones. It was pointed out earlier that in all probability methylene is formed not in its singlet ground state, but rather in an excited singlet state. A particular collision partner may (bearing in mind the  $\text{NO}$  case) be very efficient in bringing about transitions from excited singlet states to less energetic singlet ones, yet will be very inefficient in effecting the final singlet to triplet transitions. This would perhaps explain the apparent equal abilities (in bringing about the singlet-triplet conversion) of such diverse gases as  $\text{N}_2$ ,  $\text{Xe}$  and  $\text{CF}_4$ . Perhaps the only comment that can be made with any certainty is that the ground state singlet to ground state triplet transition requires but little energy transfer--so little, in fact, that it can readily be transferred to translational degrees of freedom. The manner in which this is brought about is at this stage open to conjecture; the suggestions put forth earlier are only some of the many possibilities.

Besides the abilities of the inert gases in fostering the singlet-triplet transition, they also serve (along with unreacted cis-butene-2) in cooling the "hot" (vibrationally excited) 1,2 dimethylcyclopropane ( $\text{DMC}^*$ ) before it isomerizes. Unfortunately, even at the

lowest pressures of inert gas, triplet methylene is probably beginning to appear--the distinct reactions of triplet methylene toward cis-butene-2 make the reactions of excited cis-1,2-dimethylcyclopropane (formed from the reaction of butene with singlet methylene) difficult to interpret. For example, N<sub>2</sub> would appear to be inefficient at cooling CDMC\* (as indicated by a low percentage CDMC of the total DMC), whereas this may be due entirely to the appearance of triplet methylene. On the positive side, since Xe, CF<sub>4</sub> and N<sub>2</sub> are all alike in their behavior in bringing about triplet methylene, one can argue that the low pressure behavior is a measure of the ability (of the inert gas in question) to cool vibrationally excited cis- and trans-DMC. CF<sub>4</sub> is clearly the best (as seen in Figs. (5, 6, 7) followed by N<sub>2</sub>; He and Ar show identical behavior within experimental error. Too few low pressure runs were done with Xe as third body, but it would appear on the basis of these few runs that it is somewhat poorer than CF<sub>4</sub>. The relative differences in the behavior of these M gases lies in their abilities to accommodate the vibrational energy of the hot adduct in their own vibrational, rotational and translational modes--clearly, the hot dimethylcyclopropane is in a singlet state, and, probably, the ground state singlet, thus precluding the need for electronic transitions. (Setser and Rabinovitch (26), using kinetic data, deduced that the excited DMC should have an energy content of 110 kcal/mole, well below the excitation energy for the lowest lying singlet state). The transfer of excess vibrational energy to a monatomic collision mate (He, Ar, Xe) may, in theory, proceed in several ways. If the collision has a finite lifetime (complex formation), there is the possibility that vibrational energy may be accommodated by the increased number of vibrational and rotational modes of the complex. In the present

case, this does not appear to be an important way of losing energy, since, if it were, the complex formed between  $\text{DMC}^*$  and  $\text{N}_2$  would be more efficient in vibration-rotation energy transfer than the  $\text{DMC}^*$ -argon complex, due to the expected larger moments of inertia of the former; yet as experimental results show,  $\text{N}_2$  is no more efficient than Ar in cooling vibrationally excited 1,2-dimethylcyclopropane. As mentioned previously, if there is a momentary complex formed, and if it has a lifetime as long as the period of one vibration, one might expect an energy distribution among all the bonds in the complex; when the complex decomposes, the collision partner would be expected to have more energy than it would have if it underwent a "hard sphere" collision. Thus, in the cases of He, Ar and Xe, the excess vibrational energy of the  $\text{DMC}^*$  would appear only as translational energy of these gases; the differing "cooling" abilities of these three monatomics would perhaps be determined by the strengths of the bonds formed in the complex. In the case of  $\text{CF}_4$ , a long-lived collision would enable a distribution of energy among a larger number of bonds resulting in a more efficient energy exchange, especially since  $\text{CF}_4$  would be expected to have a few near-resonant vibrating frequencies. The relative inefficiency of  $\text{N}_2$  along these lines can be related to its high vibrational frequencies, which are much higher than those of  $\text{CDMC}^*$ , making  $\text{N}_2$  poor as far as vibration-vibration relaxation is concerned. The behavior of  $\text{N}_2$  along such lines is not peculiar to the  $\text{DMC}^*$  system, as it is also rather inefficient in carrying off the excess energy of the excited sec-butyl radical (43); this, in spite of  $\text{N}_2$ 's vibrational ability. The conclusion reached in that work is the same reached in the present work, i.e. the vibrational frequencies are so high that the vibrator is not able to accommodate

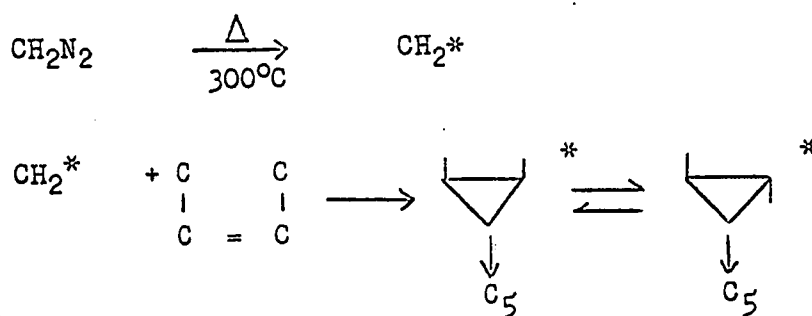
the available energy with ease; indeed, Kohlmaier and Rabinovitch find that  $N_2$  is only as good as Ar in deactivating sec-butyl radicals, the same results found in this present work in regards to deactivating DMC\*. If molecules having so-called resonant frequencies are efficient collision partners, one would expect hydrocarbons, which have many different vibrational frequencies near the expected ones for the "hot" species, to be efficient collision partners. This is true in this present work, where cis-butene-2 approaches  $CF_4$  in deactivating ability. In the work concerning excited sec-butyl radicals,  $SF_6$  was found to be more effective in collisional deactivation than cis-butene-2.

