being fruitless since a small reduction in volume sometimes occurred after six half-lives. This was not a leak since the volume reduction, <1 ml, occurred even if the pressure in the apparatus was less than atmospheric.

Rate constants were calculated by the least-squares method using the 12–22 points accumulated during the first 90% of reaction. The data were plotted as ln $(V_m - V_t)$ *vs.* time, where V_m is the maximum volume of gas produced during the timed portion of the run and V_t is the volume of gas produced at a particular time. The computations were performed on the Michigan Terminal System IBM 360 computer. Yields of propene produced were calculated from the weight of sulfoxide introduced and the total volume of propene produced, corrected to STP. Activation parameters were computer calculated by a least-squares method using points on a plot of log 10 k_1 *vs.* $1/T$ and, for computation of ΔH and ΔS, at 175°, a temperature which was common to all of the compounds. Two or more runs were made on each compound at each temperature, except where noted in Table I. The reaction constant, ρ, was computed by the least-squares method using σ values[5] and the logarithms of the rate constants.

Registry No.—Phenyl *n*-propyl sulfoxide, 21865-07-6; *p*-chlorophenyl *n*-propyl sulfoxide, 21865-08-7; *p*-tolyl *n*-propyl sulfoxide, 21865-09-8; *p*-methoxyphenyl *n*-propyl sulfoxide, 21865-10-1; *p*-nitrophenyl *n*-propyl sulfoxide, 21865-11-2.

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The Photolysis of 2-Methyl-5-Phenyltetrazole

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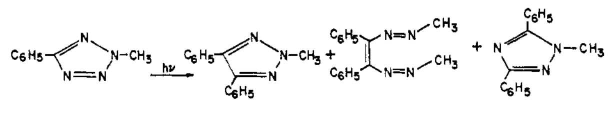
The photolysis of 2-methyl-5-phenyltetrazole has been found to produce 2-methyl-4,5-diphenyl-1,2,3-triazole (**2**) in 22–27% yield and 1,2-di(methylazo)-1,2-diphenylethylene (**3**) in 6–10% yield. In contrast to previous studies on the photolytic behavior of tetrazoles, no evidence of production of a nitrilimine was found. The product formation is rationalized *via* an intermediate photodimer. The structure of the triazole was confirmed by an independent synthesis, while the structural assignment for the bisazoethylene rests on spectral evidence.

In the last few years, much attention has been devoted to the photolysis of a variety of heterocyclic aromatic compounds,[2] and most recently the behavior on irradiation of several tetrazoles has been examined.[3] Huisgen and coworkers[3a] studied the photolysis of 2,5-diphenyltetrazole, and Moriarty and coworkers studied the photolysis of 1,5-dicarbomethoxytetrazole[3b] and 1,5-diphenyltetrazole[3c] (also studied by Kirmse[3d]). This year, a paper by Scheiner[3e] on the photolytic behavior of 5-phenyltetrazole and its anion has appeared. We now wish to report an investigation of the photolysis of 2-methyl-5-phenyltetrazole.[4] The photolytic behavior of this compound is found to differ strikingly from that reported previously for any other tetrazoles.[5]

Irradiation of a solution of 2-methyl-5-phenyltetrazole (**1**) in 1,4-dioxane using a Hanovia 450-W medium pressure mercury lamp for 3 hr caused the consumption of 88% of the tetrazole. Following purification of the reaction mixture by two careful chromatographic separations, three compounds were isolated in pure form. The first of these, formed in 22% yield, was a white solid, **2**, whose identity was established by chemical and spectroscopic means as 2-methyl-4,5-diphenyl-1,2,3-triazole. The second product, a red solid, was formed in 6% yield. This compound is tentatively assigned the structure 1,2-diphenyl-1,2-di(methylazo)-ethylene (**3**), having a *cis* arrangement of the phenyl groups about the ethylenic bond and both a *cis* and a *trans* azo group. The third identifiable product, 1-methyl-3,5-diphenyl-1,2,4-triazole (**4**), was formed in a yield of less than 4%. The photolysis reaction is summarized in eq 1.

(1)



1 2 3 4

Since thin layer chromatography showed that at least five additional products were present in the crude photolysate, the reaction was also studied in two other solvents, benzene and isooctane. In these solvents, there were fewer side products formed, but the yields of **2** and **3** increased only slightly to 25 and 10%, respectively. The effect of varying the tetrazole concentration (0.09–0.38 *M* in benzene) was found to be negligible. The yield of **4** varied from 4 to 7% in the latter solvents.

