PHOTOLYSIS OF THE TETRAZOLE RING

by

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PREFACE

This thesis is concerned with the photolysis of the tetrazole ring. The thermolytic behaviours of a number of tetrazoles have been known for a long time, but there is almost no report in the literature concerning the photolysis of the tetrazole ring. This prompted us to study the photolytic behaviours of the various substituted tetrazoles.

The author wishes to express his thanks to Professor R. R. Fraser, under whose direction and constant supervision the work described in the second part of this thesis was carried out. Throughout the course of this research and in the preparation of the manuscript, Professor Fraser was always prepared to give freely his time and advice. Without his ideas, inspiration and patience, this research, as well as the writing of this thesis, could not have come to a successful conclusion.

The author also wishes to thank Mr. Paul Hanbury for proofreading a part of this thesis, and Mrs. A. Eriksen for typing the entire thesis.

The author would like to extend his particular thanks to his wife for proofreading a part of the thesis and for her encouragement and patient understanding throughout the course of this work.

Finally, the author wishes to thank the Canadian Commonwealth Scholarship and Fellowship Committee for the award of a scholarship for the last 3-1/2 years.

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The preparationsof 5-ethoxycarbonyltetrazole, 5-phenyltetrazole, 1-methyl-5-phenyltetrazole, 2-methyl-5-phenyltetrazole, 5-p-nitrophenyltetrazole, 1-methyl-5-p-nitrophenyltetrazile, 2-methyl-5-p-nitrophenyltetrazole, 1-methyl-3,5-diphenyl-1,2,4-trai zole and 2-methyl-4,5-diphenyl-1,2,3-triazole have been described.

Photolysis of 5-phenyltetrazole produces 3,6-diphenyl-s-tetrazine and 1,4-dihydro-3,6-diphenyl-s-tetrazine, whereas the latter undergoes smooth oxidation with bromine producing 3,6-diphenyl-s-tetrazine. Several attempts were made to trap the possible nitrilimine intermediate by photolysing 5-phenyltetrazole in the presence of norbornene and ethyl acrylate, but in neither case was any pyrazoline derivative obtained. The production of 1-4-dihydro-3,6-diphenyl-s-tetrazine through the possible photodimer or free radicals formations has also been discussed.

Photolysis of 2-methyl-5-phenyltetrazole produces 2-methyl-4, 5-diphenyl-1, 2, 3-triazole in addition to some other yet unidentified products. The structure of 2-methyl-4, 5-diphenyl-1, 2, 3-triazole has been confirmed by its independent synthesis starting from benzil.

Several attempts were made to trap the possible C-phenyl-N-methyl-nitrilimine by photolysing 2-methyl-5-phenyltet razole with benzonitrile, but no change in the total yield of 1, 2, 3-triazole derivative was observed. The formation of 2-methyl-4, 5-diphenyl-1, 2, 3-triazole through a possible photodimer of 2-methyl-5-phenyltetrazole has also been assumed.

As 2-methyl-4, 5-diphenyl-1, 2, 3-triazole on heating up to 220-225° for 6 hours did not produce any 1-methyl-3, 5-diphenyl-1, 2, 4-triazole, the idea of the formation of 1-methyl-3, 5-diphenyl-1, 2, 4-triazole via 2-methyl-4, 5-diphenyl-1, 2, 3-triazole during the thermolysis of 2-methyl-5-phenylterrazole was given up. It has been shown, by using the Vycor filter, that radiations above 2400 Å are responsible for effecting the photolysis of 2-methyl-5-phenyltetrazole.

Several attempts were made to effect the photolysis of 1-methyl-5-phenyltetrazole by direct irradiation and once with the sensitizer, benzophenone, but in all cases 1-methyl-5-phenyltetrazole was found to be stable towards ultraviolet irradiation. 2-methyl-5-p-nitrophenyltetrazole, which has been isolated in 93% yield by methylation of 5-p-nitrophenyltetrazole , has been found to be stable towards the direct ultraviolet irradiation.

The magnetic anisotropy-effects on the ortho protons of the phenyl rings of 2-methyl-5-phenyltetrazole, 5-phenyltetrazole, 5-p-nitrophenyltetrazole, 2-methyl-5-p-nitrophenyltetrazole and 1-methyl-3, 5-diphenyl-1, 2, 4-triazole and 3, 6-diphenyl-s-tetrazine have been discussed.

Infrared, ultraviolet and n.m.r. spectra were used extensively in the structure determinations of these compounds.

PHOTOLYSIS OF THE TETRAZOLE RING

INTRODUCTION

A. General Introduction

The beginning of photochemistry probably coincided with the first rays of sunlight. As a matter of fact, photochemical reactions, such as photosynthesis, have always played an important role in the development of life.

Reports of organic photochemical reactions are to be found even in the earlier chemical literatures. However, in those days, the discovery and study of photochemical reactions were often the result of an accident. Only recently has quantum mechanics clarified the effect of light on matter. During the primeval ages of photochemistry (from about 1850 to 1920), numerous and wondrous photochemical reactions were discovered, but most of them were lacking any useful application, as well as any unifying theory behind those transformations. Among the pioneers in this field were Ciamician and Silber[1] and Paterno[2], who obtained exciting and at the same time discouraging results, because the photochemical reaction mixtures were hopelessly complex and no methods were then available to standardize their reactions. From 1920-1950, photochemistry was perhaps considered in the domain of the physical chemists who concentrated on the study of relatively simple systems, with particular emphasis on the secondary free-radical processes in the gas phase[3,4]. In the last decade, organic photochemistry has become more popular, resulting in a surge of interest and activity in this field. The reasons for this are several, but the most important of them are:

(a) the development of a number of spectroscopic and analytical techniques, which have enormously simplified the challenging complexity of the problems of structure and purification associated with many photochemical programmes, and

(b) the advent of somewhat belated appreciation by the organic photochemists of the theoretical concepts and methods of electronic spectroscopy and quantum mechanics[4]. Besides these it has also been realised that photochemistry often provides a shorter route for the synthesis of compounds than conventional synthetic methods and sometimes provides the only route.

A photochemical reaction is any chemical reaction initiated by ultraviolet or visible light. So for a photochemical reaction to occur, light must be absorbed by the molecule or by a certain part of the molecule[5].

Photochemical transformations may be divided into several categories depending on the nature of the operations. The light used may be ultraviolet or visible and the reactions may be promoted with or without a sensitizer. Reactions may be induced in the vapor, liquid or solid phases, with notable differences in products. Beside these, other physical factors such as temperature may be of importance[6].

Photochemical reactions will be of use to the synthetic organic chemists, when one or other of the following conditions are fulfilled[7]:

(1) The number of molecules reacting per quantum of light absorbed is quite large;

(2) The products can be synthesized either more easily or in a higher state of purity.

(1) The Overall Photochemical Process[3, 8, 9]

"The primary photochemical process comprises the series of events beginning with the absorption of a photon by a molecule and ending either with the disappearance of that molecule or with its conversion to a state such that its reactivity is statistically no greater than that of similar molecules in thermal equilibrium with their surroundings". So in the primary photochemical process one of the electrons in the stable orbitals, that is the ground singlet state, Sg, is excited to an unoccupied orbital of higher energy - an antibonding molecular orbital. Since spin must be conserved in this transition, the excited state will be an upper singlet state, Sn (n = 1, 2, 3 ...). The initially excited molecule may find itself in any of the allowed vibrational levels of the Sn electronic excited states, but rapidly, in the order of 10^{-13} sec., it decays to the lowest vibrational level of the Sn state. If Sn is a higher energy state than the lowest or the first excited singlet state (i. e. $n > 1$) it will quickly decay non-radiatively by a process called "internal conversion" in the order of 10^{-11} sec. to the Si state, which has a longer lifteime of 10^{-8} to 10^{-7} sec. (Fig. 1, modified Jablonski diagram)[3]. At this point,

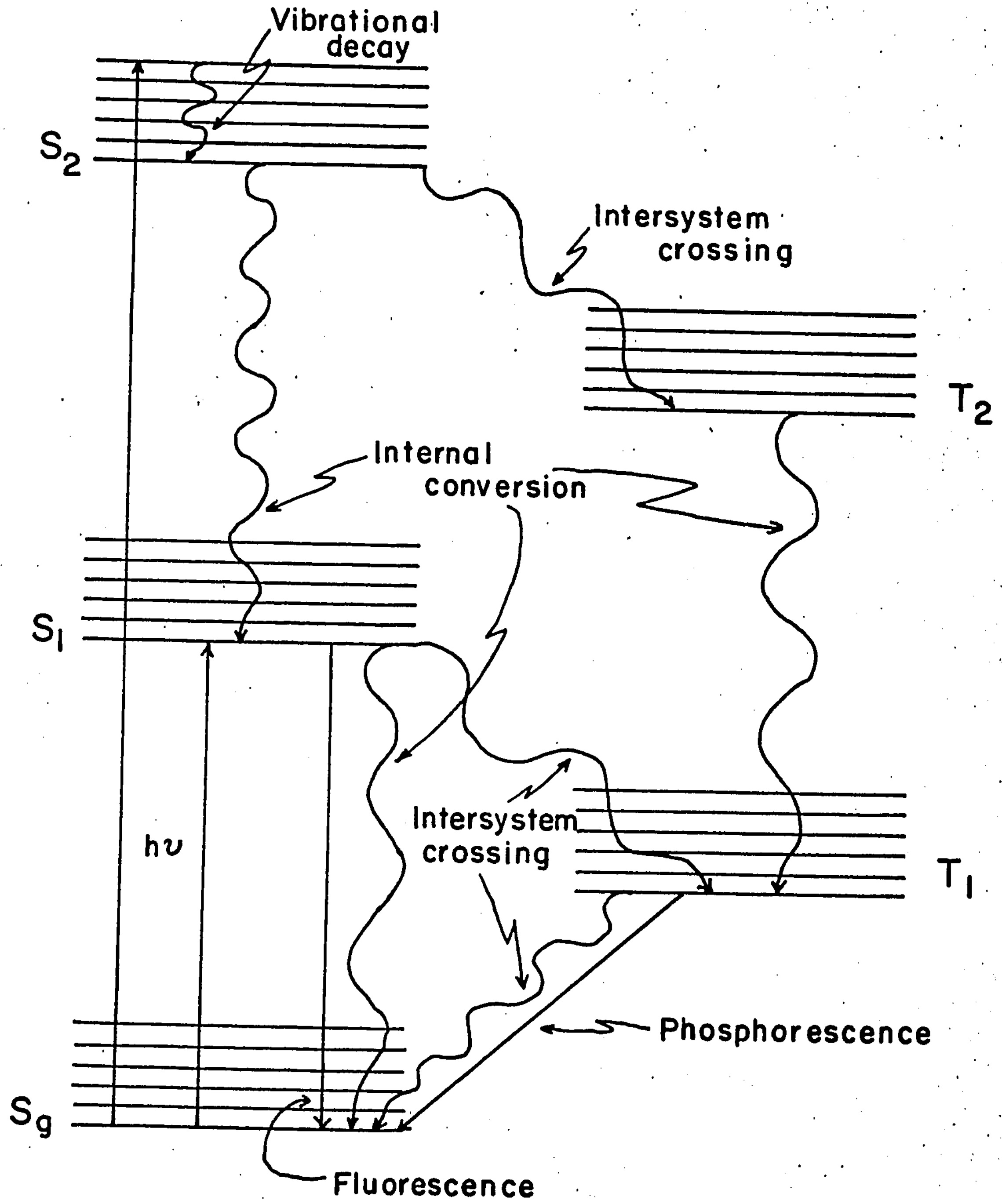


Fig. I. Modified Jablonski Diagram.

there are a number of paths available for the decay of the S_1 state depending upon the nature of the molecule, temperature and physical state. A molecule in an S_1 state may return directly to the ground state by emission of a photon (a radiative process) called fluorescence, or by internal conversion, the non-radiative process in which energy is thermally dissipated to the surrounding molecules. The molecule in an S_1 state may also undergo a secondary process, where new products of chemical interest are formed. Again the molecule may revert directly to the ground state and excite a neighbouring molecule to an electronically excited singlet state of equal or lower energy. And finally, the molecule in the S_1 or S_2 or Sn state can undergo a non-radiative process called intersystem crossing to the triplet states, T_1 or T_2 or Tn. The triplet state has net spin one and hence a multiplicity of three. Intersystem crossing is formally forbidden because it involves a change in the electronic spin; but it occurs very easily in the order of 10^{-9} sec. in certain organic molecules, particularly many aromatic and carbonyl containing compounds. A triplet state has a longer lifetime than the corresponding singlet state. If a higher triplet state is formed by intersystem crossing, this triplet will undergo rapid internal conversion to the lowest triplet, T_1 state. An excited triplet molecule dissipates its energy both by radiative and non-radiative paths. The $T_1 \longrightarrow Sg$ radiative transition is known as phosphorescence (usually observed at low temperature such as that of liquid nitrogen and at longer wavelengths). The non-radiative paths are (a) simple thermal decay to the ground state, (b) photochemical reactions to yield new molecules, (c) energy transfer to a neighbouring molecule so that the latter in turn is excited to a triplet state of equal or lower energy. If the T_1 state of the neighbouring molecule (i. e. the potential acceptor) is higher in energy than the T_1 of the donor, then the excitation transfer will not occur. A fascinating field of photochemistry is the study of chemical reactions taking place in the acceptor molecules after it has been "sensitized" or energized by the triplet donor[3, 8, 9, 10].

(2) Transition Probability and Energy Transfer[3, 4]

"The transition probability is a measure of probability that a photon, possessing the appropriate energy (i. e. of the right wavelength) rather than passing directly through a molecule, will be absorbed causing an electronic transition". As it has been mentioned previously, an excited molecule in an S_1 or T_1 state can, along with other possible paths of decay, transfer its excitation-energy to the neighbouring molecules (acceptors). If D is the donor or sensitizer and A is the acceptor, the process may be written:

$$D \xrightarrow{h\nu} D^*$$
$$D^* + A \longrightarrow D + A^*$$
$$A^* \longrightarrow A + h\nu$$
$$A^* \longrightarrow A + \text{heat}$$
$$A^* \longrightarrow \text{Products}$$

Energy transfer of singlet excitation, observable by the induced fluorescence and fluorescence depolarisation, has been well-documented by Reid[11] and Forster[12]. Forster[13] has developed a theory of long range (40-100 Å) single step excitation transfer which has recently been established by Dexter[15] and Bennett[16]. This theory is based upon the coupling of the transition dipoles of sensitizer and acceptor molecules. This mechanism is also known as the resonance transfer mechanism[14]. When the dipole transition in one or both molecules is forbidden, a second mechanism comes into effect. This is the exchange or collisional mechanism[17]; by which excitation transfer occurs through the collision between D* and A.

Transfer of triplet excitation was first reported by Terenin and Ermolaev[18, 19, 20], who observed induced phosphorescence at low temperature. Both theory and experimental results[21] indicate that transfer of triplet excitation must involve molecular contact between the donor and the acceptor (quencher) molecule which is initially in its ground electronic state. Although triplet-triplet transfer is strongly forbidden by the resonance mechanism[15], it is completely allowed by the collisional energy transfer mechanism, provided that the triplet energy of the donor be greater than the corresponding triplet energy of the acceptor, and the lifetime of D* must be sufficiently long to allow an encounter between D* and A.

(3) Limitation of Light Sources and Reaction Vessels[7]

The usefulness of photochemical reactions is determined to some extent by the availability of the reaction vessels and steady light source. Infrared radiation produces little effect but to raise the temperature in the system. Visible light (7000 Å - 4000 Å) will frequently, if absorbed, produce chemical changes. Ultraviolet light induces many photochemical reactions. Most of the photochemical studies have been done mainly in the near ultraviolet region, which roughly extends to 2000 Å. Relatively little work has been done in the far ultraviolet region.

Soft glass transmits visible light satisfactorily, but stops transmitting at about 3500 Å. Pyrex transmits light of wavelengths greater than 3000 Å. Fused quartz in small thickness (~1 mm.) may transmit as far as 1650 Å to 1750 Å. For still shorter wavelengths, a few substances such as calcium fluoride and lithium fluoride, may be used as windows.

(4) Light Sources[7, 8]

In recent years, various types of lamps which give a very high light intensity for a very short period of time have found many applications[8]. Thus a photolysis lamp is used to produce a photochemical reaction and a spectroflash lamp is employed to determine the absorption of the transient species produced by high intensity photolysis flash.

High Pressure Lamp - This is a lamp filled with mercury or Xenon vapor (or a mixture of them) to about ten or more atmospheres of pressure. Although the total energy output is very high, the emission is largely above 3000 Å.

Medium Pressure Lamp - This is a lamp filled with mercury vapor to a pressure of one atmosphere. The total intensity in the near ultraviolet and visible light is lower than that of a high pressure lamp, but photochemically useful light at wavelengths less than 3000 Å is produced.

Resonance Lamp - Such lamps (also known as "Low pressure lamps") are often used as line sources in photochemical studies. These lamps usually contain a small amount of a metal vapor (such as mercury, cadmium, zinc etc.) and several mm. pressure of a rare gas. They operate at relatively low current and high voltages. Most of the radiation is concentrated in the resonance lines[3] at 1849 and 2537 Å.

Sunlight - Naturally, it is an inexpensive source of light, but to obtain approximately monochromatic light, suitable color filters should be used. Sunlight can rarely be observed to extend below 2900 Å, and the intensities at the shorter wavelengths are quite small. Much, but not all of the infrared may be removed by water. A flask filled with water may be used to focus sunlight or light from the filament lamps; but this will not prevent the increase in temperature, so that thermostatting is necessary.

Filament Lamps - For those reacting systems which absorb in the visible and near ultraviolet region, 500-1000 watt Mazda lamps can be very useful. Since these lamps emit a considerable amount of infrared, the reaction vessel should be thermostatted and shielded by a layer of water from the light source.

Hydrogen discharge[7] - When a continuous source of radiation up to 4000 Å is required, an uncondensed high potential discharge through hydrogen at low pressure is satisfactory. Radiation of high intensity may be obtained with a hydrogen discharge, but the light is far from monochromatic. The range covered extends down to 1200 Å.

Sparks - Sparks between aluminum electrodes are useful in the region between 1800 and 2000 Å. Zinc sparks are also very useful for wavelengths somewhat greater than 2000 Å.

(5) Concept of Quantum Yield[7, 4]

When a molecule absorbs light, it receives energy in the form of discrete units or quanta. A quantum of the radiant energy is $h\nu$ ergs, where h is Plank's constant and ν is the frequency of radiation. The value of a quantum is $1.983 \times 10^{-8}/\lambda$ ergs, where λ is the wavelength in Angstrom units, 10^{-8} cm. In order to determine the quantum yield (ϕ), it is necessary to measure in absolute units the amount of light absorbed by the reaction system per unit time and to determine simultaneously the number of molecules of product or number of molecules disappearing per unit time. Thus in the reaction

$$CH_3COCH_3 \xrightarrow{h\nu} C_2H_6 + CO$$

one may consider either the quantum yield of carbon monoxide formation, the quantum yield of ethane formation or the quantum yield of acetone disappearance. So,

$$\emptyset = \frac{\text{Number of molecules undergoing a particular process}}{\text{Number of quanta absorbed by the system.}}$$

(6) Photochemical Laws[4]

Four important photochemical laws or rules have evolved so far over the years that apply quite generally for organic photochemistry:

(1) Only the light absorbed by a system is effective in producing a photochemical change:

(2) Each photon or quantum absorbed activates one molecule in the primary excitation step of photochemical sequences;

(3) Each photon or quantum absorbed by a molecule has a certain probability of populating either the lowest excited singlet state S_1 or lowest triplet state T_1;

(4) The lowest excited singlet (S_1) or triplet (T_1) states are the starting points (in solution) of most organic photochemical processes.