The Thermal Reaction: Diazomethane with Cis-Butene-2

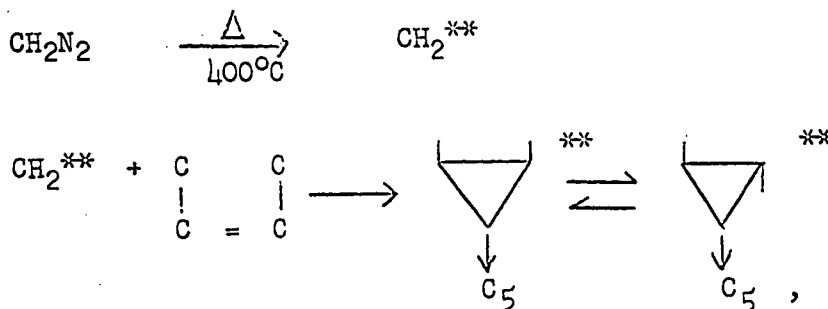
Introduction

Having the results of the reaction of singlet methylene with diazomethane (from Frey) on hand, an easy comparison with the results obtained with triplet methylene was possible. Setser and Rabinovitch (26) studied the reaction of cis-butene-2 with singlet methylene derived from the thermal decomposition of diazomethane, to give the same products (and product dependence with increase in substrate pressure) as the singlet photolysis. In general, thermolysis reactions have the advantage of allowing one to vary the temperature, thereby enabling one to prepare Arrhenius plots and determine activation energies, rate constants and the like. One of the complaints which accompanies the photolysis is that this mode of methylene generation always imparts large excesses of translational and vibrational energy to methylene. This, in turn, transfers its energy to the adduct formed with the reactant partner (butene-2) resulting in very highly excited intermediates. By irradiation with light of longer wavelengths, less energetic methylene, and hence less energetic "hot" molecules can be formed. In this way, a study can be made, as done by Frey (11), on the effects on the overall production of  $C_5$  products as a function of this excess energy. This procedure is limited by the fact that diazomethane does not have continuous absorption, and a complete survey of reactions involving methylene with varying amounts of energy would therefore be impossible. If, on the other hand, singlet methylene is produced by thermal decompositions of diazomethane, a complete range of methylene with varying amounts of energy may be produced.

Setser and Rabinovitch (26) have reported that methylene prepared from the thermal decomposition of diazomethane at 350°C had almost the same energy as the methylene produced from the photolytic decomposition of diazomethane at 4358 Å at 25°C. Decomposing diazomethane at higher and higher temperatures results in methylene having more and more energy. For example,



whereas,



where double asterisked quantities indicate more energy (internal and translational) than those compounds with a single asterisk. In other words, higher pressures of substrates would be needed to cool  $\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C} \end{array}^{**}$  to  $\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C} \end{array}$  than would be needed to cool  $\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C} \end{array}^*$  to  $\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C} \end{array}$ . Alternatively,  $\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C} \end{array}^{**}$  would tend to undergo structural isomerization to the other C<sub>5</sub> compounds more easily than would  $\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C} \end{array}^*$ .

In brief, the main reason for attempting the thermal reaction of diazomethane with cis-butene-2 was to see if, upon the addition of inert gas (N<sub>2</sub>) triplet behavior would be observed, just as it was with the photolytic procedure. The following figures (Figs. 16a, c) have

been constructed from the analytical results of Frey (11) and Setser and Rabinovitch. Figures (16 b, d) and (17) are the results of the present work.

Inasmuch as Setser and Rabinovitch have pointed out that thermolysis results are nearly identical with photolysis results (at least for the isomeric dimethylcyclopropanes), it was felt (in the present work) that the thermolysis with inert gas would show approximately the same behavior as observed in the photolysis.

#### Results and Discussion

The actual behavior is as shown in Fig. 17. The results shown here for the dimethylcyclopropanes appear startling. Concerning Fig. 17, three factors are particularly worthy of note:

1. There appears to be little triplet methylene at high pressures of inert gas, as evidenced by the small percentage of trans-1,2 dimethylcyclopropane formed; i.e., there is no evidence for random methylene addition to the carbon-carbon double bond.

2. If there is no triplet methylene present, there probably is no singlet methylene present, for, if there were, it would have easily been converted to the triplet form with excess inert gas.

3. The overall percentage of trans-1,2 dimethylcyclopropane is very low (compared with photolysis) throughout the entire pressure range.

These phenomena may be satisfactorily explained, it is felt, by a mechanism involving the molecular addition of diazomethane (NOT  $\text{CH}_2$ ) to cis-butene-2 followed by decomposition of the initially formed adduct. The following literature evidence in support of this theory is cited.

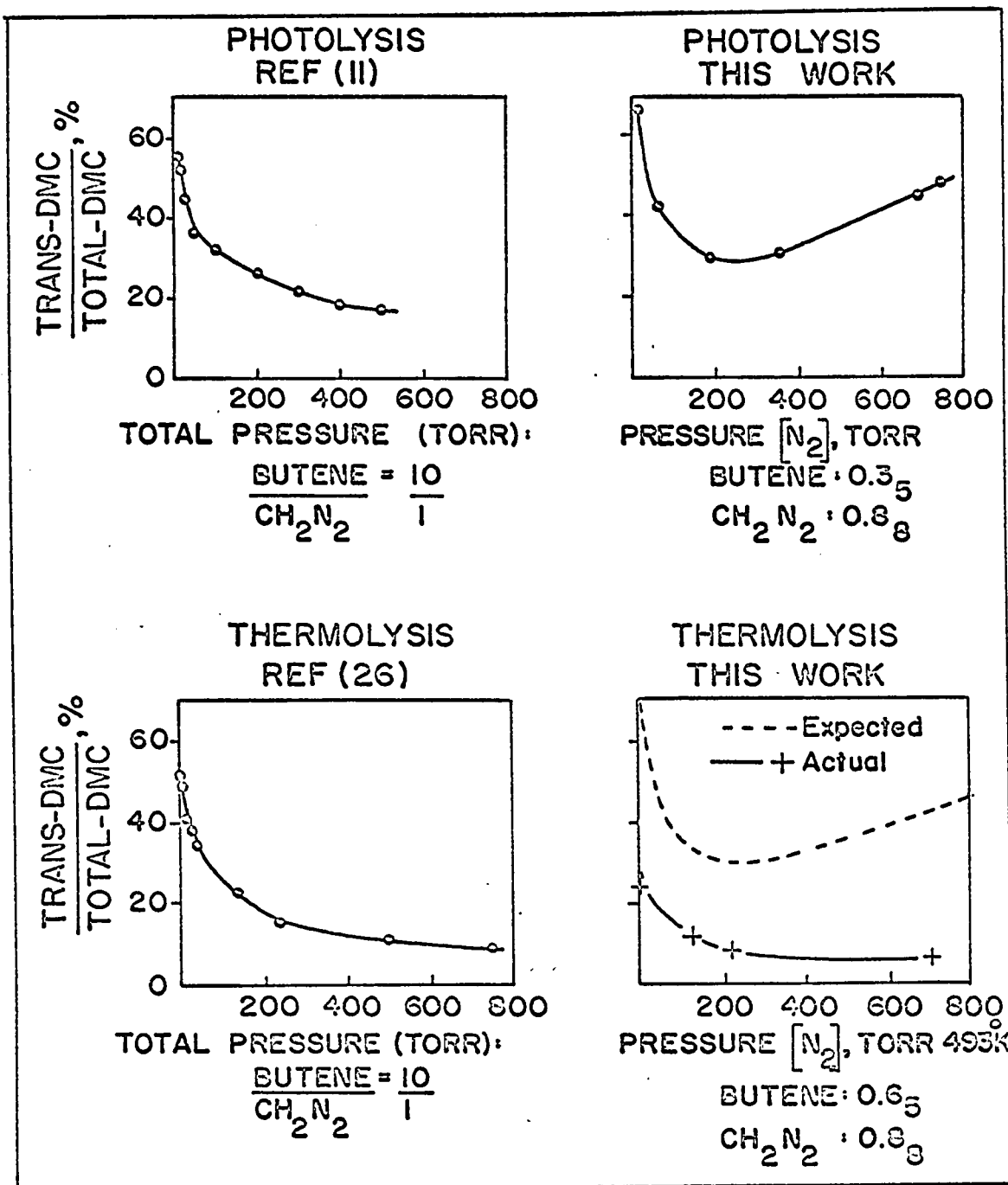


Figure 16 Comparison of Trans- 1,2-dimethylcyclopropane (as a Percent of the Total Dimethylcyclopropane) vs Inert Gas Pressure for Photolyses and Thermolyses