Huisgen and coworkers[3a] have reported that the photolysis of 2,5-diphenyltetrazole produces diphenylnitrilimine and nitrogen. This was deduced from the observations that essentially identical yields of two isomeric pyrazoline adducts were obtained from the photolysis and from dehydrochlorination of N-(α-chlorobenzylidene)-N′-phenylhydrazine. Fragmentation to phenylnitrilimine and nitrogen has been proposed by Scheiner[3e] as the major reaction during the photolysis of 5-phenyltetrazole. In contrast, the

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[1] The major part of this paper is taken from the Ph.D. Thesis of K. E. Haque, University of Ottawa, Dec 1966.

[2] For a brief review of reactions to the end of 1967, see *Ann. Rept. Progr. Chem.*, *B*, **64**, 191, (1967).

[3] (a) J. S. Clovis, A. Eckell, R. Huisgen, and R. Sustmann, *Chem. Ber.*, **100**, 60 (1967); (b) R. M. Moriarty, J. M. Kliegman, and C. Shovlin, *J. Amer. Chem. Soc.*, **89**, 5958 (1967); (c) R. M. Moriarty and J. M. Kliegman, *ibid.*, **89**, 5959 (1967); (d) W. Kirmse, *Angew. Chem.*, **71**, 537 (1959); (e) P. Scheiner, *J. Org. Chem.*, **34**, 199 (1969).

[4] The Ph.D. thesis of K. E. H. also includes a study of the photolysis of 5-phenyltetrazole. Since our findings on the latter topic agree with those reported by Scheiner,[3e] we will confine our discussion to the photolytic behavior of 2-methyl-5-phenyltetrazole.

[5] A number of recent papers describe the photolysis of 1,2,3-triazoles, none of which shows similarity to the photoreactions reported herein. These include (a) E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, **90**, 1923 (1968); (b) T. S. Cantrell and W. S. Haller, *Chem. Commun.*, 977 (1968); (c) J. H. Boyer and R. Selvarajan, *Tetrahedron Lett.*, 47 (1969).

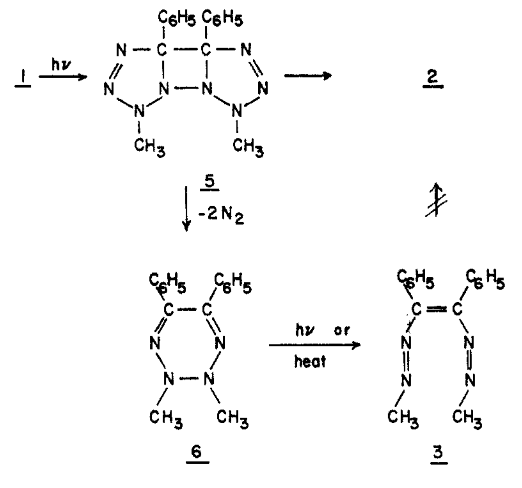
evidence below fails to support N-methyl-C-phenylnitrilimine as an intermediate in the photolysis of **1**.

It has been observed that, when diphenylnitrilimine or either of the isomeric phenylmethylnitrilimines add to benzonitrile, a 1,2,4-triazole is produced.[6] That **2** cannot have been formed indirectly from **4** was established by the observation that **4** was stable under the irradiation conditions. The alternate possibility that the observed thermal decomposition of 2-methyl-5-phenyltetrazole produces **2** first, which then rearranges thermally to **4**, was also ruled out when **2** was observed to be stable when heated to 220° for 6 hr, the conditions under which **4** is formed from **1**.

An attempt to trap any nitrilimine by using an excess of benzonitrile during the photolysis of **1** failed, the yield of products being unchanged. Since dimerization of diphenylnitrilimine has been found to produce the head-to-tail dimer 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine,[7] it is unlikely that **3** has resulted from nitrilimine dimerization. Both facts indicate that the photolysis of 2-methyl-5-phenyltetrazole does not involve N-methyl-C-phenylnitrilimine as an intermediate.

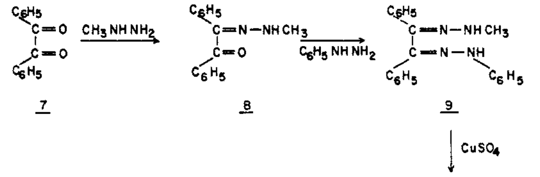
The mechanism by which **2** is formed merits consideration. Since 2 mol of **1** are required for the formation of **2**, a dimer would be a plausible intermediate.[8] Photodimerizations of aromatic heterocyclic compounds are well known and have involved 2 + 2 cycloadditions in the cases of thymine and uracil[9] and 4 + 4 cycloadditions in the dimerization of pyridones.[10] A tetrazole dimer may possibly have been formed in the photolysis of dimethyl diazidomalonate.[3b] In the photolysis of **1**, a 2 + 2 cycloaddition could produce a dimer having the head-to-head structure **5**, as shown in eq 2. Subsequently, this dimer would undergo fragmentation, losing methyl azide and nitrogen to form **2**. Intermediate **5** can also serve as the precursor of **3**. Loss of two nitrogen molecules would form the dihydrotetrazine **6**. A concerted electrocyclic rearrangement of **6** would result in its stereospecific conversion into **3**.[11] The possibility that **3** might be a precursor of **2** is ruled out by our observations that **3** is inert to the photolysis conditions and also to heating to its melting point. The remaining identified product, **4**, may have been produced from either a nitrilimine or a head-to-tail dimer. Although we have been unable to obtain evidence for the production of nitrilimine, we cannot rule out the alternative possibility that the nitrilimine is formed first and adds to a molecule of tetrazole, and the resultant adduct loses methyl azide, forming **2**.