B. Organic Photoreactions

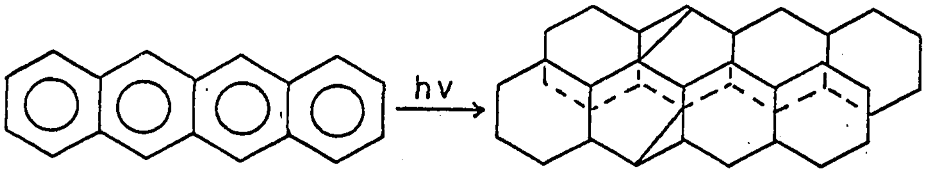
Organic photochemistry is a field of increasing activity and interest. The accumulated mass of information concerning the photochemical transformations such as isomerisations, rearrangements, addition, dimerisation, polymerisation, oxidation, reduction, alkylation, sulfonation, ring enlargement, ring contraction, carboxylation, chain reaction, dissociation, solvolysis, synthesis of various organic compounds and many more unclassified photoinduced reactions, has enabled organic photochemistry to occupy a distinct position in the field of organic chemistry.

In this rapidly expanding field, it has been observed that considerably less work has been performed in the field of heterocyclic aromatic compounds, compared to the benzenoid aromatic, alicyclic and aliphatic systems. So far not a single study has been reported where photolysis has been carried out on the tetrazole ring itself. This five membered ring contains two double bonds, one carbon and four nitrogen atoms. Although tetrazole itself is transparent[100] to the ultraviolet light throughout the range of 230-450 $m\mu$, the 1, 2 or 5-aryl tetrazoles have appreciable absorption in that range[23]. Although tetrazole has aromatic-like resonance stability, its acidic nature and the accumulation of π-electrons, and the lone pairs on the nitrogen atoms make it considerably less aromatic. Considering all these factors it was presumed that the tetrazole ring could be appreciably susceptible towards ultraviolet irradiation. Therefore, a photochemical study of substituted tetrazoles has been undertaken. In the succeeding chapters of this thesis, the techniques of approach and the various findings are described in detail and interpreted in the light of modern theory of photochemical transformations.

Photoisomerisation and Photodimerisation

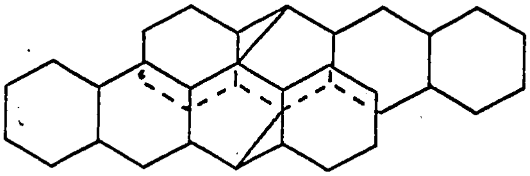
Photoinduced isomerisation is one of the most rapidly expanding branches of organic photochemistry. A number of reviews and articles on this subject have already been published[24, 25, 26]. Photoinduced isomerisation, dimerisation and cycloaddition reactions are found in all types of organic compounds, though mainly with compounds containing unsaturation[27, 28, 29].

The phenomenon of photoinduced dimerisation is well established in the field of photochemistry, one of the oldest examples being a polynucleated aromatic compound, anthracene[30]. Apart from anthracene and related compounds, some other polynucleated aromatic systems have been reported to undergo photoinduced dimerisation[31], as for example tetracene (I) on irradiation produced α- and β-ditetracene (II) and (III).



I

II



III

A great number of photoinduced dimerisations have been reported from α-, β-unsaturated carbonyl compounds[32, 33].

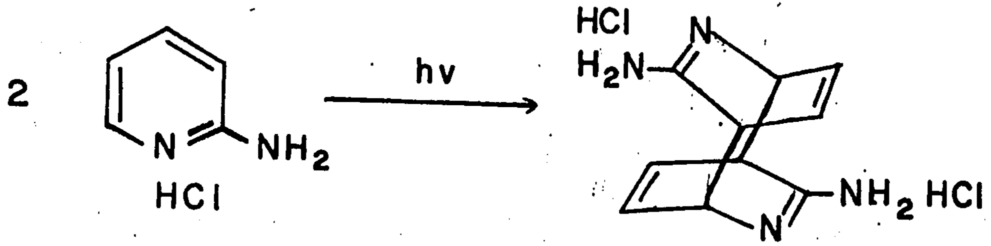
Photoinduced dimerisation in heterocyclic compounds is not as common as in the polynucleated aromatic compounds. However, several cases are of interest. Taylor[34, 35] isolated photodimers from the irradiated reaction mixture of 2-aminopyridine-hydrochloride (IV) and 2-pyridone (V) but the correct assignments to their structures (VI and VII) were reported by Mayo and Ayer[36] as well as by Slomp and co-workers[37].

It has also been reported by Slomp and Paquette[38] that variously substituted 2-pyridones on irradiation produce 3,7-diazatricyclo$[4,2,2,2^{2,5}]$dodecane-9,11-diene-4,8-dione.

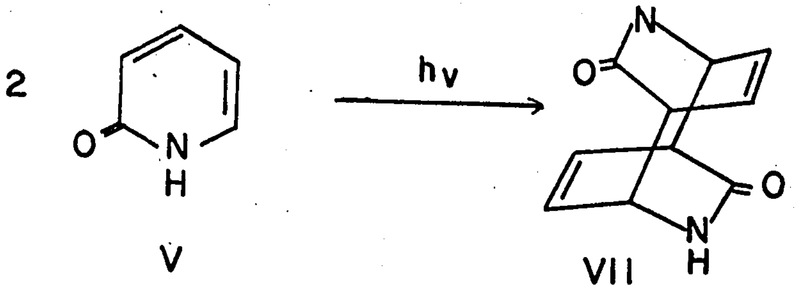
Half closed and caged-dimers have been obtained from quinones[39, 40] and pyrones[41, 42, 43] by irradiation in ultraviolet light as well as in sunlight.

Thymine(VIII)[46] and Uracil[45] form photodimers on irradiation in frozen aqueous solution and in aqueous solution. The correct assignment to the structure (head to head) of thymine dimer (IX) was later on reported by Blackburn and Davies[44].

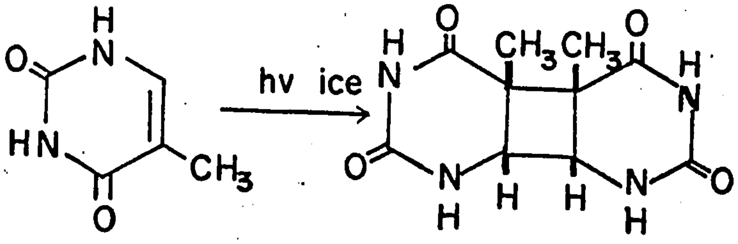
With a very few exceptions, polynucleated aromatic compounds, as well as their derivatives, usually undergo photodimerisation, while benzene and its various derivatives usually undergo photoinduced isomerisation, producing unexpectedly interesting compounds. Lately Blattmann and co-workers[47] have reported an example of photoinduced valence tautomerism in a polynuclear aromatic system. They isolated the compound (XI), having a metacyclophane structure, from the irradiation of trans-15,16-dimethyldihydropyrene (X). Presently, a revolutionary interest is being observed in the photoinduced valence tautomerism in benzene and a variety of substituted benzenes, Fulvene (XII) and the various fulvene derivatives are obtained when benzene, toluene, isopropyl benzene and anisole are irradiated[28].



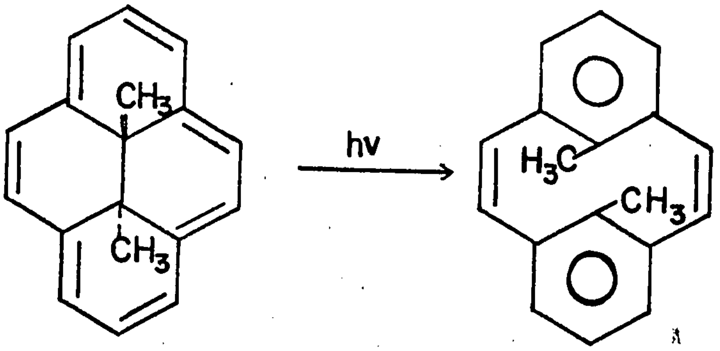
IV VI



V VII

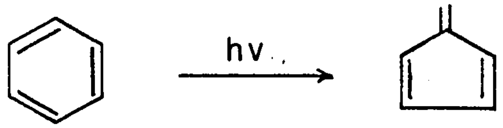


VIII IX

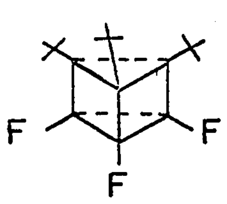


X XI

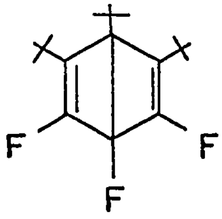
When 1, 2, 4-tri-tertiarybutylbenzene was irradiated in ultraviolet light, a bicyclo-[2, 2, 0]-hexa-2, 5-diene or "Dewar benzene" derivative was produced[29]. Subsequently, these authors[48] were able to prepare Dewar benzene itself by the oxidative decarboxylation of bicyclo-[2, 2, 0]-hexa-5-en-2, 3-dicarboxylic acid anhydride. Beside this, several other attempts were made by various groups of people to prepare and isolate Dewar benzene hydrocarbon or its derivatives. Griegee and Zanker[49] isolated dimethyl "Dewar tetramethylphthalate"; and Ivan Haller[50] lately has isolated photolytically produced Dewar hexafluorobenzene. H. G. Viehe and co-workers[51] have isolated derivatives of prismane (XIII), Dewar benzene (XIV) and benzvalene (XV) from the spontaneous trimerisation of t-butylfluoroacetylene.



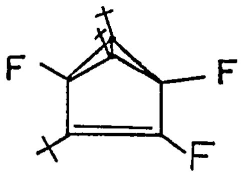
XII



XIII



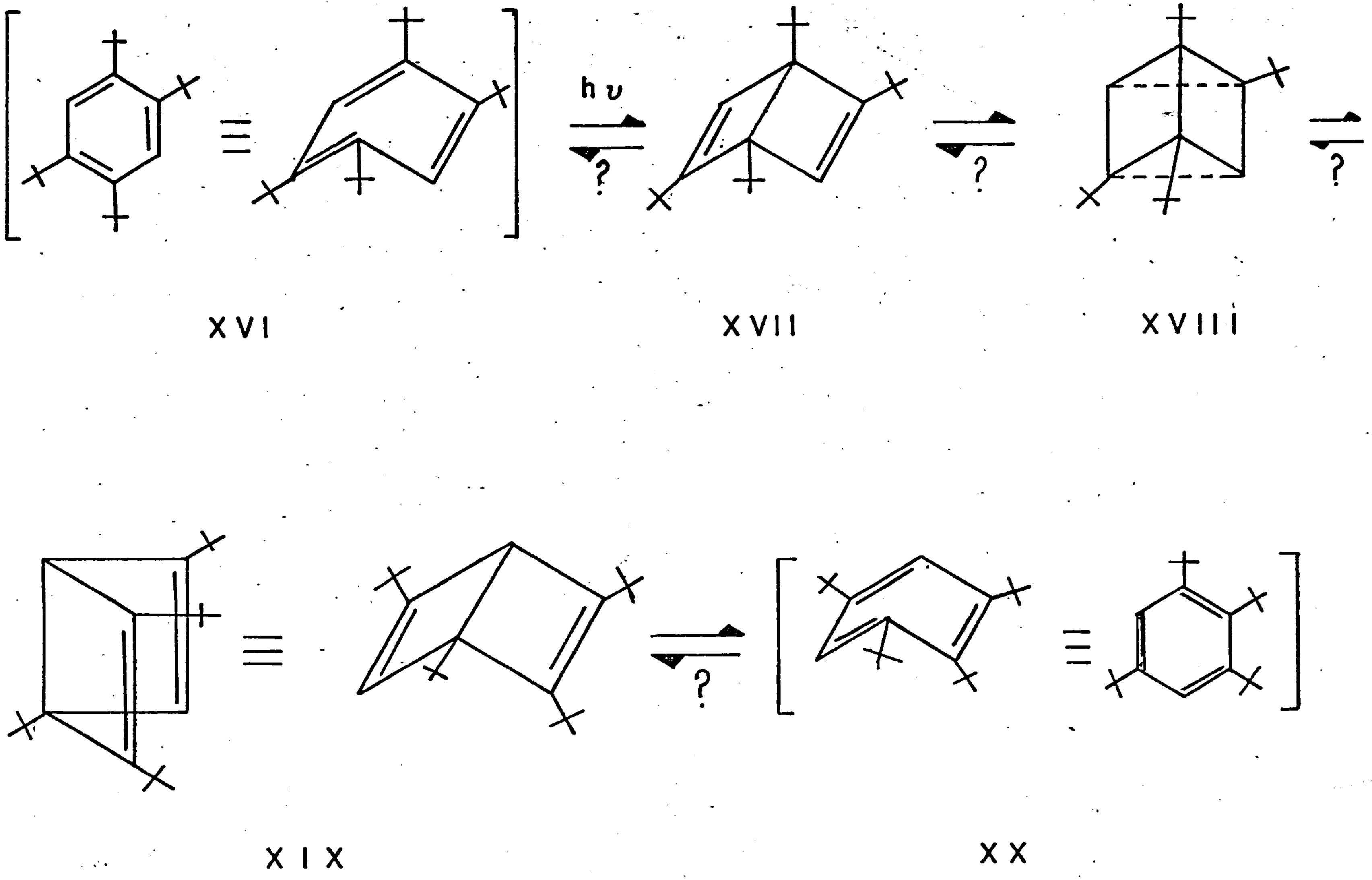
XIV



X V

Before the isolation and characterisation of benzvalene[51] the photoinduced valence-tautomerism of benzene and its derivatives was thought to proceed via the "Dewar benzene" intermediate; but the more strained Ladenburg type intermediate (i.e. prismane) was also considered in certain cases. Arnett and Bollinger[52] preferred the Ladenburg type intermediate in the photoinduced isomerisation of 1, 2, 4, 5-tetratertiarybutylbenzene into 1, 2, 3, 5-tetratertiarybutylbenzene. The authors presumed that the starting material 1, 2, 4, 5-tetratertiarybutylbenzene (XVI) was probably wrapped into a boat configuration due to strong steric interaction between the tertiary butyl groups in the planar configuration. Then this boat configuration easily converted into the Dewar benzene configuration (XVII) under the photochemical excitation. This Dewar benzene configuration easily reorganized into prismane (XVIII), then direct reversion of the prismane configuration to the Dewar configuration (XIX) and finally rearranged to the end product (XX).

Afterwards it is noticed that the idea of benzvalene comes into force to interpret photoinduced valence tautomerism in benzene as well as in the substituted benzene. Wilzbach[53] presumed that the 1, 2 shift of the methyl groups in the photoinduced isomerisation of mesitylene labelled at C_3 with ^{14}C into 1, 2, 4-trimethylbenzene labelled at the 1, 2 and 4- positions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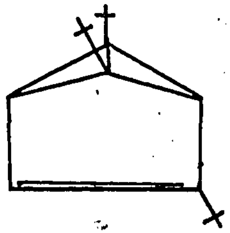
XVI
XVII
XVIII
XIX
XX

was due to ring carbon interchange. Although a Dewar benzene intermediate was considered in this transformation, the benzvalene type intermediate was highly advocated, particularly in solution, where it was assumed that the excess energy in benzvalene, could be drained off by solvation. Subsequently, Wilzbach and Kaplan[54] were able to isolate and characterise the benzvalene (XXI) in addition to the Dewar benzene (XXII) and the prismane (XXIII) from the irradiation products of 1, 2, 4- or 1, 3, 5-tritertiary-butylbenzene.

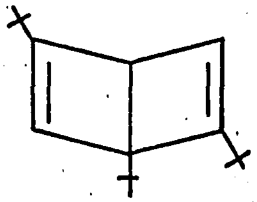
Further evidence[55, 113] in support of the benzvalene intermediate came from the products (XXIV) and (XXV), which were formed during the photolysis of benzene in trifluoroethanol at 2537Å.

The valence bond tautomerism is not limited to the benzene nucleus; Wynberg and Driel[56] have observed a photoinduced valence tautomerism in arylthiophenes. They have isolated 3-phenylthiophene (XXVIII) and 2, 3-dithienyl (XXIX) as well as 3, 3-diethienyl (XXX) by irradiating 2-phenylthiophene (XXVI) and 2, 2-dithienyl (XXVII) with ultraviolet light at 80°C in benzene solution.

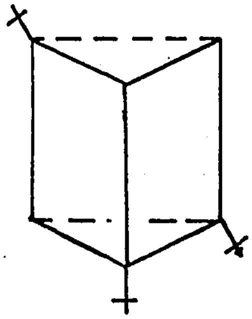
These authors[56] first explained these valence bond tautomerisms as proceeding via (XXXI),