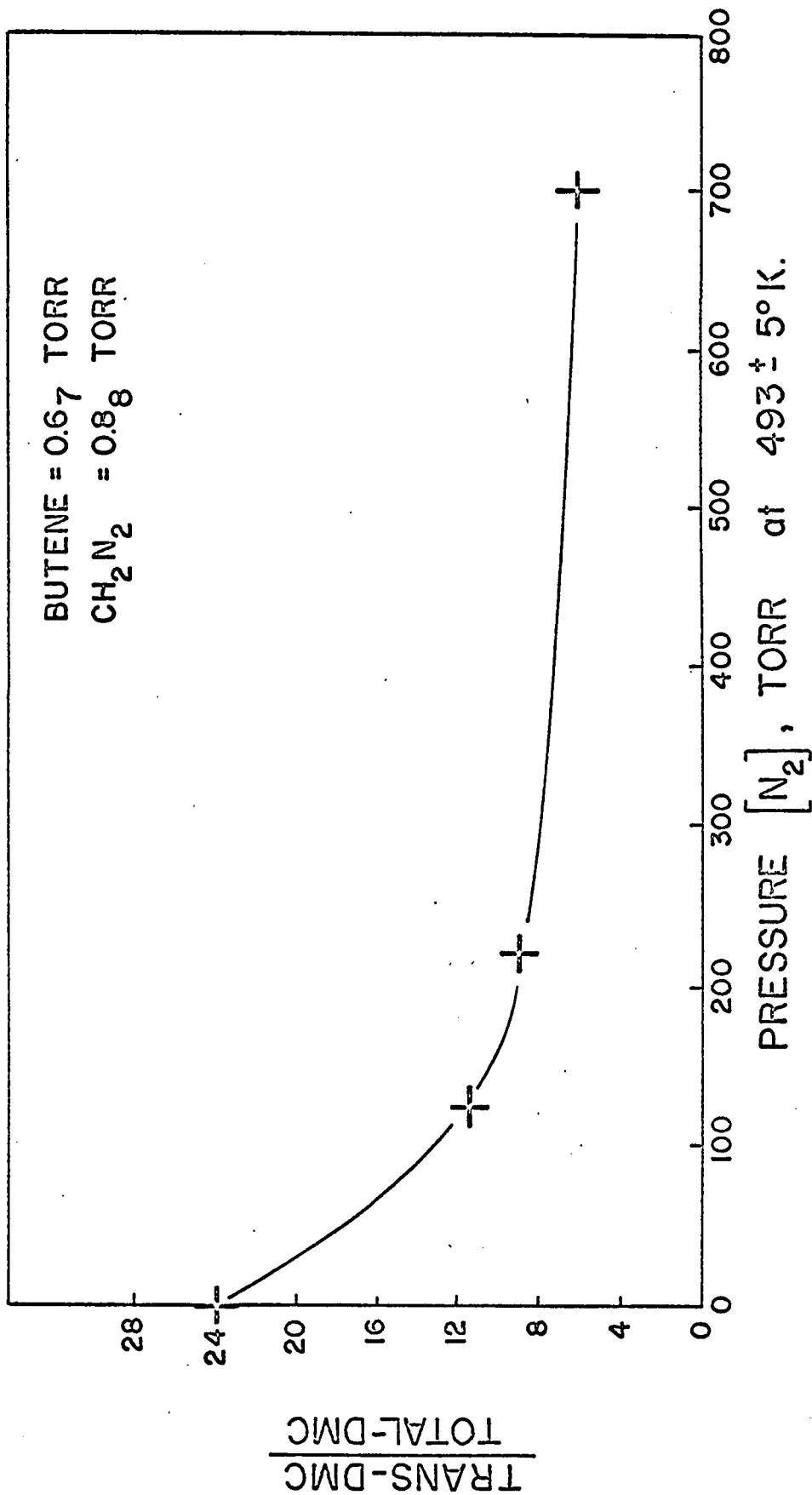
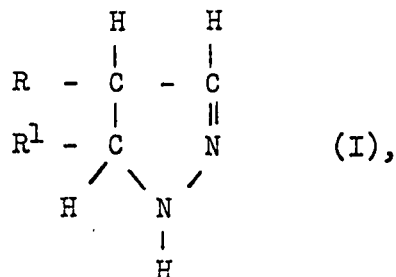


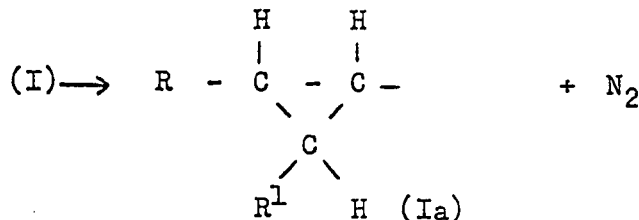
Figure 17 Trans-1,2-dimethylcyclopropane (as a Percent of the Total Dimethylcyclopropane) vs Inert Gas Pressure for the Thermal Reaction of Diazomethane with Cis-Butene-2



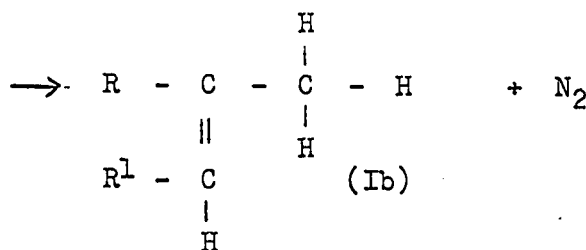
resulting in the stereospecific addition product



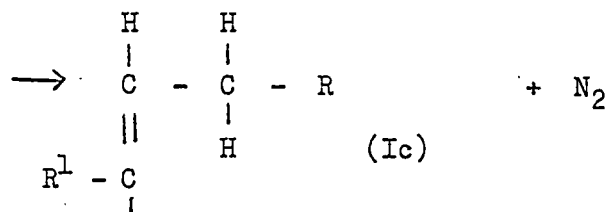
which may be isolated (depending on the nature of R and R<sup>1</sup>). Three alternative reaction paths are now open to (I):



Cis-1,2 dialkylcyclopropane



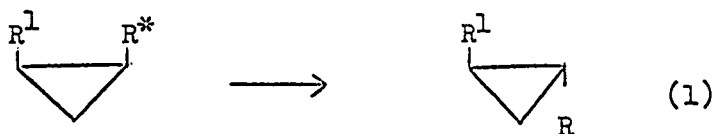
Cis-olefin



Trans-olefin

(Ib) and (Ic) are cis-trans (geometrical) isomers, which, in the case of cis-butene-2 (R= CH<sub>3</sub>, R<sup>1</sup>= CH<sub>3</sub>) are cis- and trans-pentene-2 respectively. It should be pointed out that the trans-1,2 dialkylcyclopropane is formed only in very small yields. Apparently, then, a reaction