(2)



Synthesis and Spectral Properties of 2.—The proof of structure of **2** was provided by its synthesis using the unambiguous route shown, eq 3. Benzil was converted into its monomethylhydrazone **8**, then by reaction with phenyl hydrazine into the mixed osazone **9**. This compound was not isolable, but oxidation of the crude reaction product with cupric sulfate followed by chromatographic separation gave the pure triazole **2** in a 2% yield from **8**. This latter oxidation step is a well-known method for the synthesis of osotriazoles.[14] The poor yield in the synthesis of **2** points to the photochemical method as the only practical one for its synthesis.

(3)



The nmr spectrum of **2** showed absorption at τ 2.3–2.7 (10 H) and 5.75 (3 H). It is interesting to note that the deshielding effect of a heterocyclic nitrogen atom on the *ortho* protons of an adjacent phenyl group is not observed in **2** but is present in one of the phenyl groups of **4**, whose nmr showed a two-proton multiplet at τ 1.8. This contrasting behavior is entirely normal, since deshielding has been observed in heterocyclics bearing a phenyl group only when the phenyl and heterocyclic rings can attain coplanarity.[15]

The mass spectra of **2** and its isomer **4** are both consistent with the assigned structures. Fragmentation patterns similar to those exhibited by tetrazoles occur,[15] and they are not significantly dependent upon isomeric constitution.

Structural Assignment of 3.—From the spectral characteristics of the red solid, **3**, given in the Experimental Section, a logical structure can be assigned. The empirical formula $C_{15}H_{16}N_4$ is established by elemental analysis and the parent and parent + 1 peak ratios in its mass spectrum. The nmr spectrum of **3** shows absorption for ten aromatic protons and for two N-methyl groups in different magnetic environments. These facts alone indicate **3** to be an asymmetrical dimer of C-phenyl-N-methylnitrilimine. The elec-

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(6) R. Huisgen, R. Grashey, M. Seidel, G. Wallbillich, N. Knupfer, and R. Schmidt, *Ann.*, **563**, 105 (1962).

(7) R. Huisgen, J. Sauer, and M. Seidel, *Chem. Ber.*, **94**, 2503 (1961).

(8) D. G. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967, p 100, points out that the lack of a concentration dependence in the yield of product does not eliminate the possibility of a dimeric intermediate.

(9) H. Isihara and S. Y. Wang, *Nature*, **210**, 1222 (1966).

(10) (a) W. A. Ayer, R. Hayatsu, P. De Mayo, S. T. Reid, and J. B. Stothers, *Tetrahedron Lett.*, 648 (1961); (b) G. Slomp, F. A. MacKellar, and L. A. Paquette, *J. Amer. Chem. Soc.*, **83**, 4472 (1961); (c) E. C. Taylor, R. O. Kan, and W. W. Paudler, *ibid.*, **83**, 4484 (1961).

(11) The ring opening of a cyclohexadiene to a hexatriene is thermally disrotatory[12] and photochemically conrotatory.[13] It is not obvious that the dihydrotetrazine can be considered isoelectronic with cyclohexadiene; nor are the conformations of the methyl groups known. It can be said, however, that an electrolyclic rearrangement would be expected to be stereospecific.[13]

(12) R. J. de Hock, N. G. Minard, and E. Havinga, *Rec. Trav. Chim. Pay-Bas*, **79**, 922 (1960).

(13) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(14) H. E. Khadem, *Advan. Carbohyd. Chem.*, **18**, 99 (1963).

(15) R. R. Fraser and K. E. Haque, *Can. J. Chem.*, **46**, 2855 (1968).

tronic spectrum and red color indicate the presence of an extensively conjugated chromophore. The bisazoethylene structure **3** possesses all the requirements of the above data. Furthermore, there is an authentic example in the literature[16] of a red compound having a bisazoethylene structure. The compound, 1,2-di(triphenylmethylazo)-1,2-diphenylethylene, possesses an absorption at 450 mμ (ε 560) with shoulders at 317 mμ (ε 8600) and 257 (14,000). This similarity to the uv of **3** [394 mμ (ε 932), 302 (3760), and 235 (18,500)], bearing in mind that differences due to *cis–trans* isomerism are likely, supports the assigned structure. Curtin and coworkers point out that certain structural ambiguities remain, one possibility being that it is a mixture of triene and its vicinal dihydrotetrazine tautomer. In the case of **3**, our nmr evidence excludes the presence of tautomeric **6**. Evidence on the configuration about the carbon–carbon double bond of **3** is not available, but a *cis* configuration is considered likely because of the previously proposed origin of **3** from **6** by a stereospecific electrocyclic reaction.