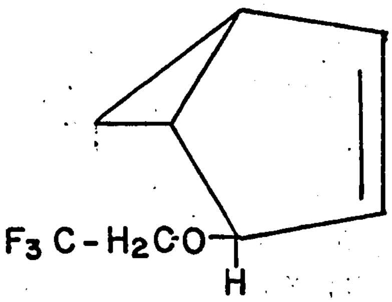
XXI



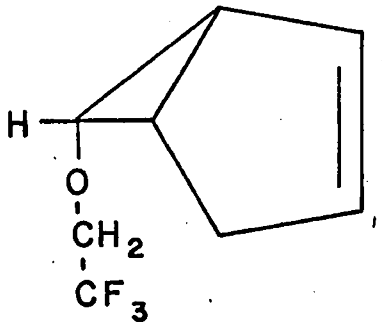
XXII



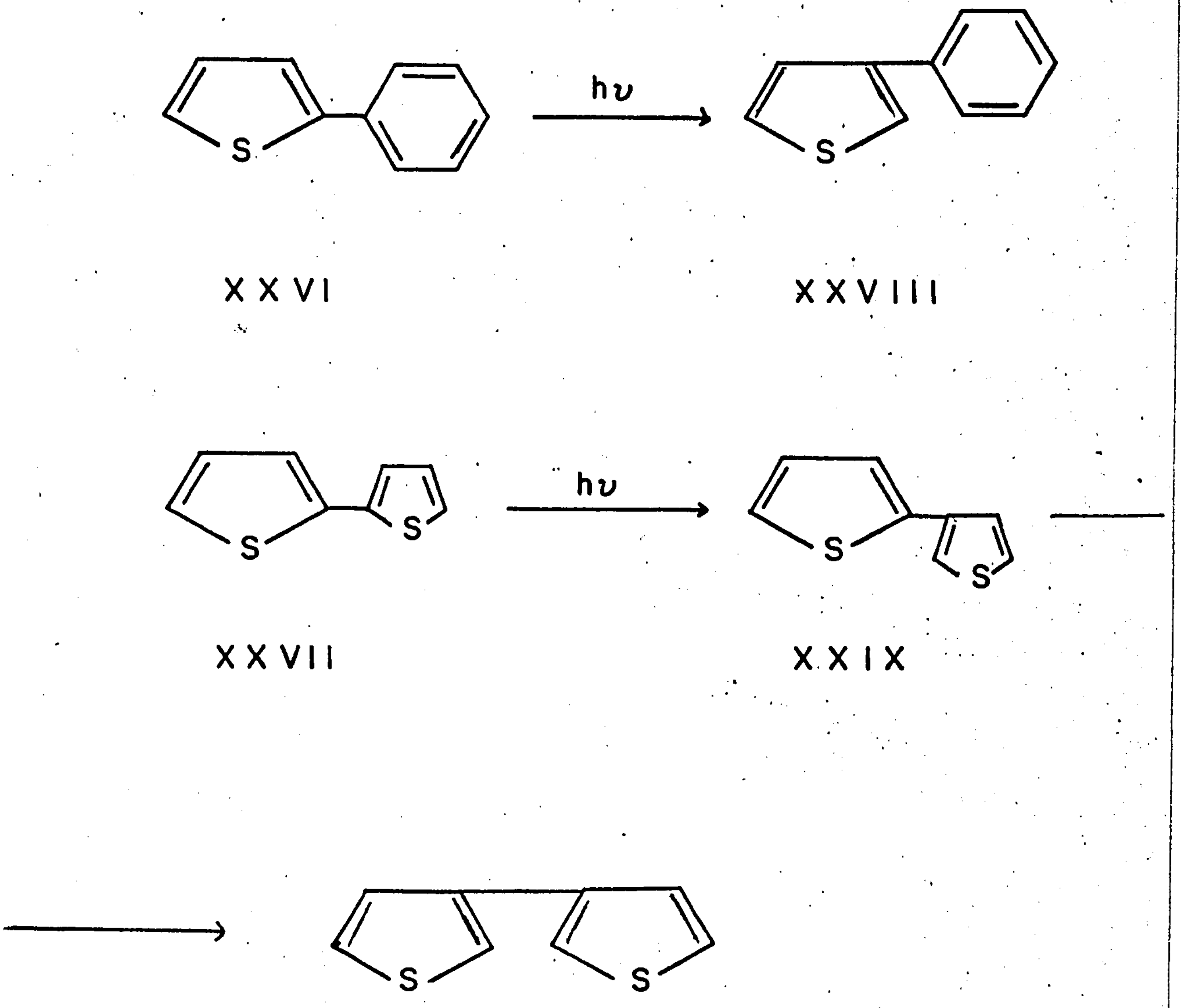
XXIII



XXIV



XXV



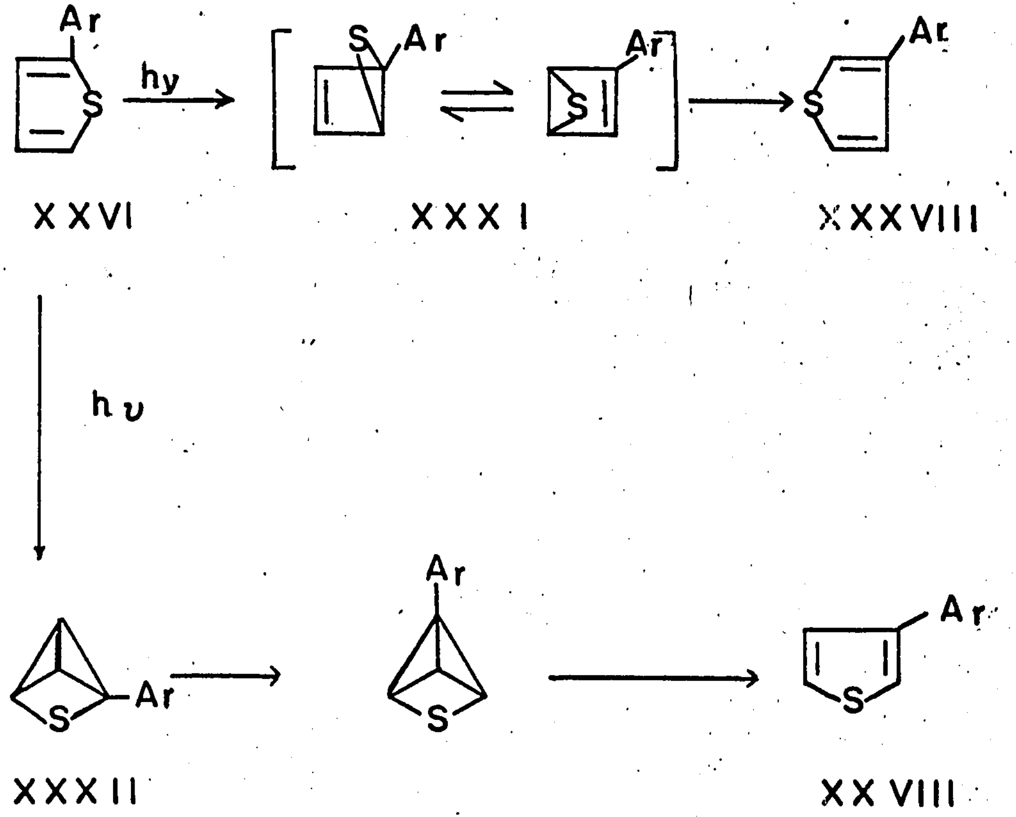
XXVI

XXVIII

XXVII

XXIX

XXX



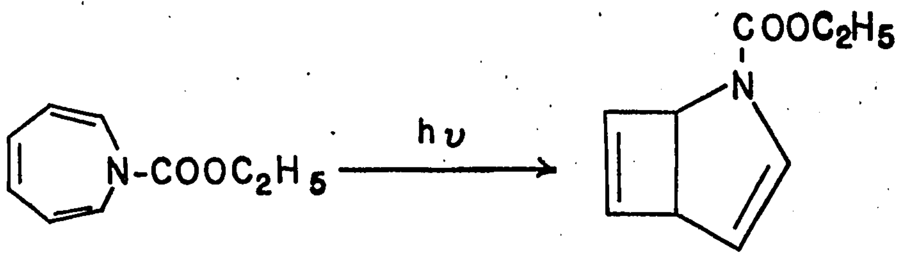
XXVI XXXI XXXVIII

XXXII XXVIII

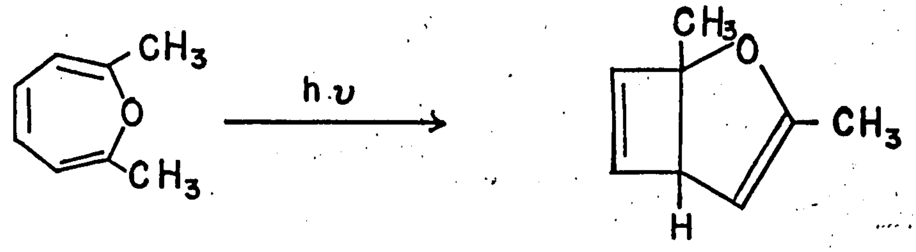
and valence bond structure intermediates (XXXII). Subsequent[126] studies have led them to postulate (XXXII) as the intermediate.

A number of other heterocyclic compounds have been found to undergo photocatalyzed valence tautomerism. Heteroatomic 8π-electrons system, like N-carboethoxyazepin (XXXIII) and 2, 7-dimethyloxepin (XXIV) undergo photoinduced valence tautomerisation to the bicyclo[3, 2, 0]hepta-3, 6-diene systems (XXXV) and (XXXVI)[57, 58]. Photocatalysed skeletal rearrangements have been observed in heterocyclic compounds like 2, 3-dihydropyrazin (XXXVIIa, b)[59] and 3, 5-diphenylisoxazole (XXXVIII)[27]. The former rearranged to N-methylimidazole (XXXIVa, b) and the latter to 2, 5-diphenyloxazole (XL).

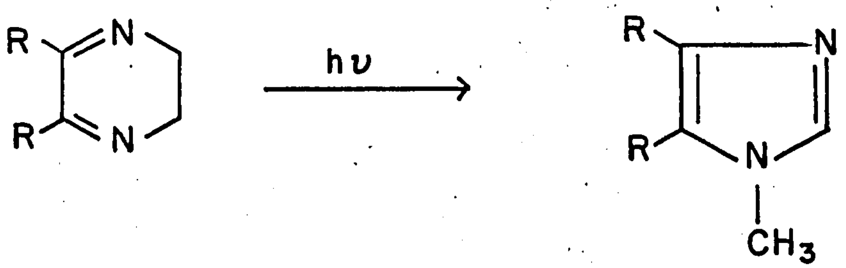
The phenomenon of light catalysed oxidations and reductions have been observed for a long time; one of the well-known examples being that of the photoinduced reduction of benzophenone to benzopinacol in isopropyl alcohol[60]. Usually photoinduced oxidation takes place in the presence of free oxygen; while photoreduction is usually brought about by hydrogen abstraction from the solvent[24, 61]. A major group of photochemical reduction reactions are oxidation reduction processes, e.g. phenazine was reduced by ethanol to give dihydrophenazine[62] while ethanol was oxidised to acetaldehyde.



XXXIII XXXV



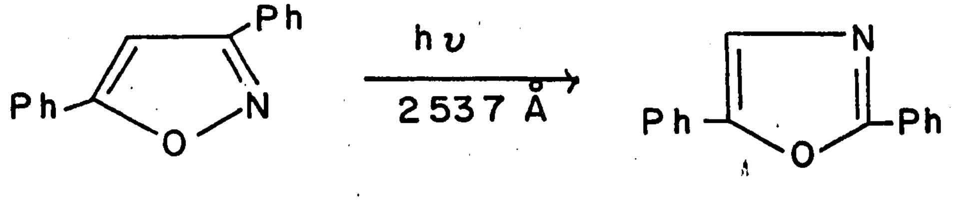
XXXIV XXXVI



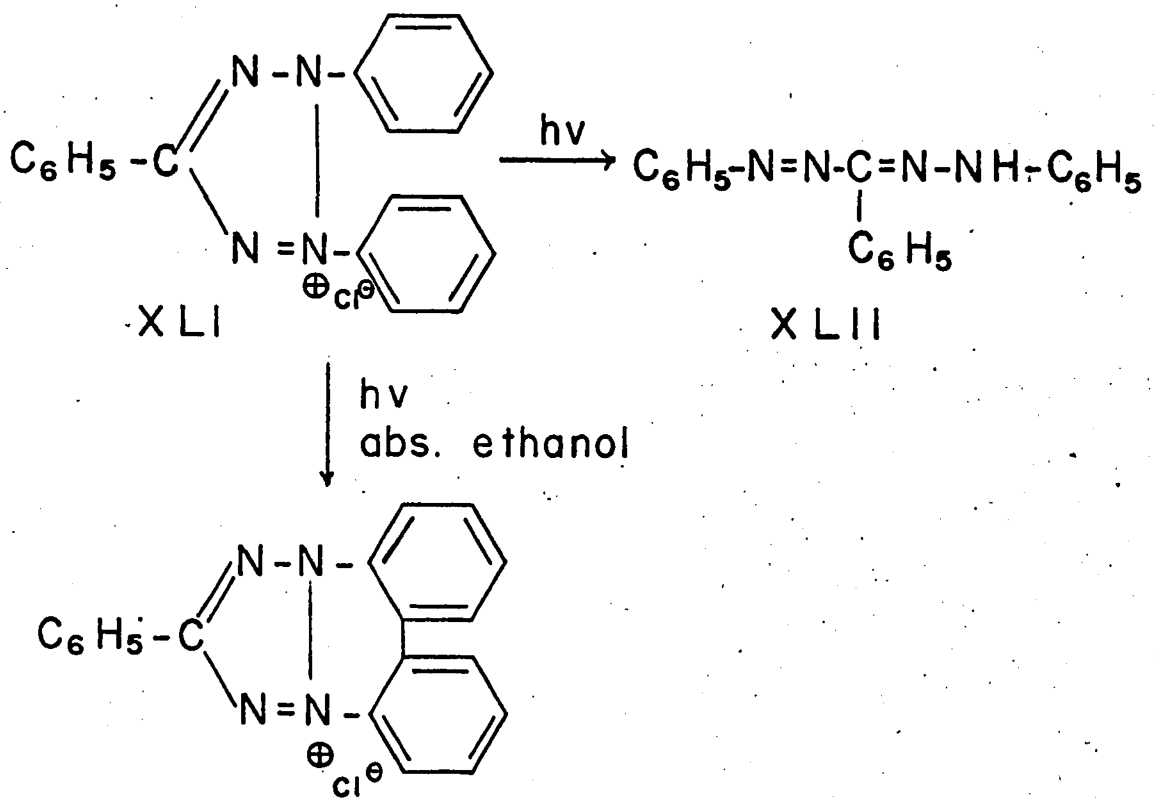
XXXVII XXXIX

a, R = Ph

b, R = CH$_3$

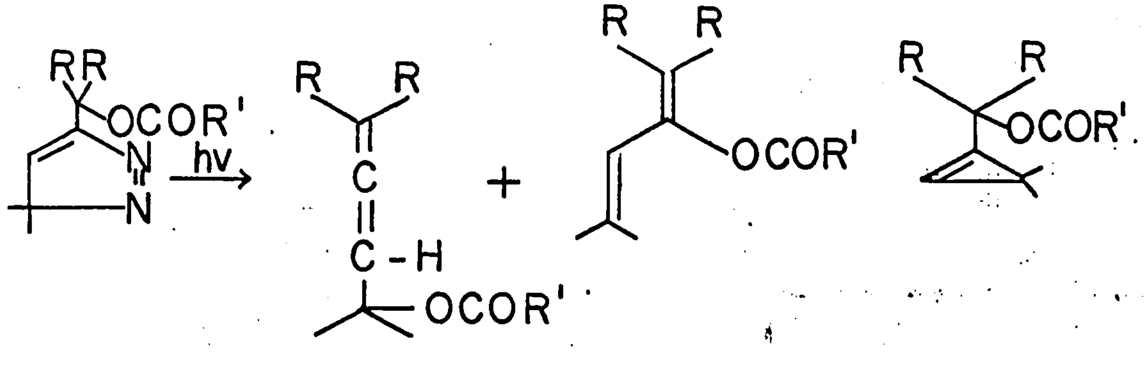


XXXVIII XL



XLI XLII

XLIII



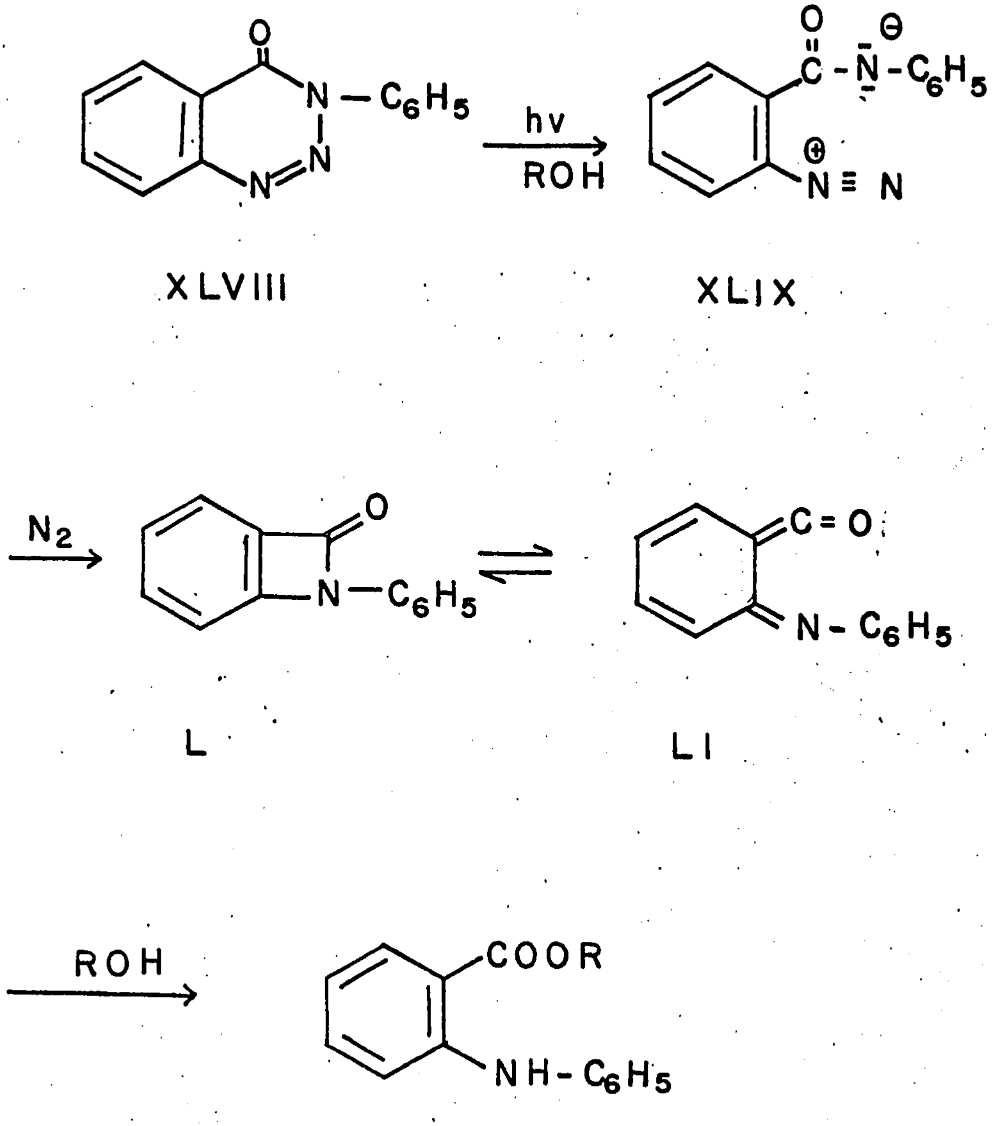
XLIV XLV XLVI XLVII

(a) R = R' = Me;
(b) R = Me, R' = Et;
(c) R = Et, R' = Me.
(d) R = R' = Et.

Until now, the only tetrazole compound which has been subjected to photochemical transformation, is the photo-oxidation and reduction of 2, 3, 5-triphenyltetrazolium chloride (XLI), which in aqueous solution on irradiation was reduced to triphenyl formazan (XLII), but in absolute ethanol under the same reaction conditions, tetrazolium ring was intact, but dehydrogenation of the adjacent phenyl groups took place producing a biphenyl compound[63, 64, 65] (XLIII).

C. Miscellaneous

Pyrazolines and pyrazolenines undergo light induced decomposition producing cyclopropane and cyclopropene derivatives, e.g. photolysis of 3-carbomethoxy-cis-3, 4-dimethyl-1-pyrazoline, produced cis-1, 2-dimethylcyclopropane-1-carboxylate[24, 66] and photolysis of 3, 3-dimethylindiazene-6-carboxylate produced 1, 1-dimethyl-3-carbomethoxybenzocyclopropene[67]. However, contrasting results have been obtained by irradiation of certain pyrazolenines; e.g. Day and Whiting[68], upon irradiation of pyrazolenine esters of the type (XLIV), obtained a mixture of isomeric allenes (XLV and XLVI) instead of the expected cyclopropene (XLVII).



XLVIII

XLIX

L

LI

LII

R = CH_3 or C_2H_5

Ege[69] isolated N-phenylanthranilic ester (LII) in 90% yield, when 3,4-dihydro-4-oxobenzo-3-phenyl-1,2,3-triazene (XLVII) was irradiated in methanol, ethanol or iso-propanol. In this transformation it was assumed that the starting compound (XLVII), dissociated into (XLIX), from which nitrogen was split off with the formation of (L), which was converted to (LI) followed by addition of the alcohol present in the medium to form N-phenylanthranilic ester (LI).

Light catalysed ring enlargements and ring contractions are also found in heterocyclic nitrogen compounds. For instance, pyrroles, carbonylisoxazoles, and indoles on irradiation in aqueous ammonia produced pyrimidines, s-triazines and quinazolines[24, 70], whereas o-quinone-diazides, undergo photoinduced ring contraction[24, 99].

At present, several organic-photo-chemical reactions are being used as routine synthetic methods. These include the introduction of a functional group into non-activated sites of the steroid nucleus by photolysis of the appropriate nitrites (i.e. the Barton reaction)[71, 72, 101] and the production of nitrenes, by the photolysis of azides, which has opened an important route into the synthesis of new organic compounds[73, 74, 75, 76].

As time passes, other new aspects of organic photochemistry are appearing, offering a wider scope to the practical organic chemists as well as to the theoretical and physical chemists who are interested in the mechanisms of these reactions. Still, we are at the beginning of a photochemical renaissance, and the survey presented in this section is very brief, with particular emphasis on the heterocyclic and aromatic compounds, because the problem of interest to us involves a heterocyclic ring, the tetrazole ring.

EXPERIMENTAL

Description of the General Methods:

The melting points (uncorrected) were determined on an electrically heated copper block using glass capillaries.

The infrared spectra were measured as films or nujol mulls on a Perkin-Elmer "Infracord" Model 137, and Beckman "Infrared Spectrophotometer", I. R-8.

The ultraviolet spectra were recorded using Perkin-Elmer "Ultraviolet-Visible Spectrophotometer", Model 202.

The nuclear magnetic resonance spectra were obtained from 15 to 20% solution in a solvent as noted. The instrument, a Varian V-4302 high resolution spectrometer, operating at 60 Mc/S, was modified to HA-60/DA-60 specification; manufacturer - Palo Alto, California. The chemical shifts are reported on Tier's scale[112].