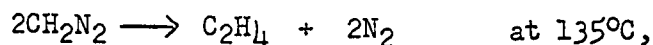
involving the isomerization of excited cis-1,2 dialkylcyclopropane to the corresponding trans isomer does not occur very readily, i.e.,



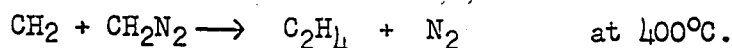
is not important in solution, probably because in solution, like high pressures in the gas phase, collisional deactivation occurs before isomerization. In the present work, however, there is a distinct pressure dependence involving the dimethylcyclopropanes which would indicate that there probably is some trans-DMC appearing because of the isomerization of hot cis-DMC (eq. (1) above). Moreover, the olefinic compounds cis- and trans-pentene-2 and 2-methylbutene-2 (but not 3-methylbutene-1) are also found as products in the present work; these compounds may arise through an excited molecule (trans-DMC\*) mechanism. The pressure dependencies of the yields of these C<sub>5</sub> hydrocarbons are given in table 8 page 37. Unfortunately, too few thermal experiments were performed and so trends with increasing pressures of inert gases are unrecognizable. However, these olefinic compounds also appear at the highest pressures of inert gas utilized, which is evidence, perhaps, that they are formed directly from the heterocyclic intermediate. The formation of cis- and trans-pentene-2 from this nitrogen containing intermediate requires rearrangements involving methyl group migrations, most probably through radical intermediates. The amounts of 2-methylbutene-2 formed in the low temperature reaction is surprising, totalling, in some cases, as much as 30% of the total yield of C<sub>5</sub> hydrocarbons. The formation of this compound from the heterocyclic intermediate does not require methyl group migration (but does require H migration). The outcome of these thermal experiments

gives a method whereby gas phase reactions involving diazomethane may be tested for the appearance of "free" methylene (rather than molecular reactions involving diazomethane).

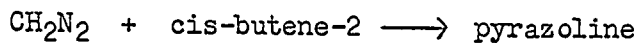
Of course, the original purpose of the thermal work (to follow the reactions of triplet methylene with increases in pressure) still remains to be done. It is interesting to note in this regard that Setser and Rabinovitch report that at temperatures below 225°C reproducible data could not be obtained, probably because of heterogeneity. In the present work (220°C  $\pm$  5) there was no evidence for heterogeneity with regard to wall effects, probably because of the very large volume/surface ratio used (3 liter reaction bulb). Also of interest are the two different mechanisms for the reaction of diazomethane alone, at high and low temperatures. In the reaction studied by Steacie (65), no free methylene is formed at low temperatures, reactions proceeding molecularly:



while at high temperatures, as reported by Pearson, Purcell and Saigh (66) the reaction is



Thus, it seems reasonable to assume that at temperatures of around 225°C the reaction



is important, whereas at higher temperatures the methylene reaction predominates. In this regard, it is noteworthy that the reaction of diazomethane with cis-butene-2 at 150°C did not produce any products (this work) even though reaction time exceeded 15 hours (compare  $\frac{1}{2}$  hours at

225°C). This is in keeping with the theory of pyrazoline formation from diazomethane and cis-butene-2; 150°C is not a sufficiently high enough temperature to decompose this product.

An interesting observation made by Kirkbride and Norrish (42) indicates that under certain conditions the photolysis of diazomethane (alone) results in a brownish, nitrogenous liquid residue, having a low vapor pressure and basic character. In this present work, a similar (in appearance) residue was observed when mixtures of large amounts of diazomethane and butene-2 were photolyzed. Previous to the work of Kirkbride and Norrish, Azzarello (67) had found that diazomethane reacted with ethylene (gas phase) to give an adduct which readily lost hydrogen to give the corresponding (stable) pyrazole.

Still further evidence against free methylene reaction at the temperatures studied is the low yields of butene-1 product (table 11 b, p. 83). As mentioned earlier, this compound probably arises from methylene reaction either across the double bond (of propylene) or direct insertion into a carbon-hydrogen bond. Failure to produce this compound is taken as further evidence that no methylene is produced.

Spin-Orbit Interactions

At the very heart of the question of singlet to triplet transitions lies the problem of spin-orbit coupling. Before discussing the method and results of the latest calculations involving the resonance splitting found in methylene, a short introduction would be helpful.

For a linear symmetrical molecule, the orbital angular momentum about the molecular axis is given the notation  $\Sigma$ ,  $\Pi$ ,  $\Delta$  ... which denotes a value of 0, 1, 2... (units of  $\hbar$  for the angular momentum). For linear methylene, we may have the orbital angular momentum of each electron adding vectorially to produce a total angular momentum of 0 and 2, i.e.,  $\Sigma$  and  $\Delta$  states. The multiplicity associated with each state is signified by a superscript, and for the methylene case this would be either a singlet or triplet state, resulting in six wave equations overall (see p. 116). Bent states are designated by Roman letters, for example,  $^1A_1$ , where again the superscript refers to the multiplicity. This symbol is called a "species" or an "irreducible representation" of a certain symmetry group. All the irreducible representations (of the symmetry group) define the eigenfunctions of molecules belonging to particular point groups (i.e. the eigenfunction must transform as one of the irreducible representations of the point group). In the case of the linear configuration of  $CH_2$ , this molecule belongs to the  $D_{\infty h}$  point group having the irreducible representations  $^1\Sigma_g^+$ ,  $\Sigma_g^-$ ,  $\Delta_g$ , etc. The bent case belongs to the  $C_{2v}$  point group, having the irreducible representations  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$ , where, again, these terms describe how the molecule behaves when the symmetry

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1 for a complete discussion, see G. Herzberg, Infrared and Raman Spectra, D. Van Nostrand Company, Princeton, New Jersey, 1962

operations of point group  $C_{2v}$  are applied.

As a first approximation, it may be assumed that there is no interaction between the orbital angular momentum and the spin vector of the electron. For very light atoms this is a justifiable approximation, and the spin orbit interaction may be added as a perturbation. For elements of high atomic number ( $Z$ ) spin-orbit coupling is too large to be treated as a perturbation and the orbital and spin angular momentum quantum numbers no longer have meaning. If a  $^3B_1$  and a  $^1A_1$  state mix very strongly, the very terms used to describe these states have no significance since they do not represent the true picture, since the spin and orbital angular momentum are not separately conserved or quantized but only their sum. The quantum numbers used to identify these states, then, are not "good quantum numbers". On the other hand, for atoms of small  $Z$ , this strong interaction is replaced by a perturbation, with the quantum numbers in this case being "almost good quantum numbers". The possibility of mixing in this case will be small, but definite, and the actual probability for the crossing may be calculated.