The mass spectra wererecorded using the RMU-6D mass spectrometer, manufactured by Hitachi, Tokyo, Japan.

The photolyses were carried out by using the Hanovia Medium pressure 450 watt, mercury vapor ultraviolet lamp, No. 679A36, using water-cooled inner jacket.

All the elemental analyses were reported by the "Midwest Microlab, Inc.", Indianapolis, Indiana, U.S.A.

1. Preparation of 5-Ethoxycarbonylmethyltetrazole

The general method for the synthesis of 5-substituted tetrazoles reported by Robert Loftquist[77] was followed in the preparation of this tetrazole. A mixture of ethyl cyanoacetate (22.6 g., 0.2 moles), sodium azide (14.3 g., 0.22 moles), ammonium chloride (5.3 g., 0.1 mole) and N,N-dimethylformamide (100 ml.) was placed in a round bottomed flask (250 ml.) fitted with a reflux condenser and an efficient magnetic stirrer. The stirred reaction mixture was heated in an oil bath at 95° for a period of 8 hours. All the solvent was removed under reduced pressure. The reaction mixture was dissolved in water (100 ml.) and acidified with concentrated hydrochloric acid to pH 2. After cooling to 5°C in an ice-water bath, the product was removed by filtration, washed with several portions of ice-water and dried. The product (25.0 g., 80%) after recrystallization from 2-propanol melted at 129-130°C (reported[77] m.p. 128-130°C) and showed λ_{max}^{EtOH} 204 mμ and 273 mμ. The infrared absorption spectrum (mull) showed strong bands at 1725 cm^{-1}, 1200 cm^{-1}, 1025 cm^{-1} and 935 cm^{-1}.

2. Attempted Photolysis of 5-Ethoxycarbonylmethyltetrazole

A solution of 5-ethoxycarbonylmethyltetrazole (3.0 g.) in dry dioxane (150 ml.) was irradiated for three hours. The reddish solid residue obtained after evaporating all the solvent with a flash evaporator was crystallised from 2-propanol. The crystallised product (2.82 g.) had the same melting point and λ_{max}^{EtOH} as those of the starting compound.

Subsequently several experiments were carried out in the same solvent and under the identical irradiation conditions, extending the irradiation period over 6 hours, 12 hours, 20 hours and 24 hours, but in each case more than 95% of the total pure tetrazole was recovered.

As this particular tetrazole was found to be inert towards photolysis, we turned our attention to other 5-substitutedtetrazoles.

3. Preparation of 5-Phenyltetrazole[77]

A mixture of benzonitrile (62.0 g., 0.6 mole), sodium azide (43.0 g., 0.66 mole), ammonium chloride (16.5 g., 0.31 mole) and N,N-dimethylformamide (300 ml.) was heated in an oil bath at 120-125°C for 8 hours. All the solvent, N,N-dimethylformamide, was evaporated under reduced pressure. The residual colorless liquid together with the suspended solid was dissolved and diluted in cold water (200 ml.). The aqueous solution was acidified with concentrated hydrochloric acid to pH 2 and cooled down to room temperature. The white precipitate was filtered and washed several times with cold water. It was purified by crystallisation from water; the product (80.0 g., 90%), melted at 214-215°C (reported[77] m.p. 213-215°), had λ_{max}^{EtOh} 207 mμ and 241 mμ (ϵ = 11.8 x 10^3) [reported[78] λmax. 239 mμ (ϵ = 10.9 x 10^3)]. The compound showed strong absorption in the infrared spectrum at 1600 cm^{-1}, 1550 cm^{-1}, 1160 cm^{-1}, 1050 cm^{-1}, 1035 cm^{-1}, 730 cm^{-1} and 690 cm^{-1}. Its proton magnetic resonance spectrum in a mixture of deuterochloroform and dimhthylsulfoxide (1:1) showed absorptions at τ 1.91 (m)* and τ 2.49 (m)* with an integrated intensity ratio of 2 to 3.

4. Photolysis of 5-Phenyltetrazole

A solution of 5-phenyltetrazole (4.5 g., 0.031 mole) in dry dioxane (150 ml.) was irradiated for three hours. All the solvent was evaporated from the clear red solution by a flash evaporator. The red liquid residue was dissolved in ether (180 ml.). This ethereal solution was washed with water (25 ml. portions) once making the whole solution alkaline by adding aqueous sodium hydroxide (40%). The ethereal solution was further washed with water (25 ml. portions) making it acidic by adding hydrochloric acid (10%). Thus the ethereal extract obtained was the neutral fraction. The basic fraction was extracted with ether by basifying the combined aqueous layer with aqueous sodium hydroxide (40%). The acidic fraction was extracted with ether by acidifying the aqueous layer with hydrochloric acid (10%). Thus neutral, basic and acidic fractions were separated.

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* multiplet

recovered starting material (5-phenyltetrazole), and the basic fraction (3.25 g., 72%) crystallised from methanol. It had a melting point range 150-160°C and was also found to be a mixture of red and yellow varieties of crystals. In order to separate the yellow and the red crystalline materials, the crystal-mixture was dissolved in hot, dry chloroform. On cooling the chloroform solution, the first crop of the product (1.1 g.) was long needle-shaped yellow crystalline material. After recrystallisation from pure ethanol, the yellow crystalline material, 1,4-dihydro-3,6-diphenyl-*S*-tetrazin[82], melted at 198-200°C (reported[103] m.p. 190-192°) had λ_{max}^{EtOH} 205 mμ and 245 mμ (ϵ = 24.3 x 10^3). The proton magnetic resonance spectrum in deuterochloroform solution showed absorption at τ2.55 (m).* The infrared spectrum in chloroform solution showed strong absorptions at 3410 cm^{-1}, 3020 cm^{-1}, 1450 cm^{-1}, 1385 cm^{-1}, 1200 cm^{-1} and 690 cm^{-1}.

Anal. Calculated for $C_{14}H_{12}N_4$: C, 71.16: H, 5.12: N, 23.72. Found: C, 71.38; H, 5.38; N, 23.71.

Another solid crystallised from the concentrated mother liquor as long red prisms (2.5 g.). This product was actually 3,6-diphenyl-s-tetrazine[82]. It had melting point of 192-193°C (reported m.p. 192-193°C), λ_{max}^{EtOH} 205 mμ , 297 mμ (ϵ = 30.85 x 10^3) and 554 mμ (ϵ = 421)

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* m = multiplet

sublimed at 55°C at 0.05 mm/Hg. Its infrared spectrum showed absorptions in chloroform solution at 3020 cm^{-1}, 1390 cm^{-1}, 1200 cm^{-1}, 1105 cm^{-1}, 690 cm^{-1}. The proton magnetic resonance spectrum of 3,6-diphenyl-s-tetrazine in chloroform solution showed absorptions at τ2.4 (m) and τ1.37(m). Anal. Calculated for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.96; H, 4.52; N, 23.84.

5. Attempted Reduction of trans Stilbene by 1,4Dihydro-3,6-diphenyl-s-tetrazine

A mixture of 1,4-dihydro-3,6-diphenyl-s-tetrazine (1.0 g.) and trans stilbene (0.5 g.) dissolved in dry dioxane (100 ml.) was refluxed for 25 hours under dry nitrogen atmosphere. The yellow cake obtained after evaporating all the solvent was partially dissolved in ether. The insoluble yellow material was filtered out from the reddish mother liquor. The yellow material (0.9 g.) melted at 196-200°C and had the same u.v-absorption maxima as the 1,4-dihydro-3,6-diphenyl-s-tetrazine.

6. Oxidation of 1, 4-Dihydro-3, 6-diphenyl-s-tetrazine

1, 4-Dihydro-3, 6-diphenyl-s-tetrazine (0.12 g.) (0.5 mmole) was dissolved in dry ethanol (40 ml.). A few drops of concentrated hydrochloric acid were added to the clear ethanolic solution, which was cooled in an ice bath. Bromine was added from a dropping funnelto this cold stirred solution ($\sim 10^{\circ}$C) until the bromine colour became persistent. After stirring for fifteen minutes more in the cold bath, all the solvent was evaporated with a flash evaporator. In order to make the residue free from hydrochloric acid, hydrobromic acid and free bromine, this evaporation was repeated several times with the fresh addition of ethanol. The red stout needle-shaped crystalline product (0.102 g.) obtained from ethanol had melting point at 192-193°C. No depression in the melting point was observed when the product was mixed with the authentic 3, 6-diphenyl-s-tetrazine. The u.v., i.r. and n.m.r. spectra were in agreement with thisstructure.

7. Attempted Photolysis of 5-Phenyltetrazole in the Presence of Norbornene

A mixture of 5-phenyltetrazole (2.0 g.) and norbornene (6.0 g.) dissolved in dry dioxane (150 ml.) was irradiated for three hours. The red solid residue obtained after evaporating all the solvent with a flash evaporator was separated into the basic, the acidic and the neutral fractions. The crude basic fraction (1.6 g.) had the same pattern of infrared spectrum as that of the crude basic fraction obtained from the photolysis of 5-Phenyltetrazole alone. The crude acidic fraction (0.4 g.) melted at 200-205°C and was found mostly to be the starting material, 5-phenyltetrazole. In the neutral fraction practically nothing was obtained.

8. Attempted Photolysis of 5-Phenyltetrazole in the Presence of Ethyl acrylate

A mixture of 5-phenyltetrazole (2.0 g.) and ethyl acrylate (10.0 g.) dissolved in dry dioxane (150 ml.) was irradiated for three hours. The red solid residue obtained after evaporating all the solvent was separated into the basic, the acidic and the neutral fractions. The crude basic fraction (1.3 g.) had the same pattern of infrared and ultraviolet absorption spectra as those of the crude basic fraction obtained from the photolysis of 5-phenyltetrazole alone. The crude acidic fraction (0.4 g.) was found to be the starting material, 5-phenyltetrazole. The small amount of the crude neutral fraction (0.1 g.) was not further investigated.

9. Preparation and Purification of 1-Methyl-5-Phenyltetrazole and 2-Methyl-5-Phenyltetrazole

These tetrazoles were prepared following the method reported by Henry[79]. A solution of methyl iodide (25.0 g.) in acetone (285 ml.) was added to a solution of 5-phenyltetrazole (25.0 g.) and sodium hydroxide (14.1 g.) in water (70 ml.). The reaction mixture was refluxed for two hours: at the end of the first hour an additional amount of methyl iodide (25 g.) was added to make up the loss due to evaporation. The solution was cooled and 300 ml. of benzene was added, and washed with water till the washing was no longer alkaline towards the pH paper. After drying the benzene layer with anhydrous calcium chloride, all the solvent was evaporated, giving a crude yellowish colored liquid (27.0 g.). The crude reaction product, dissolved in a mixture of diethyl ether (225 ml.) and benzene (30 ml.), was left in the refrigerator overnight.

The needle shaped crystalline product (4.3. g.), 1-methyl-5-phenyltetrazole, melted at 101-103° (reported[79] m.p. 101-102°), had λ_{max}^{EtOH} 206 mμ and 232 mμ ($\epsilon = 10.8 \times 10^3$) (reported[78] 232 mμ, $\epsilon = 10.8 \times 10^3$). The infrared spectrum in chloroform of 1-methyl-5-phenyltetrazole had strong absorption[83] at 3000 cm^{-1}, 1600 cm^{-1}, 1565 cm^{-1}, 1475 cm^{-1}, 1460 cm^{-1}, 1290 cm^{-1}, 1110 cm^{-1}, 1070 cm^{-1}, 1030 cm^{-1} and 690 cm^{-1}.

Its proton magnetic resonance spectrum in deuterochloroform showed absorptions at τ2.33 (m) and τ5.85 (s*) with an area ratio of 5 to 3.

The filtrate was decolorised with Norite A. All the solvent was evaporated: the solid residue (16.2 g.) melted at 45-48°C. (The reported[79] m.p. 50-51° for 2-methyl-5-phenyl-tetrazole). This solid crystalline product contained a considerable amount of 1-methyl-5-phenyltetrazole. In order to purify 2-methyl-5-phenyltetrazole, this impure crystalline 2-methyl-5-phenyltetrazole was partially dissolved in warm petroleum ether (b.p. 30-60°C). The clear solution was decanted from the solid residue. The clear decanted solution, on concentration and cooling, gave long stout needles of pure 2-methyl-5-phenyltetrazole., m.p. 50-51°C (reported[79] 50-51°C), λ_{max}^{EtOH} 207 mμ and 240 mμ (reported[78] 242 mμ),($\epsilon = 11.3 \times 10^3$). Its infrared spectrum[84] in chloroform exhibited strong absorptions at 3050 cm^{-1}, 1600 cm^{-1}, 1545 cm^{-1}, 1450 cm^{-1}, 1375 cm^{-1}, 1075 cm^{-1}, 1050 cm^{-1}, 1015 cm^{-1} and 690 cm^{-1}.

The proton magnetic resonance spectrum in deuterochloroform showed absorptions at τ1.87 (m) and τ2.59 (m) for five aromatic protons and τ5.75 (s)* for the three protons of the methyl group.

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*s = singelt

10. Attempted Photolysis of 1-Methyl-5-Phenyltetrazole

1-Methyl-5-phenyltetrazole (2.0 g.) dissolved in dry dioxane (150 ml.) was irradiated for three hours. The yellowish solid residue obtained after evaporating all the solvent was separated into the basic, the acidic and the neutral fractions. Both the basic and the neutral fractions, which accounted for 1.8 g. of the total product, were found to have the same melting point, i.r. and u.v. spectra as those of the 1-methyl-5-phenyltetrazole. 50-60 mg. of the gummy material was obtained from the acidic fraction, which was not further investigated.

About 95% of the starting material was recovered in the subsequent attempts of the photolysis of 1-methyl-5-phenyltetrazole, extending the irradiation period over 6 hours, 10 hours and 12 hours.

11. Photolysis of 2-Methyl-5-Phenyltetrazole

A solution of 2-methyl-5-phenyltetrazole (2.5 g.) in dry dioxane (150 ml.) was irradiated for three hours. The red liquid residue (2.5 g.) obtained after evaporation of all the solvent with a flash evaporator was separated into neutral, basic and acidic fractions. Both the acidic and the basic fractions (0.15 g.) and (0.25 g.) respectively were viscous material.

The crude neutral fraction (1.5 g., 60%) showed ultraviolet absorption maxima at 207 mμ and 249 mμ. The infrared spectrum as a film showed strong absorption characteristic of a 1,2,3-triazole[92] at 1010 cm^{-1} and 990 cm^{-1}.

The crude neutral fractions (3.0 g.) collected from two irradiations of 2-methyl-5-phenyltetrazole were distilled under vacuum. A yellowish red viscous distillate (0.9 g.) was collected at 125-135°C at 0.05 mm/Hg, and a considerable amount of undistilled tarry material was left in the distillation flask. The distillate was dissolved in petroleum ether (b.p. 30-60°). A small amount of yellowish solid residue (0.2 g.) was filtered. This solid residue was found to be 1-methyl-5-phenyltetrazole from its m.p., i.r. and u.v. spectral properties.

The presence of various components in the mother liquor was detected on a preparative thin layer plate (Silica gel G) eluted with a mixture of petroleum ether (b.p. 30-60°C) and chloroform (3:2). Thin layer chromatographic separation method was used for the separation of the various components from the mixture. Thin layer plates (14, each 20 cm. x 20 cm.) of thickness (0.8 mm) were made from a slurry of silica gel G (250 g.) and water (375 ml.), shaking for 12 to 15 minutes. A petroleum-ethereal solution (7 ml.) of the distillate was applied to these fourteen plates along a line.

These plates were then developed in the chromatogram jars containing (80 ml.) a mixture of petroleum ether (b.p. 30-60°) and chloroform (3:2). The developed plates were dried and the positions of the various bands were revealed under ultraviolet light. The various bands were carefully marked and scraped off separately. Fraction (i) was the least mobile band; fraction (iii) the most mobile band, and fraction (ii) the band in between (i) and (iii). The content of each of the bands was extracted separately by acetone in a Soxhlet. Fraction (ii) (0.3 g.), a light yellow viscous liquid, was dissolved in methanol. Cubical crystals were deposited which had m.p. 60-61°C and showed λ_{max}^{EtOH} at 257 mμ ($\epsilon = 13.3 \times 10^3$). The infrared spectrum of this material had strong absorption at 3000 cm^{-1}, 1690 cm^{-1}, 1475 cm^{-1}, 1010 cm^{-1}, 990 cm^{-1} and 695 cm^{-1}.

The proton magnetic resonance spectrum (in deuterochloroform) showed absorptions at τ 2.7 (m) and τ 5.88 (s) with the areas corresponding to ten and three protons.

Anal. $C_{15}H_{13}N_3$ Calc. C, 76.56; H, 5.57; N, 17.86. Found: C, 76.32; H, 5.78; N, 18.10. In the mass spectrum, a molecular ion appeared at $^m/e$ 235 in agreement with the assigned structure, 2-methyl-4,5-diphenyl-1,2,3-triazole.

Separation by Column Chromatography

The crude neutral fraction (3.0 g.) obtained from the photolysis of 2-methyl-5-phenyltetrazole (5.0 g.) was applied to an alumina column (36 cm. x 2 cm.) of activity (II). Fractions of equal volume (100 ml.) were taken during elution. Nothing was obtained from the fractions 1 - 4 eluted with petroleum ether (b.p. 30-60°C). Fractions 5-10 eluted with petroleum ether afforded 95 mg. of material, which was a mixture of two or more unidentifiable components. Fractions 11-22 and 28 eluted with a mixture of petroleum ether and chloroform (2%) afforded 1.02 g. (35%) of the product which was found to be 2-methyl-4, 5-diphenyl-1, 2, 3-triazole from its m.p. and spectral properties. Fractions 23-27 eluted by a mixture of petroleum ether and chloroform (2%) amounted to 0.185 g. (6.3%) of the product, which was a mixture of the starting material (80%), 2-methyl-4, 5-diphenyl-1, 2, 3-triazole (18%) and some other contaminantes, which were estimated from n.m.r. spectrascopy. Fractions 30-40 eluted with a mixture of petroleum ether containing 5% chloroform afforded (0.81 g.) (27%) of the product which was thought from its n.m.r. spectrum to be a mixture of 1-methyl-3, 5-diphenyl-1, 2, 4-triazole and some other contaminants (80%). Fractions 41-44 which were also eluted with a mixture of petroleum ether and 5% chloroform afforded 0.143 g. (5%) of an oil. The presence of 1-methyl-3, 5-diphenyl-1, 2, 4-triazole was suggested by the appearance of a sharp singlet at τ 6.1. The chemical shift of the N-methyl group of a sample of 1-methyl-3, 5-diphenyl-1, 2, 4-triazole is τ 6.1.

12. Preparation of 5-p-Nitro-Phenyltetrazole

By following the procedure of Loftquist[77], 5-p-nitrophenyltetrazole was prepared by heating a mixture of p-nitrobenzonitrile (15.0 g.) sodium azide (8.0 g.) ammonium chloride (4.0 g.) and N, N-dimethylformamide (50 ml.) up to 100°C for three hours. After the usual work up, 5-p-nitrophenyltetrazole (18.5 g., 96%) was obtained, melted at 220-222°C (reported[81] m. p. 218-219°) λ_{max}^{EtOH} 204 mμ and 296 mμ ($\epsilon = 10.4 \times 10^3$). Its infrared spectrum (mull) showed strong absorptions at 3400 cm^{-1}, 1550 cm^{-1}, 1390 cm^{-1}, 1095 cm^{-1}, 1160 cm^{-1}, 860 cm^{-1} and 745 cm^{-1}.

The proton magnetic resonance spectrum in acetone showed absorptions at τ1.6 (s) and τ3.48 (s) in an intensity ratio of 4:1 for the aromatic and the N-H groups.

13. Methylation of 5-p-Nitrophenyltetrazole[79]

Methyl iodide (8.25 g.) in acetone (95 ml.) was added to a solution of 5-p-nitrophenyltetrazole (7.18 g.) and sodium hydroxide (4.65 g.) in water (23 ml.). The reaction mixture was refluxed for two hours, and at the end of the first hour an additional amount of methyl iodide (8.25 g.) was added to make good the loss due to evaporation. The solution was cooled, benzene (100 ml.) was added and the mixture was washed with cold water until the washings were no longer alkaline. The benzene layer, after drying with anhydrous calcium chloride, was filtered and evaporated to dryness. The brownish solid residue was extracted with ether (3 x 40 ml.). The insoluble material melted over the range of 145 to 160°C, while the ethereal extract (after evaporating all the ether) showed melting point range from 95° to 110°C. The low melting component, 1-methyl-5-p-nitrophenyltetrazole (0.5 g., 7%) was crystallized several times from 85% isopropyl alcohol, and showed melting point at 121-123°C, reported[80] m.p. 123-126°C. 1-Methyl-5-p-nitrophenyltetrazole had λ_{max}^{EtOH} at 204 mμ and 274 mμ ($\epsilon = 9.0 \times 10^3$), and its infrared spectrum in chloroform showed strong absorptions at 3050 cm^{-1}, 1700 cm^{-1}, 1525 cm^{-1}, 1350 cm^{-1}, 1050 cm^{-1}, 1020 cm^{-1}, 870 cm^{-1} and 860 cm^{-1}.

The proton magnetic resonance spectrum in deuterochloroform showed absorptions at τ1.47 (d)* (J = 9 c.p.s.), and τ1.95 (d) (J = 9 c.p.s.) and τ5.75 (s). The areas corresponded with 2, 2 and 3 protons.

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* (d) = doublet

The high melting component (6.88 g., 93%) was crystallized several times from 85% isopropyl alcohol until the melting point became constant (171-172°C). This isomer was 2-methyl-5-p-nitrophenyltetrazole, had λ_{max}^{EtOH} 204 mμ and 285 mμ ($\epsilon = 14.18 \times 10^3$). Its infrared spectrum in chloroform solution showed strong absorptions at 3100 cm^{-1}, 1620 cm^{-1}, 1540 cm^{-1}, 1460 cm^{-1}, 1360 cm^{-1}, 1120 cm^{-1}, 1050 cm^{-1}, 1010 cm^{-1}, 1020 cm^{-1}, 860 cm^{-1} and 870 cm^{-1}. The n.m.r. spectrum in deuterochloroform showed absorptions at τ1.61 (s) and τ5.58 (s) with an intensity ratio of 4:3 for the aromatic and N-methyl protons. Anal. for $C_8H_7N_5O_2$ Calc: C, 46.93; H, 3.44; N, 34.12. Found: C, 47.23; H, 3.74; N, 34.30. Its mass spectrum showed a molecular ion at $^m/e = 205$, which agreed with the formula assigned.

14. Attempted Photolysis of 2-Methyl-5-p-Nitrophenyltetrazole

A solution of 2-methyl-5-p-nitrophenyltetrazole (2.0 g.) in dry dioxane (150 ml.) was irradiated for three hours. All the solvent was evaporated with a flash evaporator to give a solid residue (2.0 g.) whose m.p. λ_{max}^{EtOH} , i.r. and n.m.r. spectra were the same as those of the starting compound.

Several attempts were made to photolyse the 2-methyl-5-p-nitrophenyltetrazole under the same conditions by extending the irradiation period over 6 hours, 10 hours, 15 hours and 24 hours, and in all cases more than 98% of the starting material was recovered.

15. Preparation of 1-Methyl-3, 5-diphenyl-1, 2, 4-triazole

Dibenzamide, prepared by following the procedure of Titherley[85] was converted to 3, 5-diphenyl-1, 2, 4-triazole by a method reported by Wolchowe[86]. The infrared spectrum (mull) of 3, 5-diphenyl-1, 2, 4-triazole showed strong absorptions at 1650 cm^{-1}, 1380 cm^{-1}, 1120 cm^{-1}, 960 cm^{-1}, 730 cm^{-1} and 660 cm^{-1}. The n. m. r. τ values (acetone) were at 1. 9 and 2. 6 (m). 1-Methyl-3, 5-diphenyl-1, 2, 4-triazole was prepared by methylating 3, 5-diphenyl-1, 2, 4-triazole according to the method described by Atkinson[87].

It showed m. p. at 83-85°C (reported[88] m. p. 84-85°C), and, in its ultraviolet spectrum λ_{max}^{EtOH} at 247 $m\mu$ ($\epsilon = 18.7 \times 10^3$) (reported[88] 247 $m\mu$ ($\epsilon = 19.4 \times 10^3$)). Its infrared spectrum in chloroform showed strong absorptions at 3070 cm^{-1}, 1520 cm^{-1}, 1475 cm^{-1}, 1400 cm^{-1}, 1350 cm^{-1}, 1120 cm^{-1}, 1075 cm^{-1}, 1015 cm^{-1}, 980 cm^{-1}, 695 cm^{-1}.

Its proton magnetic resonance spectrum in deuterochloroform showed absorptions at τ 2. 51 (m), τ 1. 90 (m) and τ 6. 1 (s) with an intensity ratio of 10:3 for aromatic and N-methyl protons.

16. Synthesis of Benzil-Monomethylhydrazone

The method for the preparation of the benzil-monomethyl hydrazone reported by David Cardwell[89] was considerably modified. Methyl hydrazine (1.60 g.) was added to a solution of benzil (5.0 g.) in ethanol (99%, 40 ml.) and was kept at room temperature for 8 hours. Crystals of benzil monomethylhydrazone were deposited. The first crop of the product accounted for 90% of the yield. Subsequent crops obtained on further concentration of the mother liquor led up to the theoretical yield (5.57 g.).

Benzil monomethylhydrazone melted at 138° (reported[89] m.p. 138°). Its infrared spectrum in chloroform showed strong absorptions at 3400 cm^{-1}, 1645 cm^{-1}, 1550 cm^{-1}, 1340 cm^{-1}, 870 cm^{-1}, 1035 cm^{-1}, and 700 cm^{-1}.

The proton magnetic resonance spectrum in deuterochloroform showed absorptions at τ 6.95 (d), τ 3.67 (broad peak), τ 2.55 (m) and τ 2.0 (m).

17. Attempted Synthesis of Benzil-bis(N-methyl N'-phenyl)-hydrazone

Phenylhydrazine (2.16 g.), glacial acetic acid (1 ml.) were added to an ethanolic solution of benzil monomethyl hydrazone (2.55 g.). The reaction mixture was refluxed on a water bath for two hours. The crystals obtained after concentration and cooling the reaction mixture had m. p. 134°C, which is the m. p. of benzil monophenylhydrazone[90]. The infrared and n.m.r. spectra were identical with those of the benzil monophenylhydrazone. The reaction was carried out at room temperature over a period of 8 and 12 hours, but no reaction took place.

Again, benzil monophenylhydrazone (3.16 g.) prepared by the reported method[90] was dissolved in ethanol (30 ml.) and was refluxed for 12 hours together with methylhydrazine (2 ml.). The crystalline material obtained after evaporating all the solvent had the same melting point, infrared spectrum, as those of the benzil monophenylhydrazone.

18. Synthesis of 2-Methyl-4, 5-diphenyl-1, 2, 3-triazole

(i) A mixture of benzil monomethylhydrazone (0.5 g.), phenylhydrazine (0.2 g.) and two drops of glacial acetic acid sealed in a Pyrex tube was heated at 130°C in the Carius furnace for 2.5 hours. The gummy product (3.0 g.) collected from six such tubes was dissolved in dioxane (75 ml.). Cupric sulfate[91] (3.0 g.) dissolved in water (75 ml.) was added to the above solution which was then refluxed for 1.5 hours. All the solvent was evaporated from the filtrate. The black residue was extracted with ether (3 x 50 ml.). Basic, neutral and acidic fractions were separated from the ethereal extract. The crude neutral fraction (2.5 g.) was purified by the preparative thin layer chromatography. The least mobile band (1.7 g.) had λ_{max}^{EtOH} 252 mμ and characteristic 1,2,3-triazole bands (1010 cm^{-1} and 990 cm^{-1}) in the infrared spectrum[92]. But still this fraction contained a lot of impurities of carbonyl nature.

(ii) Separation of 2-Methyl-4,5-diphenyl-1,2,3-triazole by Column Chromatography

The impure triazole (1.7 g.) was applied to a column (20 cm. x 2 cm.) packed with neutral alumina of activity (11) then the column was eluted with petroleum ether (b.p. 30-60°) and fractions of equal volume (200 ml.) were collected. The infrared spectra of the fraction (2, 80 mg.) and the fraction (3, 30 mg.) eluted with a mixture of petroleum ether(b.p30-60°) and 3% benzene, showed strong carbonyl absorption. Fraction (4, 50 mg. 2%) eluted with a mixture of petroleum ether (b.p. 30-60°C) and 10% benzene had λ_{max}^{EtOH} 257 mμ (ϵ = 13.3 x 10^3). The infrared absorption spectrum in chloroform and the n.m.r. τ-values (in deuterochloroform)and the m.p., were identical with those of the 2-methyl-4,5-diphenyl-1,2,3-triazole obtained by the photolysis of 2-methyl-5-phenyltetrazole. In the mass spectrum of this compound the molecular ion appeared at

$^m/e = 235$ in agreement with the assigned structure. Strong peaks appeared at $^m/e = 192$, 165, 131, 104, 89, 77 and 51 in the mass spectrum.

19. Attempted Photolysis of 1-Methyl-3,5-diphenyl-1,2,4-triazole

A solution of 1-methyl-3,5-diphenyl-1,2,4-triazole (0.6 g.) in dry dioxane (60 ml.) was irradiated for 3 hours. The crude liquid residue obtained after evaporating all the solvent was crystallized from cold ether. The crystals (0.52 g.) melted at 85°C and had the same u.v., i.r. and n.m.r. spectral properties as those of the starting material.

20. Photolysis of 2-Methyl-5-Phenyltetrazole using a Vycor filter

A soltution of 2-methyl-5-phenyltetrazole (1.8 g.) dissolved in dry dioxane (150 ml.) was irradiated using a Vycor filter. The red liquid residue obtained after evaporating all the solvent was separated into neutral, basic and acidic fractions. The crude neutral fraction (1.12 g.) had identical infrared and ultraviolet spectra as those of the neutral fraction obtained from photolysis of 2-methyl-5-phenyltetrazole without a filter.

21. Photolysis of 2-Methyl-5-Phenyltetrazole in the Presence of Benzonitrile

Benzonitrile (1.3 ml.) was added to a solution of 2-methyl-5-phenyltetrazole (2.0 g.) in dry dioxane (150 ml.). It was irradiated for three hours. All the solvent (dioxane) was evaporated with a flash evaporator at room temperature. The residual liquid was distilled under vacuum. The distillate (0.8 ml.) which came over at 60-61° was the pure benzonitrile. On further distillation under high vacuum, benzonitrile (0.3 ml.) came over at 0.025 mm/Hg and at 20-25°C. The total benzonitrile recovery was 1.1 ml. The residue was separated into basic, acidic and neutral fractions. The crude neutral fraction (1.2 g.) was distilled under vacuum. The distillate (0.5 g.), which boiled at 115-125°C at 0.05 mm/Hg was applied to preparative thin layer plates, in order to separate 2-methyl-4,5-diphenyl-1,2,3-triazole (as in the case of experiment no. 11). The yield of 2-methyl-4,5-diphenyl-1,2,3-traizole was 0.15 g. (8 % yield).

22. Photolysis of 1-Methyl-5-Phenyltetrazole with Benzophenone

A mixture of 1-methyl-5-phenyltetrazole (3.0 g.) and benzophenone (0.2 g.) dissolved in dry dioxane (160 ml.) was placed in the irradiation vessel. Dry nitrogen gas was bubbled through this solution during the 4.5 hour period of irradiation. All the dioxane was evaporated and the reddish liquid residue was separated into acidic, basic and neutral fractions. A small amount of material (0.3 g.) was isolated from the basic fraction. Infrared and ultraviolet spectra of this material indicated it to be mainly starting material. Most of the starting tetrazole (2.5 g.) was recovered from the neutral fraction.

23. Heat Treatment of 2-Methyl-4,5-diphenyl-1,2,3-triazole

2-Methyl-4,5-diphenyl-1,2,3-triazole (30 mg.) was taken in a sealed capillary tube and heated up to 220-225° for 6 hours in the melting point apparatus. The u.v. and the i.r. spectra of the fused mass, together with its melting point were found to be identical in all respects with those of the starting triazole.

DISCUSSION

1.

A variety of methods are available for the synthesis of tetrazoles[93, 94, 95]. However, all the 5-substituted tetrazoles mentioned in this thesis have been synthesised following the method reported by Loftquist and co-workers[77], i.e. by heating a mixture of an appropriate nitrile, sodium azide and lithium chloride or ammonium chloride in N, N-dimethylformamide. The structures of the previously known compounds were established by comparing the reported and the experimental values of their melting points and spectral properties.

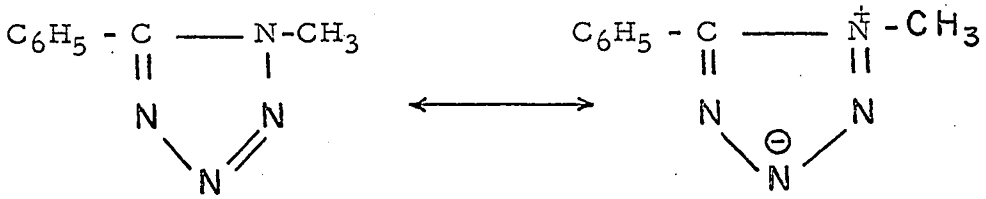
We wish to discuss briefly the spectral properties of the mono- and the disubstituted tetrazoles whose photolytic behavior is being examined. The infrared spectrum of 5-ethoxycarbonylmethyltetrazole shows the characteristic tetrazole ring vibration[97] at 1025 cm^{-1} in addition to the carbonyl band at 1725 cm^{-1}. Its ultraviolet absorption maxima appear at 203 $m\mu$ ($\epsilon = 576$) and at 273 $m\mu$ ($\epsilon = 94$). These absorptions are most probably due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions[98] of the carboxylate group. So it appears that the tetrazole ring of 5-ethoxycarbonylmethyltetrazole is almost transparent to ultraviolet light.

Two absorption maxima appear in the ultraviolet spectrum of 5-phenyltetrazole, one at 207 $m\mu$, likely being the primary band of the benzene ring[98], and the other at 241 $m\mu$ ($\epsilon = 11.8 \times 10^3$), most probably due to the $\pi \rightarrow \pi^*$

transition of the tetrazole ring[98]. The reported value[78] for its absorption maximum is 239 mμ ($\epsilon = 10.9 \times 10^3$). Tetrazole itself is transparent[100] to ultraviolet light throughout the range of 230 mμ - 450 mμ . As a phenyl group is substituted at position-5 of the tetrazole ring, a linear extended conjugation arises between these two rings giving rise to an intense absorption[98] at 241 mμ . This absorption maximum is comparable with that of biphenyl whose absorption maximum[98] is at 245 mμ . From this comparison it appears that the conjugation as well as the orientation of biphenyl and 5-phenyltetrazole are of a similar nature. The n.m.r. spectrum of 5-phenyltetrazole shows two sets of multiplets at τ1.9 and τ2.49; the former is assigned to the two ortho protons and the latter to the meta and para protons of the phenyl group. There was no visible absorption for the $>$N-H proton.

The spectral characteristics of 5-p-nitrophenyltetrazole are as follows. Its infrared spectrum shows the characteristic tetrazole ring vibration[97] at 1095 cm^{-1}. A $\pi \rightarrow \pi^*$ band appears at 296 mμ ($\epsilon = 10.4 \times 10^3$) in the ultraviolet absorption spectrum of 5-p-nitrophenyltetrazole. This higher wavelength absorption is most likely due to the extended linear conjugation of the para nitrobenzene ring with the tetrazole ring. The n.m.r. spectrum of 5-p-nitrophenyltetrazole shows a singlet for the four protons of the benzene ring at τ1.6 and a broad signal at τ3.48 for the proton of the $>$NH group.

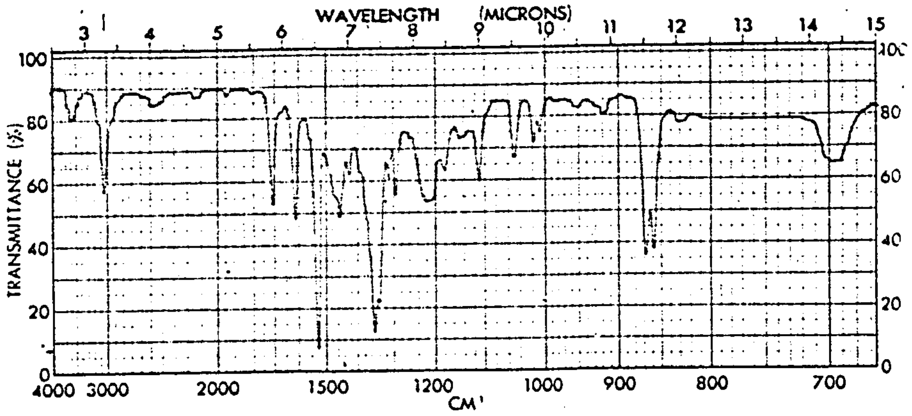
1-Methyl-5-phenyltetrazole and 2-methyl-5-phenyltetrazole were prepared by methylation of 5-phenyltetrazole following the procedure of Henry[79]. 2-Methyl-5-phenyltetrazole, which constituted 80% of the methylated product, was separated from the 1-methyl-5-phenyltetrazole by fractional crystallisation from petroleum ether (b.p. 30-60°). The absorption maximum of the tetrazole ring of 1-methyl-5-phenyltetrazole appears at 232 $m\mu$ ($\epsilon = 10.8 \times 10^{3}$), and the reported value[78] is also 232 $m\mu$ ($\epsilon = 10.3 \times 10^{3}$). A further shift towards longer lengths was expected by Nachod and **Elpern**[78] because of linear conjugation between these two rings. He then explained the unexpected low wavelength maximum on the basis of charge separation in solution which reduced this linear conjugation.



The n.m.r. spectrum(6) (field increases from left to right) of 1-methyl-5-phenyltetrazole shows a poorly resolved multiplet centered at $\tau 2.36$ due to the five protons of the phenyl ring and a singlet at $\tau 5.84$ due to the three protons of the N-methyl group.

The ultraviolet absorption maximum of 2-methyl-5-phenyltetrazole appears at 240 mμ (ϵ= 11.3 x 10^3) whereas the reported value[78] is 242 mμ (ϵ = 11.0 x 10^3). Unlike the 1-methyl-5-phenyltetrazole, Nachod and **Elpern**[78] explained this absorption maximum on the basis of cross conjugation. The infrared spectrum of 2-methyl-5-phenyltetrazole was in full agreement with the assigned structure. The n.m.r. spectrum (7) of 2-methyl-5-phenyltetrazole shows two sets of multiplets centered at τ1.9 and τ2.58. The former is assigned to ortho protons and the latter to the meta and para protons of the phenyl group. A singlet for the three protons of the N-methyl group appear at τ5.76.