With the methylene molecule our problem is concerned, first of all, with the possibility that the singlet and triplet states of  $CH_2$  may mix (if they do not, the experimental conclusions drawn in earlier sections would be false). Secondly, the extent of this perturbation (resonance splitting) has to be calculated in order that, thirdly, the actual probability of this crossing may be calculated. Before proceeding any further, reference should be made to Fig. 18, after Jordan and Longuet-Higgins (30). Here, an energy correlation diagram is shown, wherein the potential energy is shown as a function of H-C-H bond angle. In preparing such a diagram, we are aided by Hund's rules. From the

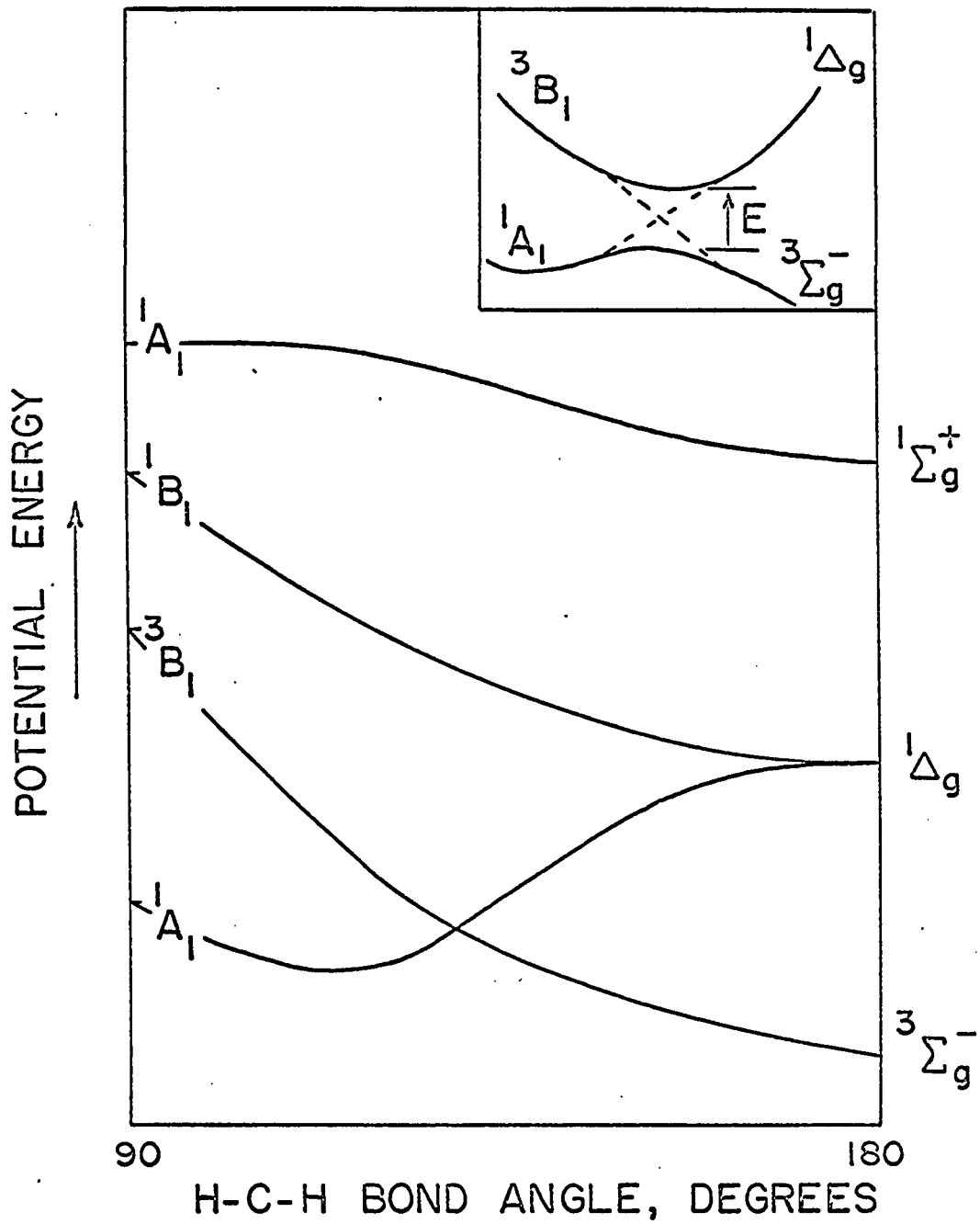


Figure 18 Correlation Diagram of Bent and Linear Configuration of Methylene with CH<sub>2</sub> Bond Angle (30)

geometry of the linear molecule, we have, as before, all the irreducible representations. According to Hund, for a given configuration, the state with the highest multiplicity lies lowest in energy--thus, as indicated in the diagram,  $^3\Sigma_g^-$  has less energy than  $^1\Sigma_g^+$ . Another of Hund's rules is that for states of the same multiplicity, and arising from the same configuration (eg.  $^1\Sigma$  and  $^1\Delta$ ), the state having the highest value for the orbital angular momentum lies lowest--in this case the  $^1\Delta_g$  state is lower in energy. For the bent case similar rules apply. What Hund's rules do not tell us, however, is the relative energy of each linear state with respect to each bent case; one may ask if the  $^1A_1$  state has a lower energy than the  $^3\Sigma_g^-$ . This question can only be unequivocally answered by experiment. Another factor not revealed by Hund's rules, yet needed for the construction of the diagram, is concerned with which linear states correlate with the bent states of the methylene molecule. This question may be answered by a study of symmetry properties, as outlined below.

The electronic configuration for the linear methylene molecule is

$$1\sigma_g^2 \ 2\sigma_g^2 \ \sigma_u \ \pi_u^2,$$

where  $1\sigma_g^2$  is the molecular orbital due to the 1s electrons of carbon,  $2\sigma_g^2$  is the orbital formed from the overlapping of carbon's 2s atomic orbital with the 1s of hydrogen, and  $\sigma_u$  is the molecular orbital formed by the overlapping of the hydrogen 1s atomic orbital with the carbon  $2p_\sigma$  atomic orbital.  $\pi_u$  is the doubly degenerate molecular orbital formed from the  $p_\pi$  atomic orbital of carbon. This electronic configuration gives rise to the  $^3\Sigma_g^-$ ,  $^1\Delta_g$ , and  $^1\Sigma_g^-$  wave functions. These functions are composed of spin parts and orbital parts:

$${}^3\Sigma_g^-: \frac{1}{\sqrt{2}} \left[ \Pi_+(1) \Pi_-(2) - \Pi_-(1) \Pi_+(2) \right] \frac{1}{\sqrt{2}} \left\{ \begin{array}{l} \alpha(1) \alpha(2) \\ \alpha(1) \beta(2) + \beta(1) \alpha(2) \\ \beta(1) \beta(2) \end{array} \right\}$$