1-Methyl-5-p-nitrophenyltetrazole and 2-methyl-5-p-nitrophenyltetrazole were prepared by methylation of 5-p-nitrophenyltetrazole following the method employed for the methylation[79] of 5-phenyltetrazole. 1-Methyl-5-p-nitrophenyltetrazole, which constituted only 7% of the methylated product, melted at 121-123°, whereas the reported[102] m.p. is 123-126°. The infrared spectrum (1) of 1-methyl-5-p-nitrophenyltetrazole shows the characteristic tetrazole ring vibrations at 1120 cm^{-1}, 1050 cm^{-1} and 1015 cm^{-1} ; and the stretching vibrations of $>$C=N and -N=N- at 1545 cm^{-1} and 1450 cm^{-1} respectively. In addition to an absorption at 204 mμ , its u.v. spectrum shows an absorption at 274 mμ


WAVELENGTH (MICRONS)
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TRANSMITTANCE (%)
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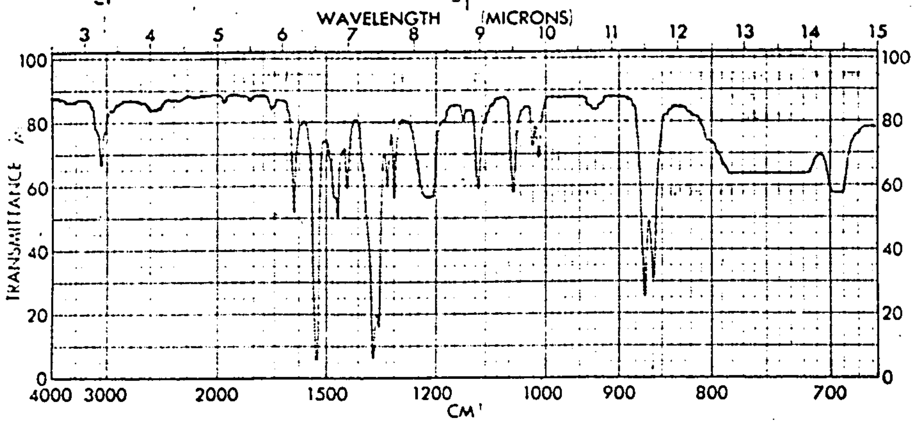
1


WAVELENGTH (MICRONS)
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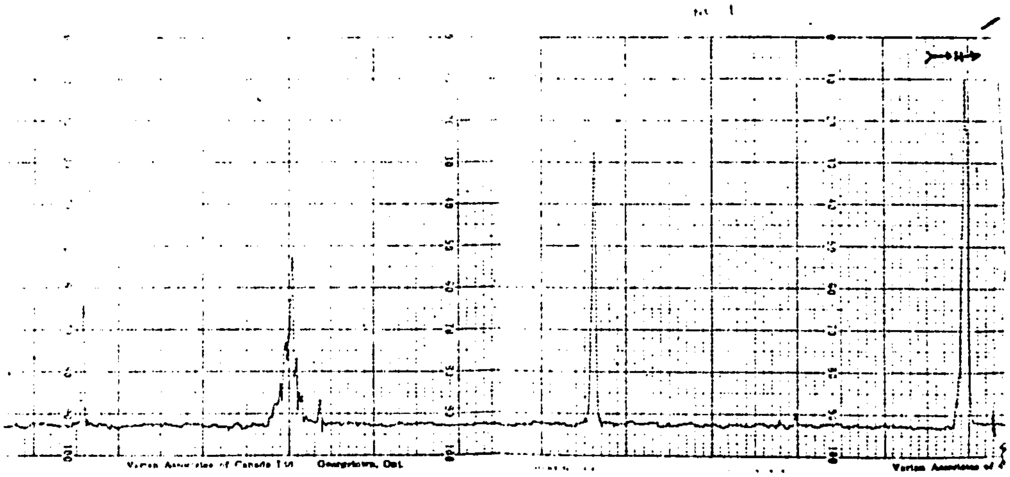
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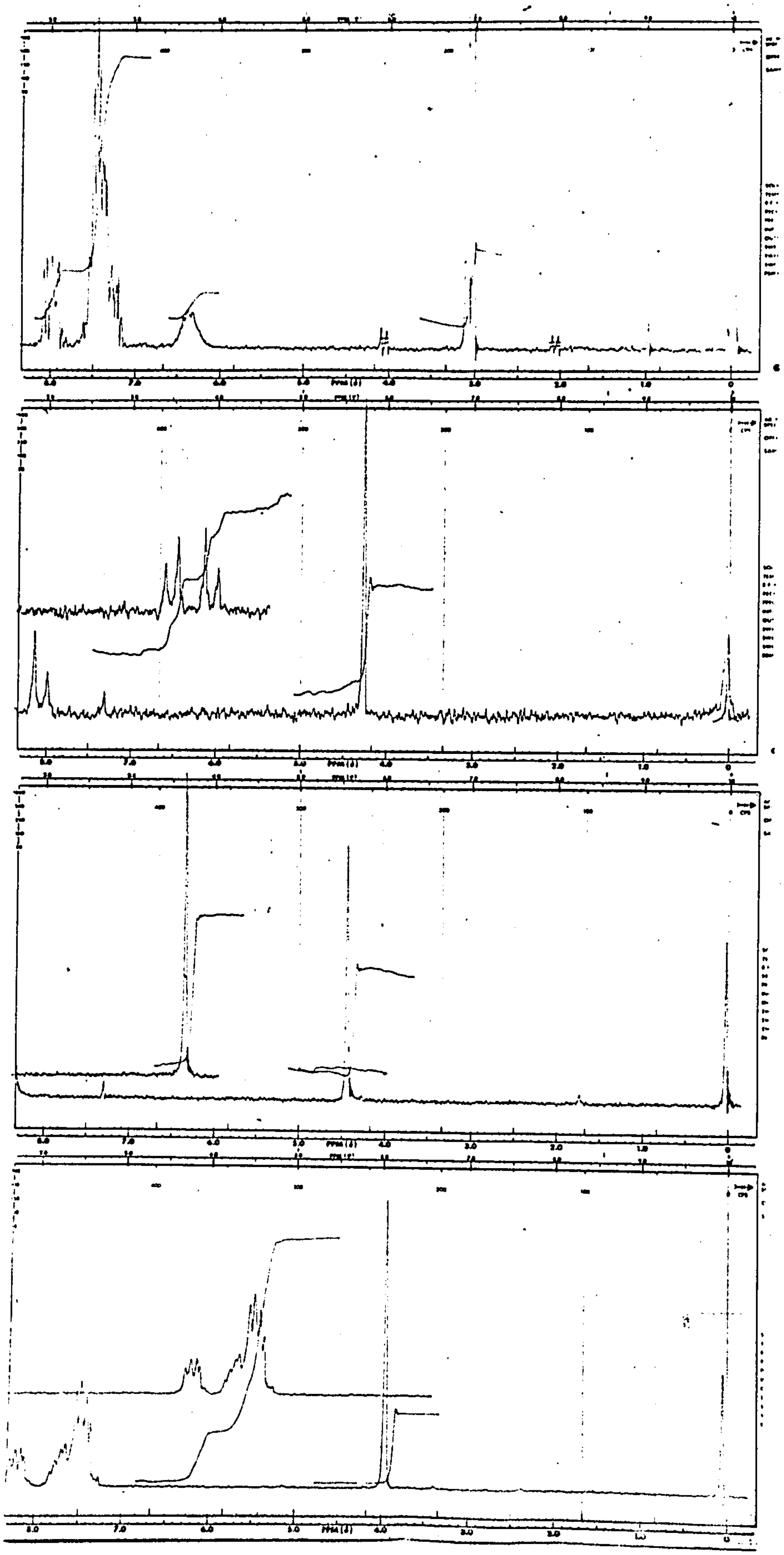
Georgetown, Ont.
Varian Associates of

6

Fig. 2.

($\epsilon = 9.0 \times 10^3$). This absorption maximum is comparable with that of nitrobenzene (λmax 269 mμ)[98]. So it appears that this absorption maximum may be due to the nitrobenzene portion whose para substituent, a tetrazole ring, contributes very little. The n.m.r. spectrum (8) (the aromatic proton resonance is offset by 120 c.p.s.) of 1-methyl-5-p-nitrophenyltetrazole shows two pairs of doublets at τ1.47 (J = 9 c.p.s.) and τ1.95 (J = 9 c.p.s.) for the four aromatic protons and a singlet at τ5.75 for the three protons of the N-methyl group.

2-Methyl-5-p-nitrophenyltetrazole, which has not yet been reported in the literature, accounted for 93% of the total methylation product. It melts at 171-172° and shows ultraviolet absorption maxima at 285 mμ ($\epsilon = 14.8 \times 10^3$) and at 204 m$\mu$. The infrared spectrum (2) of 2-methyl-5-p-nitrophenyltetrazole is in full agreement with the assigned structure. Characteristic tetrazole ring vibrations[97] appeared at 1050 cm^{-1} and 1010 cm^{-1}. The elemental analysis and the n.m.r. spectrum of 2-methyl-5-p-nitrophenyltetrazole provided further confirmation of its structure. The n.m.r. spectrum (9) shows only two singlets at τ1.79 and τ5.58 corresponding to the four aromatic and the three protons of the N-methyl group.



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8

9

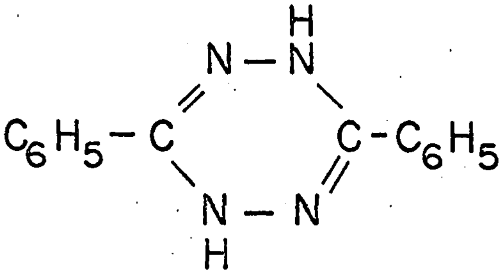
11

Fig. 3.

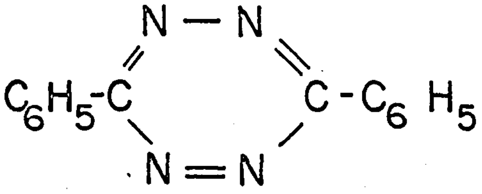
2. Photolysis of Tetrazoles

Direct irradiation of a 2% solution of 5-ethoxycarbonyl-methyltetrazole in dry dioxane did not bring about any photochemical transformations. So the inertness towards photolysis confirms the previous assignment of the u. v. absorption as due to the carboxylate group. Without further modification of the irradiation procedures, we turned our attention to the photolysis of 5-phenyltetrazole.

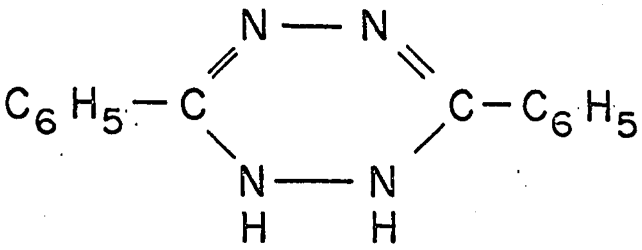
When a 2% solution of 5-phenyltetrazole in dry dioxane was irradiated by ultraviolet light two products were obtained, namely 1, 4-dihydro-3, 6-diphenyl-s-tetrazine (I) and 3, 6-diphenyl-s-tetrazine (II). The fine needle-shaped yellow crystalline 1, 4-dihydro-3, 6-diphenyl-S-tetrazine melted at 198-200°, whereas the reported melting point[103] is 190-192°. Its infrared spectrum shows a strong absorption at 3400 cm^{-1} for the -NH group. The bands at 1450 cm^{-1} and 1385 cm^{-1} are most likely due to the skeletal vibrations of the tetrazine ring[97]. The n. m. r. spectrum of 1, 4-dihydro-3, 6-diphenyl-s-tetrazine shows a set of multiplets centered at τ 2. 55 for the ten protons of the two phenyl groups. No signal for the two $>$N-H groups was observed. Its ultraviolet absorption maximum appears at 245 $m\mu$ ($\epsilon = 24.3 \times 10^3$) beside the primary band of the benzene ring at 205 $m\mu$.



I



II



III

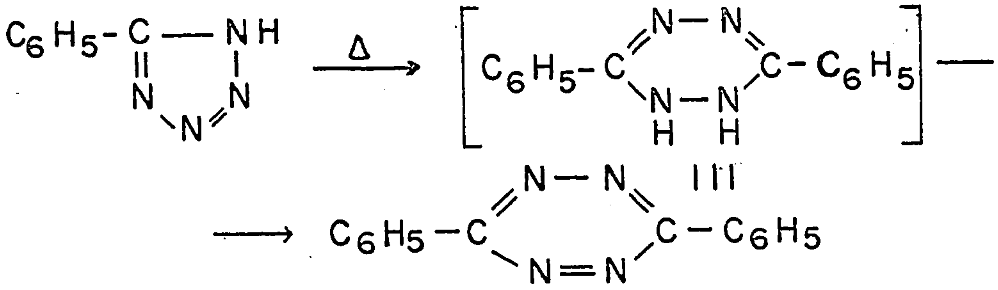
Until now there has been no report of u. v. data of 1, 4-dihydro-3, 6-diphenyl-s-tetrazine (I), but compounds of comparable chromophores, namely 2, 2-dimethyl-3-phenylazirine[121] (λmax = 245 mμ) and 2-phenyl-3-benzoylazirine[27] (λmax = 247 mμ) have absorption maxima close to the compound 1. If this compound (I) were 1, 2-dihydro-3, 6-diphenyl-s-tetrazine (III), whose melting point was reported[103, 104] to be 160°, then an extended conjugation would appear between the two phenyl rings, as in an azine. Actually, benzylideneazine[105] has an absorption maximum at 300 mμ (log ϵ = 4. 5). From these comparative studies it is concluded that the photolytically produced dihydro-3, 6-diphenyl-s-tetrazine is 1, 4-dihydro-3, 6-diphenyl-s-tetrazine (I).

If the dihydro-3, 6-diphenyl-s-tetrazine had structure (III), then it might act like a diimide towards the reduction of an olefinic system. Accordingly, an attempt was made to reduce trans-stilbene in the nitrogen atmosphere with the dihydro-3, 6-diphenyl-s-tetrazine, obtained photolytically from 5-phenyltetrazole. At the end of the experiment trans stilbene and the dihydro-3, 6-diphenyl-s-tetrazine were recovered almost quantitatively. This dihydro-3, 6-diphenyl-s-tetrazine underwent the characteristic smooth oxidation with bromine yielding 3, 6-diphenyl-s-tetrazine.

Thus chemical and spectroscopic behavior together confirm the 1,4-dihydro-3,6-diphenyl-s-tetrazine (I).

3,6-Diphenyl-s-tetrazine (II), which constituted about 65% of the total photo-products, melts at 192-193°, and the reported melting point[103] is also 192-193°C. Its n.m.r. spectrum shows two sets of multiplets centered at τ1.30 and τ2.33 corresponding to the four ortho protons and six protons from the meta and para positions of the two phenyl rings. Its ultraviolet absorption maxima appear at 297 mμ ($\epsilon = 30.8 \times 10^3$) and 554 mμ ($\epsilon = 426$). The band at 297 mμ is most likely due to the $\pi \rightarrow \pi^*$ transition of the s-tetrazine ring, while the band at 554 mμ might involved an $n \rightarrow \pi^*$ transition[106]. Its infrared spectrum was consistent with the assigned structure (II).

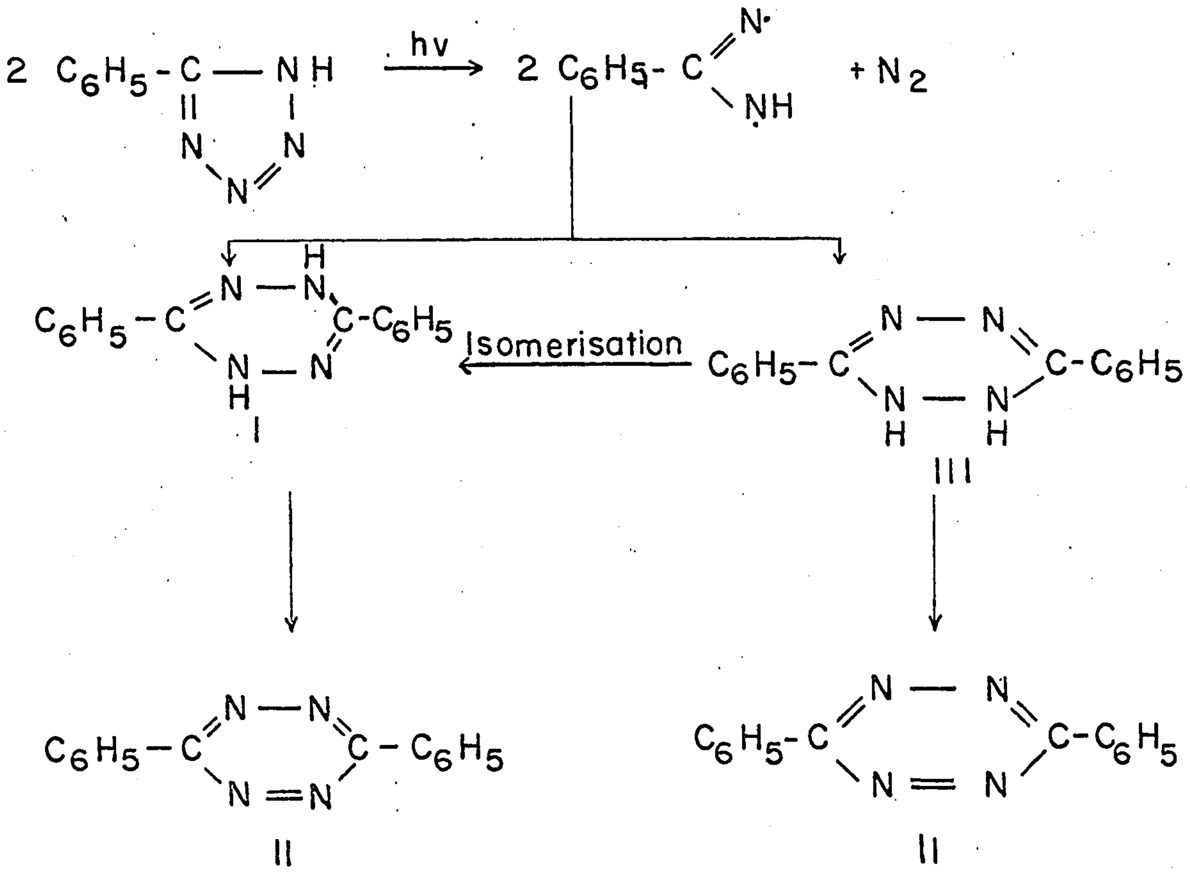
The formation of 3,6-diphenyl-s-tetrazine by heating 5-phenyltetrazole above its melting point was observed by Lossen and Statius[107] in 1887. They believed that this pyrolytic transformation went through the intermediate 3,6-diphenyl-1,2-dihydro-s-tetrazine (III), which subsequently oxidised to 3,6-diphenyl-s-tetrazine (II).



III

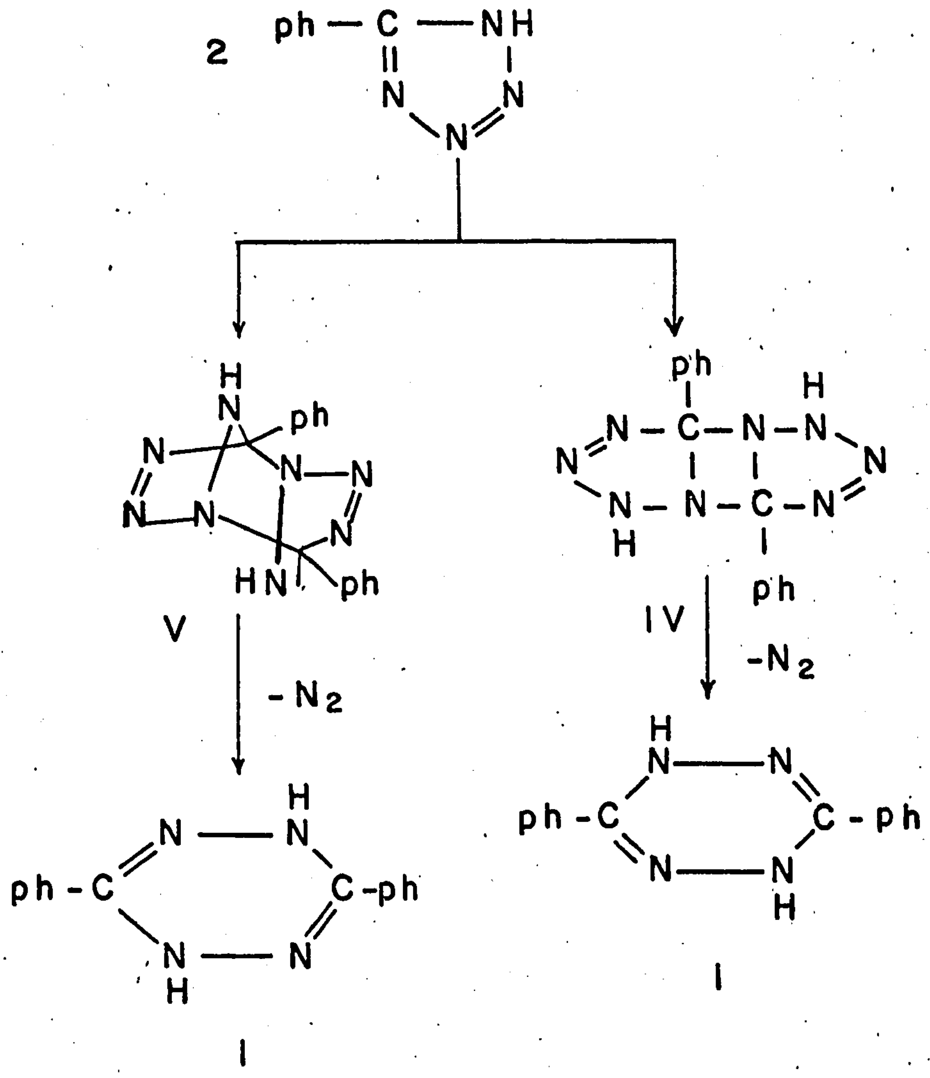
II

While the pyrolytic transformations usually proceed via the formation of free radicals, the photolytic transformation might involve the same or different intermediates. Photolytically produced free radicals from 5-phenyltetrazole could dimerise to produce 1, 2- or 1, 4-dihydro-3, 6-diphenyl-s-tetrazine. It is also possible that 1, 2-dihydro-3, 6-diphenyl-s-tetrazine is formed initially and then rapidly isomerises to 1, 4-dihydro-3, 6-diphenyl-s-tetrazine. Since 1, 2-dihydro-3, 6-diphenyl-s-tetrazine (III) is much more easily oxidised than the 1, 4-dihydro-3, 6-diphenyl-s-tetrazine[103] the former may be initially formed from the photolysis and then undergoes both the processes of isomerisation to the compound (I), and of oxidation to 3, 6-diphenyl-s-tetrazine (II). The concentrations of the final products would depend on the relative rates of both the processes. It is also possible that both 1, 2-dihydro-3, 6-diphenyl-s-tetrazine (III) and 1, 4-dihydro-3, 6-diphenyl-s-tetrazine (I), are formed at the same time by dimerisation of the free radical produced from the photolysis of 5-phenyltetrazole; then (III) gets oxidised to (II) at a faster rate than (I).



An entirely different pathway might also be involved. 5-Phenyltetrazole might dimerise initially under the influence of light to form a structure of the thymine[44, 108] (IV); pyridone[37, 36] or anthracene[123] (V) dimer, which is then converted to the final products by rearrangement and loss of nitrogen.

In addition to the above possibilities, tetrazole under the influence of ultraviolet irradiation might undergo cleavage producing nitrilimine(VI). Then


2
ph
V
IV
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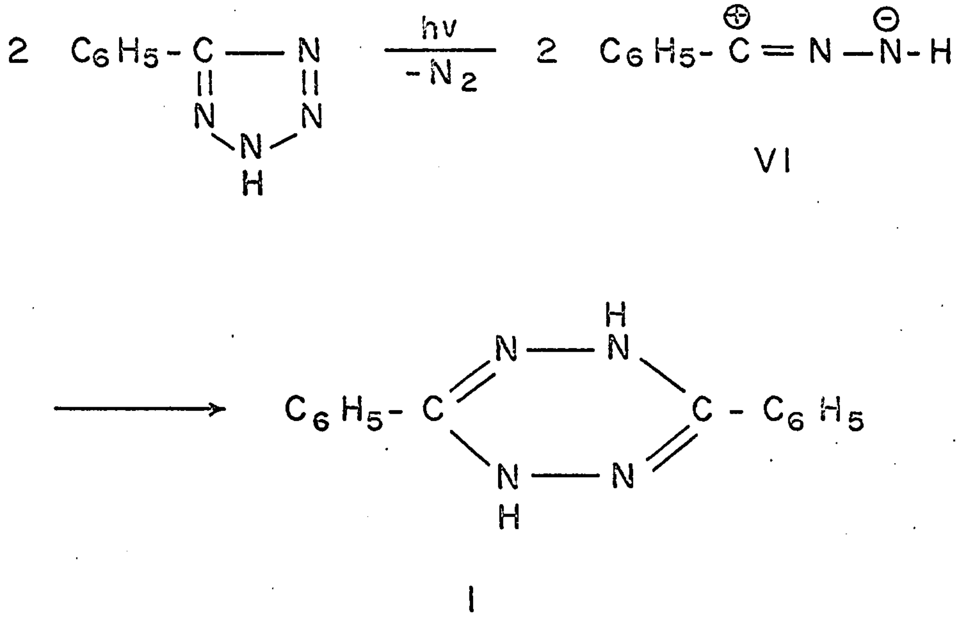
$-N_2$
I
I

two moles of nitrilimine could recombine producing 1,4-dihydro-3,6-diphenyl-s-tetrazine (I), which subsequently gets oxidised to 3,6-diphenyl-s-tetrazine (II). The only difference between this and the radical route is the multiplicity of spin in the nitrilimine.



Several attempts were made to trap the possible nitrilimine intermediate by photolysing 5-phenyltetrazole in the presenceof norbornene and ethyl acrylate in separate experiments, but in neither case was any pyrazoline derivative obtained. Moreover, the total yield of the 1,4-dihydro-3,6-diphenyl-s-tetrazine (I) and 3,6-diphenyl-s-tetrazine (II) was constant. Failure to trap the nitrilimine intermediate with norbornene and ethyl acrylate plus the absence of any other products beside the 1, 4-dihydro-3, 6-diphenyl-s-tetrazine and 3, 6-diphenyl-s-tetrazine, could be interpreted as evidence for the dimeric route to the formation of -s-tetrazine derivatives.

In order to get more information of the nature of the photolysis of 5-phenyltetrazoles, methylated 5-phenyltetrazoles were subjected to photolysis. 1-Methyl-5-phenyltetrazole, having the ultraviolet absorption maximum at 232 mμ was found to be stable towards ultraviolet irradiation even over a period of 12 hours. It was thought that by using a suitable sensitizer this tetrazole might be induced to undergo a photochemical transformation. In one trial experiment, a mixture of 1-methyl-5-phenyltetrazole and benzophenone dissolved in dry dioxane was irradiated in a nitrogen atmosphere for about four hours. All the starting tetrazole was recovered at the end of irradiation. No further photolytic experiments were performed with this tetrazole.

We then turned our interest to the photolysis of 2-methyl-5-phenyltetrazole. 2-Methyl-5-phenyltetrazole dissolved in dry dioxane, was irradiated with ultraviolet light for three hours. From the crude mixture of photoproducts, a crystaline product which melted at 60-62° was isolated in 40% yield by chromatography. Either thinlayer chromatography over silica gel or column chromatography over alumina could be used for the separation of the above crystalline compound. As a matter of fact, both of these chromatographic processes were employed in two separate experiments. The infrared spectrum (5) of the above crystalline product shows strong absorption at 1575 cm^{-1}, which was assigned to the stretching vibrations[97] of a -C=N- group. The absorptions which appear at 1020 cm^{-1}, 1010 cm^{-1} and 990 cm^{-1} were assigned eventually to the vicinal triazole ring[111, 92] vibrations. Characteristic mono substituted phenyl ring vibrations appeared in the regions of 775 cm^{-1} to 690 cm^{-1} and 1800 cm^{-1} to 2000 cm^{-1}. Its n.m.r. spectrum (10) clearly indicates the presence of an N-methyl group and two phenyl rings, because of a singlet at τ5.88 and a multiplet centered at τ2.71 having an intensity ratio of 3:10. The molecular ion appears at 235 in its mass spectrum. From the above spectral evidence, together with the elemental analysis, it was concluded that the crystalline product must be a triazole containing two phenyl groups and an N-methyl group. Its ultraviolet absorption maximum appears at 257 $m\mu$ ($\epsilon = 13.3 \times 10^{3}$), which could be assigned to the linear conjugation of benzene and triazole chromophores. Initially it was thought this crystalline material might be 1-methyl-3,5-diphenyl-1,2,4-

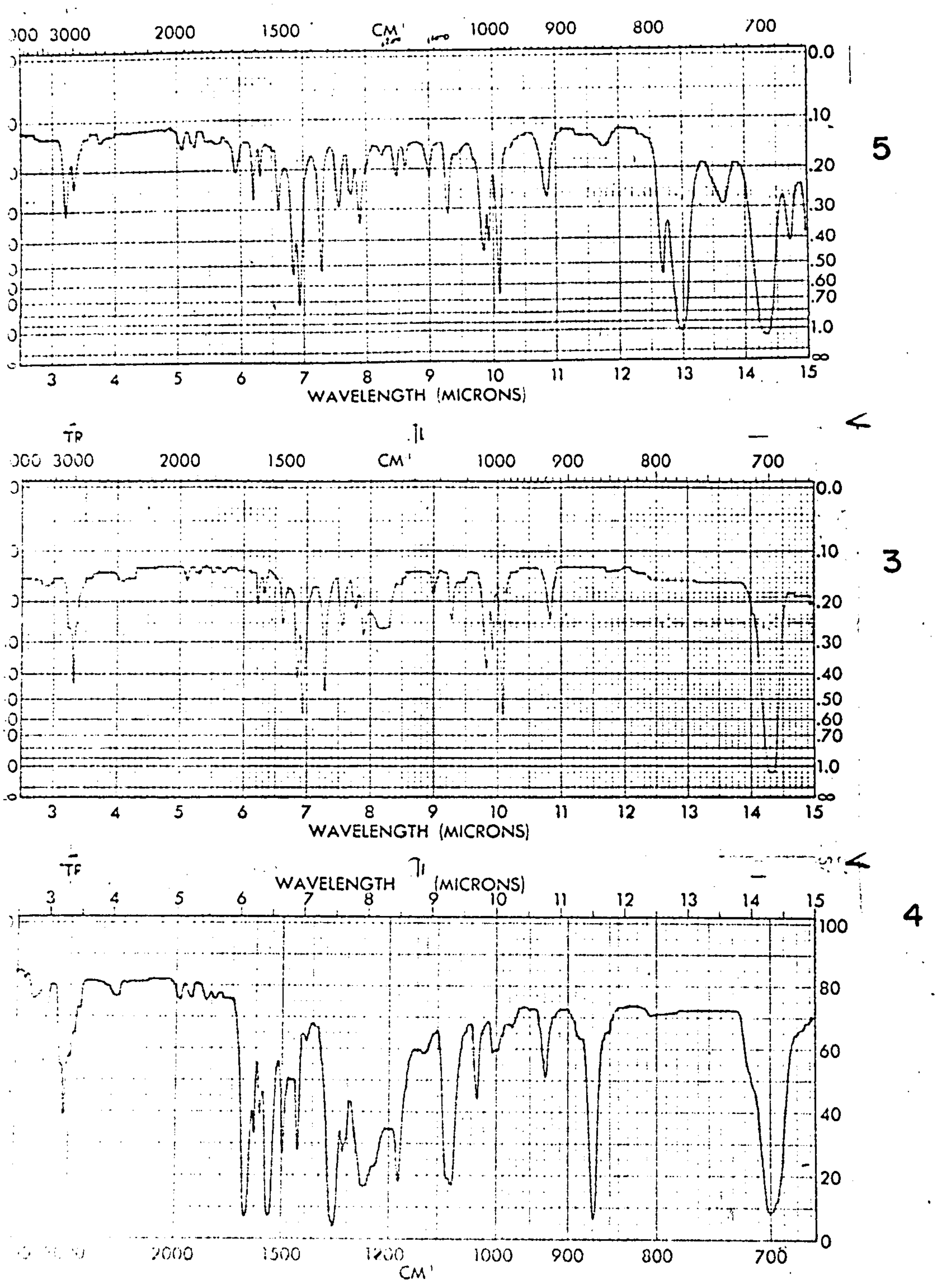

5
3000
2000
1500
CM⁻¹
1000
900
800
700
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
3
4
100
80
60
40
20
0

Fig. 4.

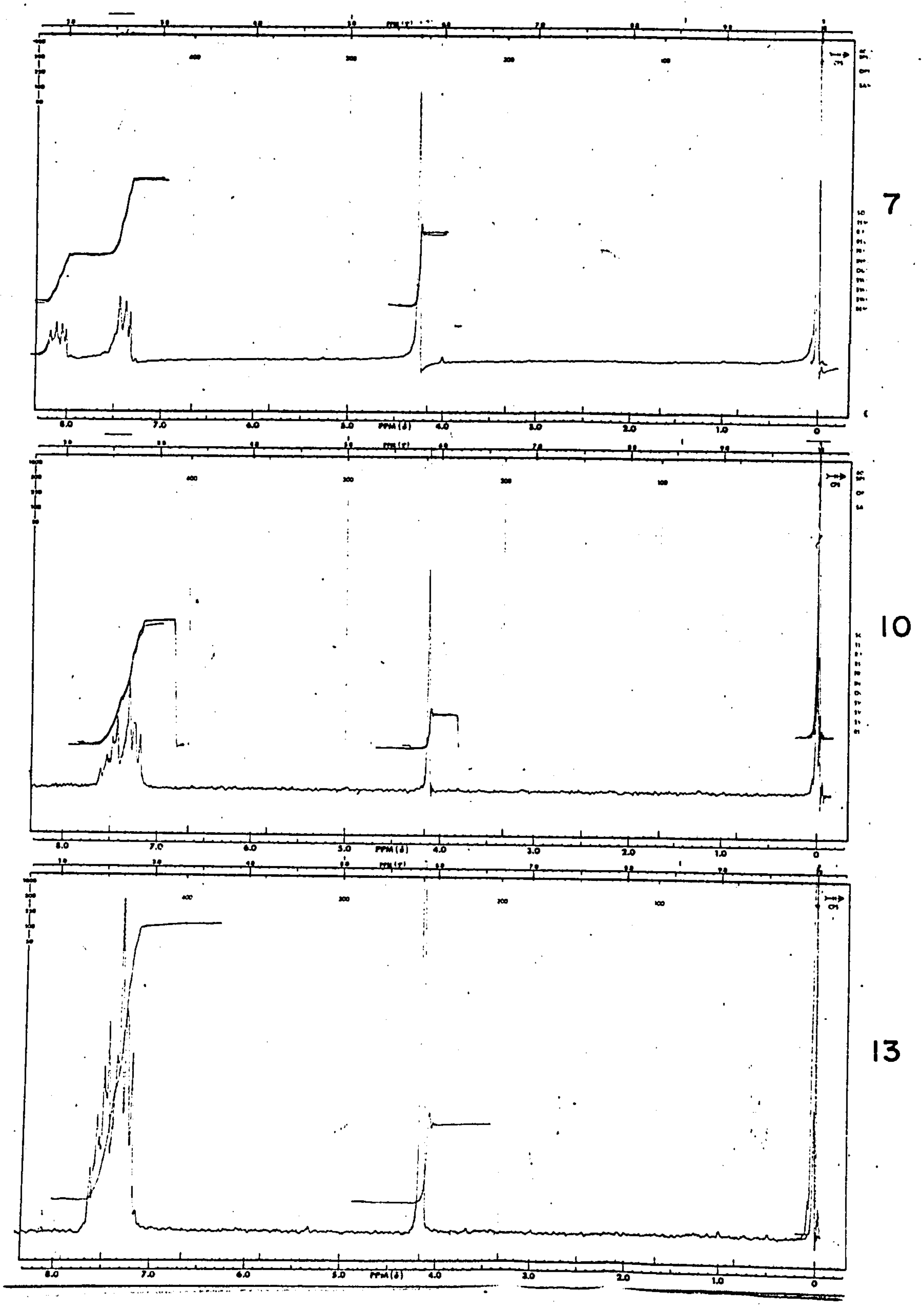
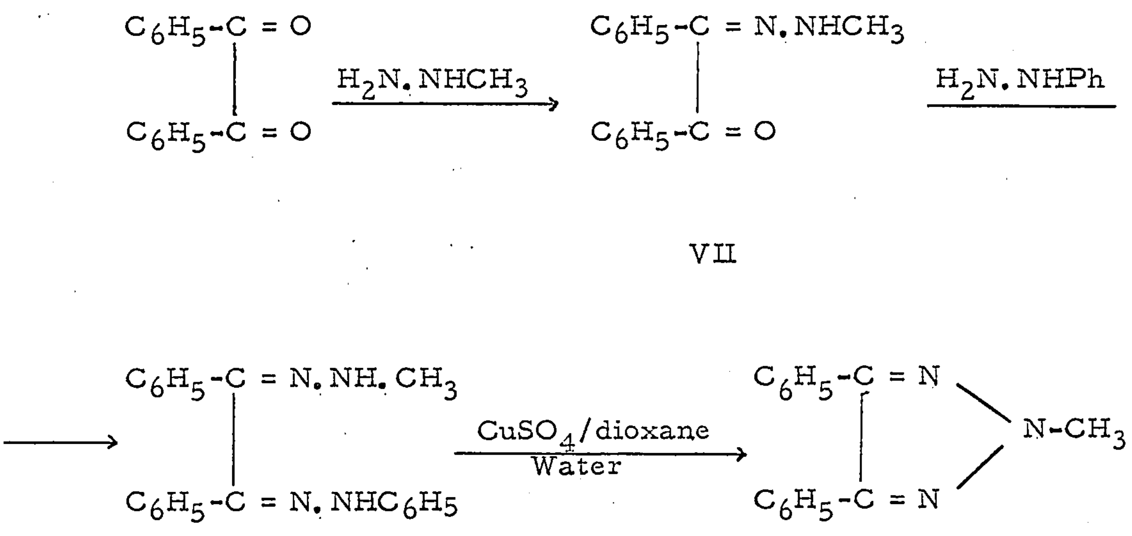


Fig. 5.

triazole. However, this compound is reported to melt at 83-85° and show an ultraviolet absorption maximum[88] at 247 mμ ($\epsilon = 19.8 \times 10^3$). Nevertheless, 1-methyl-3, 5-diphenyl-1, 2, 4-triazole was prepared by following the reported procedures[86, 85]. It not only had different melting point and ultraviolet absorption maxima, but also its n.m.r. (11) and infrared spectra were quite different from those observed in the case of the crystalline compound of melting point 60-62°.

Another possible structure for this crystalline compound was 2-methyl-4, 5-diphenyl-1, 2, 3-triazole. This particular triazole has not yet been reported in the literature. In order to confirm the structure of the photolytically produced triazole, an attempt was made to prepare 2-methyl-4, 5-diphenyl-1, 2, 3-triazole. A variety of methods are available for the preparation of 1, 2, 3-triazoles[117, 116]. Of them, the most widely employed method for the preparation of 2, 4, 5-trisubstituted-1, 2, 3-triazoles is the cyclisation of suitable osazones by refluxing with cupric sulfate in aqueous dioxane[116]. We therefore chose benzil as the starting material for the following sequence of reactions:



VII

VIII

IX

Accordingly benzil monomethylhydrazone (VII) was prepared by a modification of the method reported by Forster and Cardwell[89], which gave a quantitative yield of the product. Its melting point 138°, infrared (4) and n.m.r. (12) spectral properties were consistent with its structure (VII).