(orbital part) (spin part)

$${}^1\Sigma_g^+: \frac{1}{\sqrt{2}} \left[ \Pi_+(1) \Pi_-(2) + \Pi_-(1) \Pi_+(2) \right] \frac{1}{\sqrt{2}} \left\{ \alpha(1) \beta(2) - \beta(1) \alpha(2) \right\}$$

$${}^1\Delta_g: \begin{array}{l} \left\langle \begin{array}{l} \Pi_+(1) \Pi_+(2) \\ \Pi_-(1) \Pi_-(2) \end{array} \right\rangle \frac{1}{\sqrt{2}} \left\{ \alpha(1) \beta(2) - \beta(1) \alpha(2) \right\} \\ \frac{1}{\sqrt{2}} \left\{ \alpha(1) \beta(2) - \beta(1) \alpha(2) \right\} \end{array} ,$$

where the  $\Pi_+$  and  $\Pi_-$  symbols represent the molecular orbitals formed from the  $2p_{\Pi}$  atomic orbitals of the form  $e^{\pm i\phi}$ , and the numbers in parentheses indicate the electron in question. Rewriting the orbital function in terms of a defined coordinate system (see footnote) results in

$${}^3\Sigma_g^-: \frac{1}{\sqrt{2}} \left[ \Pi_x(1) \Pi_z(2) - \Pi_z(1) \Pi_x(2) \right] \quad \text{and}$$

$${}^1\Sigma_g^+: \frac{1}{\sqrt{2}} \left[ \Pi_x(1) \Pi_x(2) - \Pi_z(1) \Pi_z(2) \right] \quad \text{for the orbital parts}$$

$${}^1\Delta_g: \frac{1}{\sqrt{2}} \left[ \begin{array}{l} \Pi_x(1) \Pi_x(2) + \Pi_z(1) \Pi_z(2) \\ \Pi_z(1) \Pi_x(2) + \Pi_x(1) \Pi_z(2) \end{array} \right]$$

1 Each atomic orbital is a product of three functions; one radial function and two angular ones, i.e.

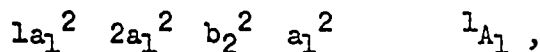
$$2p_c = R(r) \Theta(\theta) \Phi(\phi)$$

The " $\Pi$ " designation relates to the  $R(r) \Theta(\theta)$  part, while the + and - relates to the + or - coefficient of the exponent in  $e^{\pm i\phi}$ . Alternatively one may replace the  $\Pi^{\pm}$  designation by a  $\Pi_x$  and  $\Pi_z$  notation of a defined coordinate system. Both nomenclatures have their respective advantages; the + and - notations immediately define the + or - nature of the  $\phi$  dependency, whereas the x and z notation makes it easier to assign the correct behavior under the symmetry operations of the appropriate point group ( $D_{\infty h}$ ). For the case under consideration, the y axis is taken as the molecular axis ( $p_x$  and  $p_z$  will then be the  $p_{\Pi}$  orbitals in carbon).

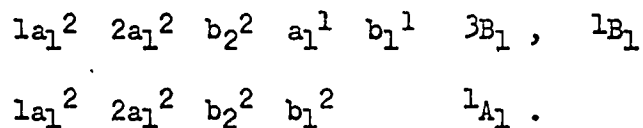
When the molecule is bent in the yz plane, the molecular orbitals correlate as follows:

<u>D<sub>∞h</sub> (linear)</u>		<u>C<sub>2v</sub> (bent)</u>
$\sigma_g$	←————→	$a_1$
$\sigma_u$	←————→	$b_2$
$\sigma_z$	←————→	$a_1^1$
$\pi_x$	←————→	$b_1$
$\pi_z$	←————→	$a_1$

The ground state configuration for the bent molecule is thus



where both  $p_{\pi}$  electrons have been placed in the  $a_1$  orbital. If one, or both electrons are excited, three other states may arise:



Noting the behavior of  $\pi_x$  ( $p_x$ ) and  $\pi_z$  ( $p_z$ ) under  $C_{2v}$ , it is seen that

<u>linear</u>		<u>bent</u>
$3\Sigma_g^-$	←————→	$3B_1$
$1\Sigma_g^+$	←————→	$1A_1'$
$1\Delta_g$	←————→	$1A_1, \quad 1B_1.$

The correlation energy diagram, Fig. 18, may now be drawn.

As mentioned previously, one of the problems to be solved concerns the possibility of mixing between the  $1A_1$  and  $3\Sigma_g^-$  states. Alter-

natively, the problem may be resolved into one of finding which states mix with  ${}^3B_1$ , since this state correlates with the  ${}^3\Sigma_g^-$  state (note that singlets correlate with singlets and triplets with triplets).

According to quantum theory, states will mix under the influence of spin only if  $\langle \Psi_a | H_{sp} | \Psi_b \rangle \neq 0$ , where  $H_{sp}$  is the Hamiltonian spin operator (68). The spin operator itself has certain symmetry properties, and contains the irreducible representations  $B_1$ ,  $B_2$  and  $A_2$ . Our problem may be restated, then, as finding the species, X, which obey the relation

$$\langle \Psi_{3B_1} | H_{sp} | \Psi_X \rangle \neq 0$$

The direct product,  $\Psi_{3B_1} \times \Psi_X$ , must then have the symmetry  $B_2$ ,  $B_1$  or  $A_2$ , so that  $\langle \Psi_{3B_1} | H_{sp} | \Psi_X \rangle$  results in non-zero solutions. Another rule pointed out (68) is that this equation will be valid only if  $\Psi_{3B_1}$  differs from  $\Psi_X$  by the spin of one electron, that is, triplets will mix under  $H_{sp}$  only with singlets. Therefore, the  ${}^3B_1$  species will mix with the  ${}^1A_1$  (or  ${}^1A_1^1$ ) species. On theoretical grounds, then, the  ${}^1A_1$  state may mix with the  ${}^3\Sigma_g^-$  state and thus the molecule may cross from the singlet to the triplet surface.

The next logical step is the calculation of the perturbation (resonance splitting) involved in the crossing of the  ${}^1A_1$  level with the  ${}^3\Sigma_g^-$  one. The method used involves perturbation theory for degenerate systems (69). Briefly, the method is this<sup>1</sup>: one assumes that there is no perturbation, and writes the general Schroedinger equation

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<sup>1</sup> For a detailed account, reference should be made to H. Eyring, J. Walter and G. Kimball, Quantum Chemistry, John Wiley & Sons, New York (1957)

$H_0 \Psi_n^{\circ} = E_n^{\circ} \Psi_n^{\circ}$ , where  $H_0$  is the Hamiltonian,  $E_n^{\circ}$  are the eigenvalues and  $\Psi_n^{\circ}$  the related eigenfunctions. Under some slight spin-orbit coupling, the Hamiltonian will be altered slightly to accommodate the perturbation. The Hamiltonian may then be written

$H = H_0 + \lambda H^{(1)}$ , where the  $H^{(1)}$  term is called the perturbation (small in comparison with  $H_0$ ).  $\lambda$  is a parameter which determines the amount of perturbation. The equation which we wish to solve, then, is

$$(H_0 + \lambda H^{(1)}) \Psi = E \Psi \quad (1)$$

Actually,  $\Psi = c_1 \Psi_1^{\circ} + c_2 \Psi_2^{\circ} + \dots + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots$ ; these  $\Psi_i^{\circ}$ 's correspond to the wave equations describing methylene before the perturbation.  $E$  and  $\Psi$  from the preceding Schroedinger equation may be expanded in powers of  $\lambda$ , and, after expansion, re-inserted. The energy of perturbation  $H_{kj}^{(1)}$  is defined as

$$H_{kj}^{(1)} = \int \Psi_k^{\circ} H^{(1)} \Psi_j^{\circ} d\tau, \text{ where, as before, } H^{(1)}$$

is the spin operator. The equation (2), after these expansions becomes

$$(H_0 - E_1^{\circ}) \Psi^{(1)} = \sum_{j=1}^m c_j (E_1^{(1)} - H^{(1)}) \Psi_j^{\circ}$$