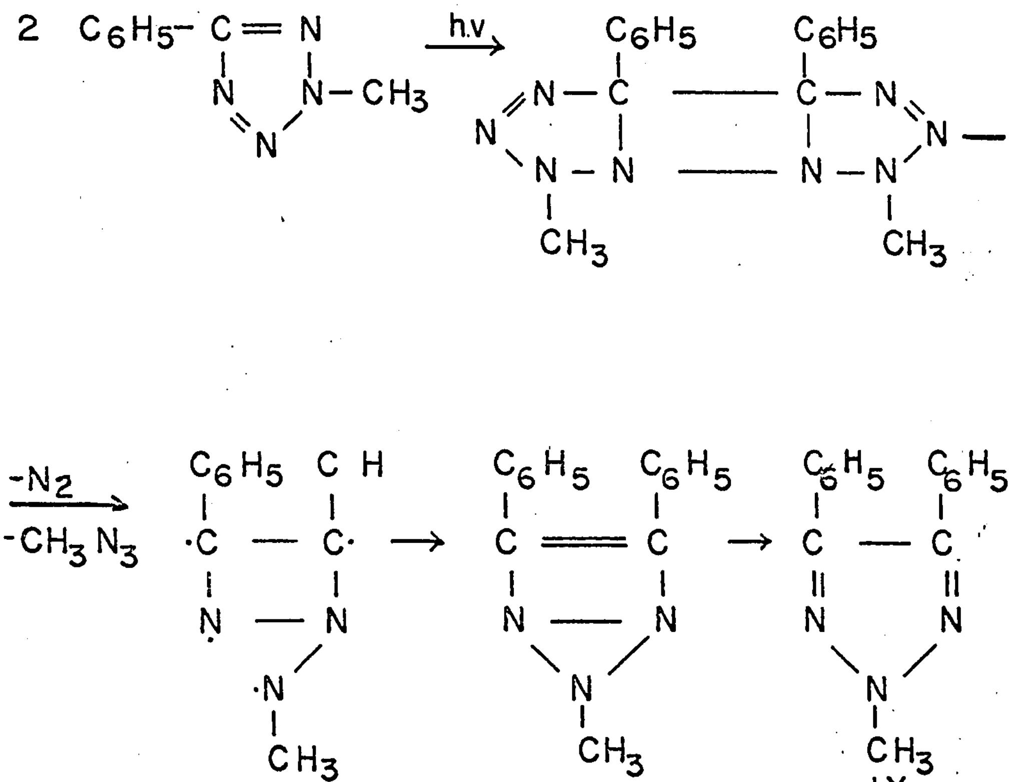
The conversion of benzil monomethylhydrazone (VII) into benzil bis-(N-methyl-N'-phenyl)hydrazone (VIII) by the action of phenylhydrazine proved very difficult. All attempts to prepare this bis-hydrazone (VIII) from (VII) with phenylhydrazine in basic, acidic, or neutral media at ordinary temperature or by refluxing over variable periods of time, resulted in the formation of benzil monophenylhydrazone with the simultaneous elimination of methylhydrazine. However, when the same operations were carried out on benzil monophenylhydrazone with methylhydrazine in basic, acidic or neutral media, standing at room temperature or refluxing over variable periods of time, nothing but the starting material was recovered.

Because we found that phenylhydrazine replaced methylhydrazine from benzil monomethylhydrazone during the preparation of the bis-hydrazone (VIII), in an open system, it was thought that if methylhydrazine would not be allowed to escape from the reaction medium, then the desired bis-hydrazone (VIII), could be formed. Accordingly a mixture of benzil monomethylhydrazone (VII) and an equivalent amount of phenylhydrazine and a few drops of glacial acetic acid was sealed in a Pyrex tube and heated up to 130° over a period of 2.5 hours. Then without isolation and purification of the bis-hydrazone (VIII), the crude reaction mixture was subsequently subjected to oxidation by refluxing with cupric sulfate dissolved in a (1:1) water and dioxane mixture. The 2-methyl-4,5-diphenyl-1,2,3-

triazole (IX) was separated and purified by a lengthy process of column chromatography over alumina. The yield of the triazole (IX) melting at 60-62° was only 2%. Its ultraviolet, infrared (3), n.m.r. (13), mass spectra and the elemental analysis agreed in all respects with those of the triazole obtained by photolysis of 2-methyl-5-phenyltetrazole.

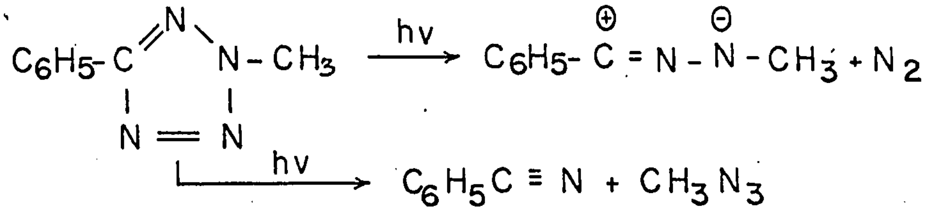
Several other compounds in addition to 2-methyl-4, 5-diphenyl-1, 2, 3-triazole were present in the crude mixture of photoproducts of 2-methyl-5-phenyltetrazole. The presence of 1-methyl-3, 5-diphenyl-1, 2, 4-triazole in the reaction mixture was suggested by the appearance of a signal at τ 6.1. Since pure 1-methyl-3, 5-diphenyl-1, 2, 4-triazole gives a peak for its N-methyl protons at τ 6.1. Several unsuccessful attempts were made to separate the 1, 2, 4-triazole by chromatography from the crude reaction mixture.

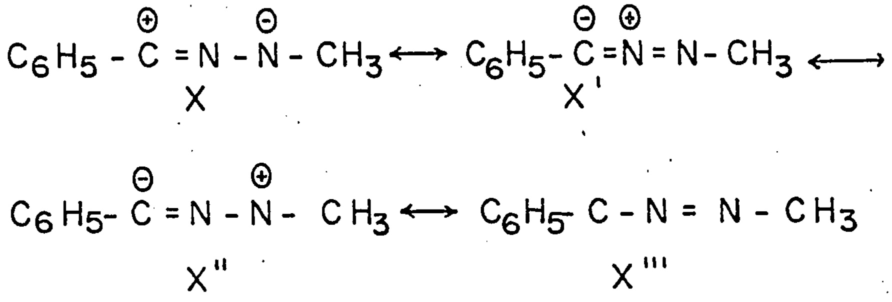
The concept of dimerisation which has been applied to explain the production of dihydrotetrazine and tetrazine from the photolysis of 5-phenyltetrazole can also be applied to explain the production of 1, 2, 3-triazole. 2-Methyl-5-phenyltetrazole may undergo head to head dimerisation which by loss of methyl azide and nitrogen, followed by rearrangement, gives the final product (IX).

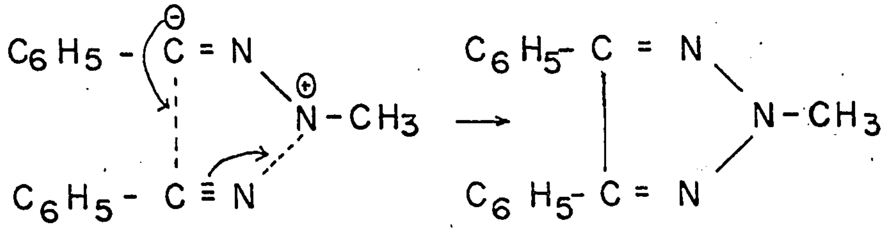


IX

Huisgen and co-workers[118] have shown that when 2-methyl-5-phenyltetrazole is heated above 225°, 1-methyl-3,5-diphenyl-1,2,4-triazole is formed. They have also shown that during this thermolysis, benzonitrile, methylazide, nitrilimine and nitrogen are formed. They concluded that benzonitrile and nitrilimine undergo 1,3-dipolar addition producing 1-methyl-3,5-diphenyl-1,2,4-triazole. So the photochemical production of 2-methyl-4,5-diphenyl-1,2,3-triazole can be rationalised in the following way:







IX

Nitrilimine (X) and nitrogen, benzonitrile and methylazide are formed from the cleavage of 2-methyl-5-phenyltetrazole under the influence of light. Nitrilimine (X) may exist in various resonance forms[96], like (X), (X'), (X'') and (X'''). Benzonitrile undergoes 1, 3-dipolar addition with (X'') to produce 2-methyl-4, 5-diphenyl-1, 2, 3-triazole.

If 1, 2, 3- as well as 1, 2, 4-triazoles could be formed by 1, 3 dipolar addition of benzonitrile with nitrilimines, the yield of either one of the above two triazoles could be increased by the addition of benzonitrile to the photolysis-medium. Therefore a photolysis of 2-methyl-5-phenyltetrazole was carried out with benzonitrile in the reaction mixture. However, the overall yield of 1, 2, 3-triazole did not alter at all; moreover, most of the added benzonitrile was recovered from the reaction mixture. There might be another possibility that 1-methyl-3, 5-diphenyl-1, 2, 4-triazole was first formed during the photolysis of 2-methyl-5-phenyltetrazole, and this triazole, under the influence of light, was converted into 1, 2, 3-triazole derivative (IX). Therefore, 1-methyl-3, 5-diphenyl-1, 2, 4-triazole was irradiated in dry dioxane for a period of three hours, but all the starting triazole was recovered from the reaction mixture at the end of irradiation.

It is possible that during the thermolysis[118] of 2-methyl-5-phenyltetrazole, 2-methyl-4, 5-diphenyl-1, 2, 3-triazole could be formed initially and then rearranged into 1-methyl-3, 5-diphenyl-1, 2, 4-triazole at the high reaction temperature. When 2-metnyl-4, 5-diphenyl-1, 2, 3-triazole was heated in a sealed tube up to 220-225°C for 6 hours, a fused mass was obtained which showed the same ultraviolet absorption maxima as those of the starting triazole. The melting point of that fused mass was 60-62°, which was actually the melting point of the starting triazole. So it is possible to make a conclusion that 2-methyl-4, 5-diphenyl-1, 2, 3-triazole is not the initial product formed during the thermolysis of 2-methyl-5-phenyltetrazole.

It has been shown that radiation at or above 2400 Å is responsible to effect the photolysis of 2-methyl-5-phenyltetrazole, because when the latter was irradiated under the same reaction condition using a vycor filter, no change in the total yield of the triazole (IX) was observed, because the vycor filter cuts off light lower than 2400 Å.

We wished to determine the effect of a substituent capable of ionic interaction with possible excited intermediates. Thus 2-methyl-5-p-nitrophenyltetrazole dissolved in dry dioxane was irradiated.

Unfortunately, no photolysis took place even on prolonging the irradiation period up to 24 hours. This tetrazole has an intense absorption at 285 mμ, but this absorption is mostly due to the p-substituted-phenyl ring. Or in other words, the tetrazole ring is considerably transparent towards the ultraviolet light, so its inertness towards ultraviolet irradiation is not so unexpected.

At present, with this amount of data, it is not possible to make any rigorous conclusion as to the nature of photolytic cleavage of the tetrazole ring in 5-phenyltetrazole and 2-methyl-5-phenyltetrazole. It can be said that the strikingly different courses followed by 5-phenyltetrazole and 2-methyl-5-phenyltetrazole can both be rationalised on the basis of formation of a common intermediate, either a nitrilimine or a dimer. Failures to trap the nitrilimine intermediates, however, make their intervention less likely. For this reason, the formation of dimer followed by loss of nitrogen is proposed as the most likely path of reaction.

N.M.R. Studies of Tetrazoles, Triazole and s-Tetrazine

It is evident from the n.m.r. data summarised in Table I, that the signals for the ortho protons of 5-phenyltetrazole, 2-methyl-5-phenyltetrazole, 1-methyl-5-p-nitrophenyltetrazole, 1-methyl-3,5-diphenyl-1,2,4-triazole and 3,6-diphenyl-s-tetrazine appear considerably at lower field than the rest of the aromatic protons in their n.m.r. spectra.

Recently several comparable cases have been reported. Mayo and Goldstein[119] have determined the effect of magnetic anisotropy on the ortho protons of biphenyl. They found these protons to be deshielded -19.05 c.p.s. relative to benzene. Crossland[120] has found that the two ortho protons of the phenyl ring of 3-methoxy-6-p-tolylpyridazine are displaced from the rest of the phenyl protons by $\Delta\delta = 0.67$ ppm. It was proposed that the ortho protons are deshielded by the neighbour anistropy effect, which was maximum when the phenyl ring and the pyridazine ring were coplanar[120]. Independently, Lynch and Hung[110] and Tensmeyer and Ainsworth[125] have reported a similar effect on the ortho protons of the phenyl group attached to a pyrazole ring; anisotropy was again offered as an explanation for the large deshielding. In both systems,

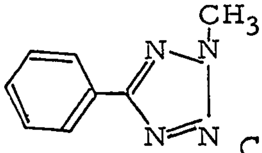
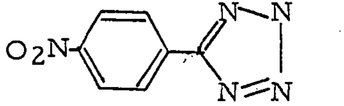
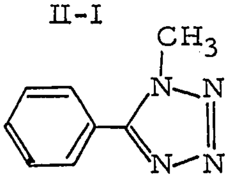
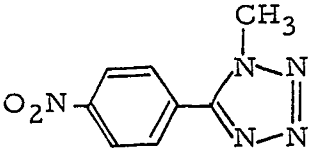
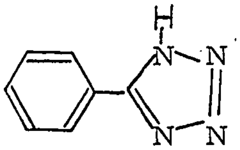
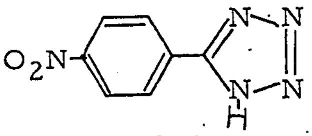
TABLE I

PROTON CHEMICAL SHIFTS (τ)

Compounds	Aromatic Protons Ortho	 Meta & Para	 N-methyl	Solvent
5-Phenyltetrazole	1.9	2.49	-	Deuterochloroform/ Dimethylsulfoxide
2-Methyl-5-Phenyltetrazole	1.87	2.59	5.75	Deuterochloroform
1-Methyl-5-Phenyltetrazole	2.36	2.36	5.84	Deuterochloroform
5-p-Nitrophenyltetrazole	1.6	1.6	-	Acetone
1-Methyl-5-p-Nitrophenyltetrazole	1.95	1.44	5.75	Deuterochloroform
2-Methyl-5-p-Nitrophenyltetrazole	1.79	1.79	5.58	Deuterochloroform
1-Methyl-3, 5-diphenyl-1, 2, 4-triazole	1.90	2.57	6.1	Deuterochloroform
3, 6-Diphenyl-s-tetrazine	1.37	2.4	-	Chloroform

TABLE II.

CHEMICAL SHIFT OF AROMATIC PROTONS (τ)

	Compounds	Ortho	Meta and Para
I		1.9 (-48 c.p.s.)*	2.6 (-6 c.p.s.)*
II		1.79 (-55 c.p.s.)	1.79 (-55 c.p.s.)
	Effect of NO_2 group II-I	(-7 c.p.s.)	(-49 c.p.s.)
III		2.36 (-20 c.p.s.)	2.36 (-20 c.p.s.)
	Effect of rotation III-I	+28 c.p.s.	-14 c.p.s.
IV		1.95 (-45 c.p.s.)	1.47 (-74 c.p.s.)
	Effect of NO_2 group IV-III	-25 c.p.s.	-54 c.p.s.
	Effect of rotation IV-II	+10 c.p.s.	-19 c.p.s.
V		1.9 (-48 c.p.s.)	2.49 (-13 c.p.s.)
VI		1.6 (-66 c.p.s.)	1.6 (-66 c.p.s.)
	Effect of nitro group VI-V	-18 c.p.s.	-53 c.p.s.

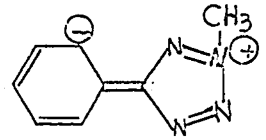
* Deviation from unsubstituted benzene (τ 2.7).

introduction of a substituent in the hterocyclic ring at a position adjacent to the phenyl ring resulted in an upfield shift.

In the present studies, it has been observed that the ortho protons of the phenyl rings of 5-phenyltetrazole and 2-methyl-5-phenyltetrazole are displaced downfield from the rest of the aromatic protons by $\Delta\delta$ = 0.59 ppm, and $\Delta\delta$ = 0.68 ppm. But in the case of 1-metnyl-5-phenyltetrazole, only one set of multiplet is observed, cantered at τ 2.36 for the five protons of the phenyl ring. So it is obvious that the two ortho protons are not subject to as large an anisotropic effect, and this could happen only when the coplanarity between the phenyl ring and the tetrazole ring is lost. The methyl group on the tetrazole ring causes this non-coplanarity.

All the four aromatic protons of 5-p-nitrophenyltetrazole and 2-methyl-5-p-nitrophenyltetrazole appear as singlets at τ 1.6 and τ 1.79 respectively. In these cases, it is obvious that both the magnetic anisotropy effect of the tetrazole ring and the nitro group exert deshielding effects on the two protons ortho to them. Incidentally, these two effects make all four aromatic protons magnetically equivalent to one another. The four aromatic protons of 1-methyl-5-p-nitrophenyltetrazole appear as an A_2B_2 pattern[109].

In Table II some of the effects are collected for comparison. It is evident that the effect of the nitro group on the protons ortho to it is significant and also comparable in 5-phenyl, 1-methyl and 2-methyltetrazole series (-53 c.p.s., -49 c.p.s. and -54 c.p.s.). As previously mentioned, the effect of an aromatic or heterocyclic ring on the chemical shift of the ortho protons on benzene rings is well known[119,120,125,110], and its origin has been ascribed to the ring anisotropy. The above series of τ values indicate such to be an oversimplification. It can be seen that there is no consistent effect of changing the methyl group from the 2- position to the 1- position of the tetrazole ring in the 5-p-nitrophenyltetrazole and 5-phenyltetrazole series. Previous studies have shown that for additivity to be followed, resonance contributions must be low[127,115,122]. It is therefore likely that there is resonance interaction such as



between the two rings, a conclusion which is substantiated by the decrease in τ-values for the meta protons (I-III) as coplanarity is prevented. That an inductive withdrawal effect is also present is suggested by the low τ-values in (III) relative to benzene. Therefore, it is concluded that resonance, inductive and anisotropy effects all contribute to the observed τ values for the aromatic protons.

Two ortho protons of one of the phenyl rings of 1-methyl-3, 5-diphenyl-1, 2, 4-triazole are shifted further downfield (τ 1. 84) than the rest of the aromatic protons. It is probable that one of the phenyl rings lies in the plane of the triazole ring, so that the two ortho protons reside preferentially near the plane of the triazole ring and are shifted downfield by its ring current. It is most likely that the phenyl ring, which is close to the $\rangle$N-CH_3 group, is out of plane of the triazole ring.

The greatest desheidling is observed for the ortho protons of 3, 6-diphenyl-s-tetrazine. Thus the large deshielding is most likely due to the sum total of resonance, inductive and anisotropy effects, and these effects become more pronounced when these three ring systems are coplanar to one another.

As we have shown above, there is strong evidence from n.m.r. data that the introduction of a methyl group in the position-1 prevents coplanarity of the bønzene and tetrazole rings. If one reconsiders the u.v. data mentioned earlier, one can then account for each absorption maximum which Nachod[78] considered to be anomalously low as actually being due to non-coplanarity of the chromophores. Biphenyl for example, exhibits this effect. Substituent in biphenyl brings about non-coplanarity which causes a decrease in the absorption wavelength and intensity[98]. For example[124], the absorption maximum of biphenyl is at 245 $m\mu$, while that of 2-methylbiphenyl is at 235 $m\mu$.

CLAIMS TO ORIGINAL RESEARCH

1. 5-Phenyltetrazole has been photolysed by ultraviolet irradiation.

1a. 1, 4-Dihydro-3, 6-diphenyl-s-tetrazine and 3, 6-diphenyl-s-tetrazine have been isolated from the photolysis of 5-phenyltetrazole.

2. 2-Methyl-5-phenyltetrazole has been photolysed in ultraviolet irradiation.

2a. 2-Methyl-4, 5-diphenyl-1, 2, 3-triazole has been isolated and identified from the photolytic products of 2-methyl-5-phenyltetrazole.

3. An independent synthesis of 2-methyl-4, 5-diphenyl-1, 2, 3-triazole starting from benzil has been described.

4. 5-p-Nitrophenyltetrazole has been methylated.

4a. 2-Methyl-5-p-nitrophenyltetrazole has been isolated from the methylated products of 5-p-nitrophenyltetrazole.

5. The magnetic anisotropy effect on the aromatic protons of 5-phenyltetrazole, 2-methyl-5-phenyltetrazole, 5-p-nitrophenyltetrazole, 2-methyl-5-p-nitrophenyltetrazole, 1-methyl-3, 5-diphenyl-1, 2, 4-triazole and 3, 6-diphenyl-s-tetrazine has been studied.

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