Now,  $\Psi^{(1)}$  may be written as a linear combination:

$$\Psi^{(1)} = \sum_j A_j \Psi_j^{\circ}$$

Likewise, for  $H^{(1)} \Psi_j^{\circ}$ :

$$H^{(1)} \Psi_j^{\circ} = \sum_k H_{kj}^{(1)} \Psi_k^{\circ}$$

The A's are constants which must be determined. After suitable substitution, one arrives at a set of m (in the case of CH<sub>2</sub>, m = 4) simultaneous equations, from which one may derive the secular equations in determinantal form:

$$\begin{vmatrix} (H_{11}(1) - E(1)) & H_{12}(1) & H_{13}(1) & H_{14}(1) \\ H_{21}(1) & (H_{22}(1) - E(1)) & H_{23}(1) & H_{24}(1) \\ H_{31}(1) & H_{32}(1) & (H_{33}(1) - E(1)) & H_{34}(1) \\ H_{41}(1) & H_{42}(1) & H_{43}(1) & (H_{44}(1) - E(1)) \end{vmatrix} = 0$$

In this determinant, the H<sub>jk</sub>'s are the actual perturbation energies, equal in value to H<sub>kj</sub>. They are

$$H_{11} = \langle +B | H_{sp} | +B \rangle = 0$$

$$H_{22} = \langle {}^oB | H_{sp} | {}^oB \rangle = 0$$

$$H_{33} = \langle -B | H_{sp} | -B \rangle = 0, \text{ where the B's donate the}$$

three (triplet) wave functions, defined as  $\Psi_1^c$ ,  $\Psi_2^c$  and  $\Psi_3^c$ , respectively, while the +, o, - symbols denote the  $\alpha\alpha$ , ( $\alpha\beta + \beta\alpha$ ) and  $\beta\beta$  spin components respectively. Also,

$$H_{14}(1) = H_{41}(1) = \langle +B | H_{sp} | {}^oA \rangle = V$$

$$H_{24}(1) = H_{42}(1) = \langle {}^oB | H_{sp} | {}^oA \rangle = 0$$

$$H_{34}(1) = H_{43}(1) = \langle -B | H_{sp} | {}^oA \rangle = V \text{ and}$$

$$H_{44} = \langle {}^oA | H_{sp} | {}^oA \rangle = 0, \text{ where } {}^oA \text{ is defined as } \Psi_4^o \text{ and } V$$

refers to the spin-orbit coupling constant of carbon. Placing these H<sub>jk</sub> values in the secular determinant gives

$$\begin{vmatrix} -E & 0 & 0 & V \\ 0 & -E & 0 & 0 \\ 0 & 0 & -E & V \\ V & 0 & V & -E \end{vmatrix} = 0,$$

since  $H_{jj} = 0$ . This determinant is an equation of the fourth degree in  $E^{(1)}$ , and will have four roots  $E_1^{(1)}$ ,  $E_2^{(1)}$ ,  $E_3^{(1)}$  and  $E_4^{(1)}$ . Solution of this determinant has the actual values  $E_1 = 0$ ,  $E_2 = 0$ ,  $E_3 = \sqrt{2} V$  and  $E_4 = -\sqrt{2} V$ . It remains to find the eigenfunctions corresponding to these eigenvalues. These functions are found by putting each eigenvalue into the set of simultaneous equations from which the secular determinant was derived. These are

$$\begin{aligned} (H_{11}^{(1)} - E^{(1)})C_1 + H_{12}^{(1)}C_2 + H_{13}^{(1)}C_3 + H_{14}^{(1)}C_4 &= 0 \\ H_{21}^{(1)}C_1 + (H_{22}^{(1)} - E^{(1)})C_2 + H_{23}^{(1)}C_3 + H_{24}^{(1)}C_4 &= 0 \\ H_{31}^{(1)}C_1 + H_{32}^{(1)}C_2 + (H_{33}^{(1)} - E^{(1)})C_3 + H_{34}^{(1)}C_4 &= 0 \\ H_{41}^{(1)}C_1 + H_{42}^{(1)}C_2 + H_{43}^{(1)}C_3 + (H_{44}^{(1)} - E^{(1)})C_4 &= 0 \end{aligned}$$

Therefore, to find the eigenfunction  $\Psi_1$  corresponding to the eigenvalue  $E_1 (=0)$ , we place this value in the simultaneous equations; this procedure is done for all the  $E$ 's. As an example, consider  $E_3$ , which equals  $\sqrt{2} V$ . If one places this value in the aforementioned simultaneous equations, the following relationships are obtained:

$$C_1 = \frac{C_4}{\sqrt{2}}, \quad C_2 = 0, \quad C_3 = \frac{C_4}{\sqrt{2}}$$

Placing these values in the equation

$$\Psi_{E=4} = C_1^+ B + C_2^0 B + C_3^- B + C_4^0 A$$

results in

$$\Psi_{E=4} = C_4 \left( \frac{+B}{\sqrt{2}} + \frac{-B}{\sqrt{2}} + {}^0A \right)$$

Normalization and collection of terms results in

$$\Psi_{E=4} = \frac{1}{2} (+B + -B + \sqrt{2} {}^0A)$$

The other wave equations, derived in a similar manner, result in

$$\Psi_{E_1} = {}^0B$$

$$\Psi_{E_2} = \frac{1}{\sqrt{2}} (+B - -B)$$

$$\Psi_{E_4} = \frac{1}{2} (+B + -B - \sqrt{2} {}^0A).$$

As noted earlier, the eigenvalues were given in terms of  $V$ , the carbon spin-orbit coupling constant. The value for carbon (70) is  $16.4 \text{ cm}^{-1}$ . The actual separation,  $E$ , of the split levels is thus

$$\sqrt{2} V - (-\sqrt{2} V) = 2\sqrt{2} \cdot 16.4 \text{ cm}^{-1} = 46.2 \text{ cm}^{-1}.$$

#### Calculation of the singlet-triplet transition probability

The probability of intersystem crossing<sup>1</sup> of states (different species) is given by the Landau-Zener equation, which is

$$P = \exp \left( \frac{-4 |V|^2 E_p^2}{h |S_1 - S_2| v} \right)$$

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1 "crossing" indicates (see Fig. 19) following the  ${}^3B_1$  surface and remaining on it, i.e. traversing from point M to point N

where <sup>1</sup>

P = probability of crossing

h = Planck's constant

E<sub>p</sub> = spin-orbit perturbation as found in methylene

|S<sub>1</sub>-S<sub>2</sub>| = absolute value for differences in slopes of the two species  
at the crossing point

v = velocity with which the system approaches the crossing point.

The perturbation (E<sub>p</sub>) has been calculated to be 46.2 cm<sup>-1</sup> or 9.18 x 10<sup>-15</sup> erg. The velocity of approach is calculated from the bending frequency of CH<sub>2</sub> and the C-H bond length (1.03 x 10<sup>-8</sup> cm), and has a value of 7.28 x 10<sup>5</sup> cm sec<sup>-1</sup> or 4.05 x 10<sup>15</sup> degrees sec<sup>-1</sup>. The value for |S<sub>1</sub>-S<sub>2</sub>| has been calculated from the results of P.C. Jordan (71) who has kindly furnished the data needed for construction of Fig. 19; this value is 4.88 x 10<sup>-14</sup> erg deg<sup>-1</sup>. Substituting these values in the Landau-Zener equation leads to a (dimensionless) value for the exponential of 2.53 x 10<sup>-3</sup>. The transmission coefficient, t, for one vibration is (41):

$$t = 2P(1-P) = \frac{8\pi^2 E_p^2}{h|S_1-S_2|v}$$

The transition rate (singlet to triplet) is given by  $t \times \nu$ , where  $\nu$  is bending frequency. Substituting these values in this relationship leads to a rate of 2.2 x 10<sup>13</sup> sec<sup>-1</sup>.

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1 see, for example, K.J. Laidler, The Chemical Kinetics of Excited States, Oxford University Press, Oxford (1955)

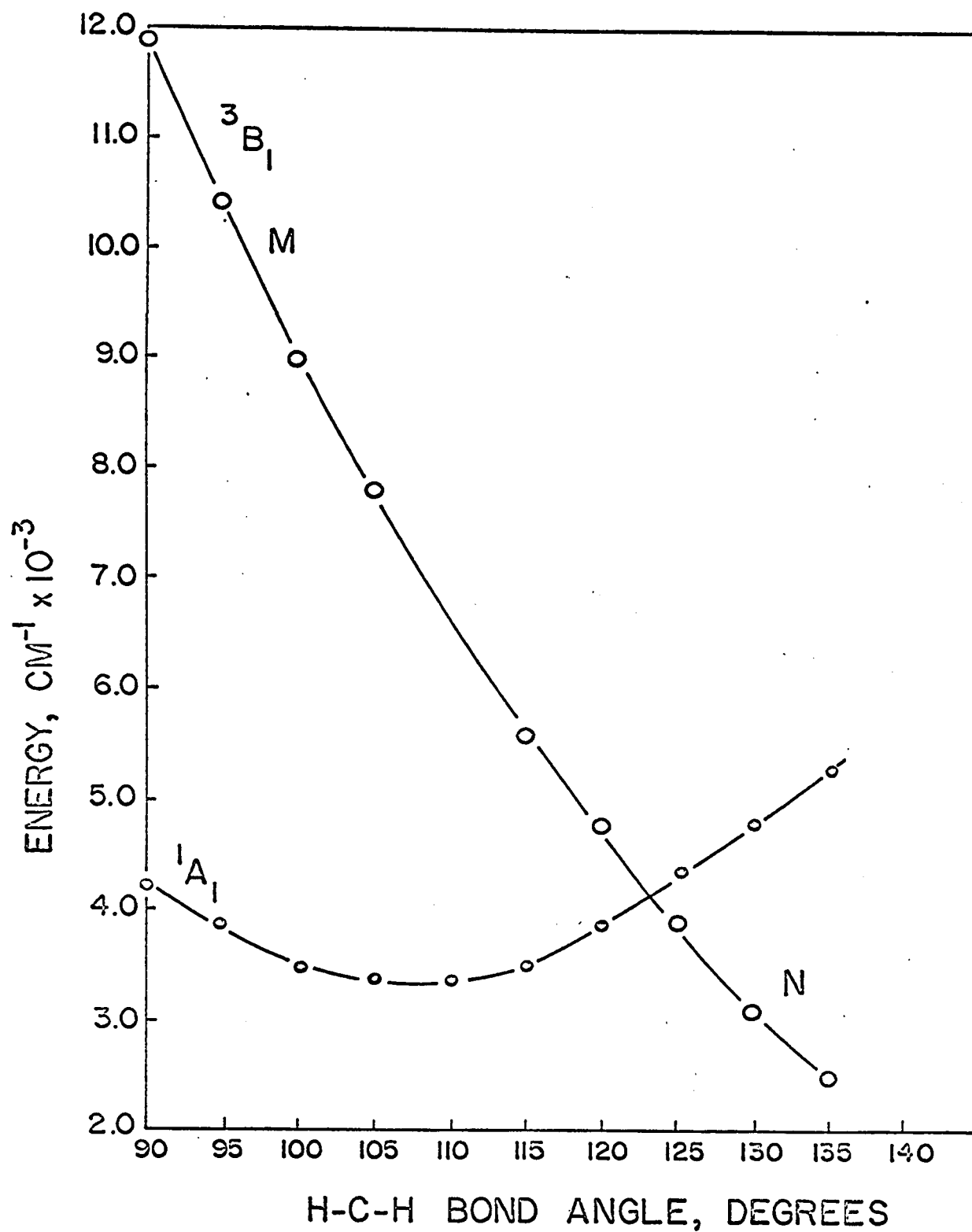


Figure 19 Expanded Potential Energy Curves For Lowest Singlet and Triplet Species for Methylene (After P.C. Jordan)

CLAIMS TO ORIGINAL RESEARCH

1. An experimental technique allowing one to follow the progression from purely singlet to mostly triplet methylene behavior has been devised.
2. Pentene formation in the photolytic reaction was followed as the change from singlet to triplet methylene occurred.
3. The relative abilities of the different inert gases in fostering the singlet-triplet transition were determined.
4. The relative abilities of the different inert gases in cooling "hot" dimethylcyclopropanes were determined.
5. Internal hydrogen abstraction mechanisms for the formation of butene-1 and 3-methylbutene-1 were proposed, consistent with the known facts.
6. The effect of molecular oxygen on the photolytic reaction of diazomethane with cis-butene-2 is negligible when singlet methylene is involved (as compared to the drastic effect on the triplet reaction).
7. Free methylene is not generated by the thermolysis of diazomethane at temperatures lower than 225°C.
8. At temperatures of 225°C, the vapor phase reaction of diazomethane with cis-butene-2 is a molecular one involving diazomethane (not methylene) reaction.
9. A method has been devised whereby one may test for the appearance of free methylene.
10. The resonance splitting between the singlet and triplet methylene species has been calculated, as well as the transition probability.

SUGGESTIONS FOR FUTURE WORK

1. Resolution of apparent similarity of some of the inert gases in effecting the singlet-triplet transition; to be accomplished mainly by decreasing the partial pressure of cis-butene-2.
2. Mercury photosensitized reactions involving diazirine (if the absorption spectrum permits; otherwise, ketene) and cis-butene-2 at relatively low pressures.
3. High temperature thermolysis ( $300^{\circ}\text{C}$  and greater) to determine if free methylene is actually formed.
4. Investigation of the high temperature thermolysis in the presence of inert gas, followed by comparison with the photolytic reaction.

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