Experimental Section[17]

Photolysis of 2-Methyl-5-Phenyltetrazole (1) in Benzene.—A solution of 3.01 g (0.0188 mol) of 2-methyl-5-phenyltetrazole in 100 ml of benzene (B. D. H., Anlar) was photolyzed for 3 hr in a reaction vessel in which was immersed a quartz-enclosed, water-cooled Hanovia 679A36 450-W medium-pressure mercury arc lamp with a Vycor 7910 filter. The solution was purged with nitrogen prior to photolysis and a flow of nitrogen was maintained during the reaction.

The volume of the crude product was reduced to about 10 ml by distillation *in vacuo* and the resulting reddish brown liquid was chromatographed on 200 g of silica gel (Mallinckrodt SilicAR CC-7, 200–325 mesh) with benzene as eluent. The total weight of the fractions collected was 1.756 g. The first fraction eluted (0.2 g) was composed of at least two products (tlc). The next fraction (0.9646 g) contained a mixture of starting tetrazole and 2-methyl-4,5-diphenyl-1,2,3-triazole (**2**). Separation of these two compounds was achieved by chromatography of the mixture on 100 g of alumina (E. Merkag, aluminum oxide G) with 20% diethyl ether in petroleum ether (bp 30–60°) as initial eluent and, after 1 l. of eluate had been collected, gradual increase of the concentration of the diethyl ether to 100%. The alumina chromatogram yielded 0.294 g of 2-methyl-5-phenyltetrazole (**1**) and 0.538 g (27.1%) of 2-methyl-4,5-diphenyl-1,2,3-triazole (**2**): mp 61.5–63°; ir ($CHCl_3$) 3040 (sh), 3020, 2960, 1460, 1443, 1438 (sh), 1373, 1013, and 989 cm^{-1}; mass spectrum *m/e* (rel intensity) 236 (20), 235 (100), 220 (5.1), 192 (8.8), 132 (8.1), 131 (11.1), 89 (8.4), and 77 (11.8); uv λ_{max}^{EtOH} 257 mμ (ε 13,000); nmr ($CDCl_3$) τ 2.48 (m, 4 H), 2.67 (m, 6 H), and 5.75 (s, 3 H).

Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.6; H, 5.6; N, 17.9. Found: C, 76.3; H, 5.8; N, 18.1.

From the later fractions of the silica gel chromatogram, 0.154 g of a red solid, **3**, was obtained. After recrystallization from benzene, **3** had mp 150.5–151.5°; ir ($CHCl_3$) 3070, 2795–2925, 1647, 1578, 1498, 1447, and 1348 cm^{-1}; mass spectrum *m/e* (rel intensity) 265 (18.8), 264 (100), 263 (13), 250 (11.5), 249 (61.8), 132 (12.5), 118 (60), 103 (25), 77 (52.5), 76 (13.7), and 51 (13.7); uv–visible $\lambda_{max}^{CH_3OH}$ 235 mμ (ε 18,500), 302 (3760), and 394 (932); nmr ($CDCl_3$) τ 2.50 (m, 10 H), 6.86 (s, 3 H), and 7.10 (s, 3 H).

Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.7; H, 6.1; N, 21.2. Found: C, 72.6; H, 5.9; N, 21.3.

In addition to the above new compounds, several other products were eluted from the silica gel chromatogram. The only other indentifiable product obtained was 0.086 g (4.3%) of 1-methyl-3,5-diphenyl-1,2,4-triazole (**4**), mp 86.0–87.0° (lit.[18] mp 84–85°). The remaining products could not be isolated in pure form by further chromatographic procedures.

Similar chromatographic procedures were used for isolation of products from the 0.09 *M* run in benzene and the 0.21 *M* run in dioxane.

Synthesis of 2-Methyl-4,5-diphenyl-1,2,3-triazole (2).—A mixture of 0.5 g (2.1 mmol) of benzil monomethylhydrazone[19] (**8**), 0.2 g (1.9 mmol) of phenylhydrazine, and 2 drops of glacial acetic acid was heated in a sealed tube at 130° for 2 hr. The gummy product from six such tubes was dissolved in 75 ml of dioxane. A solution of 3.0 g of cupric sulfate[20] in 75 ml of water was added and the resultant solution was heated under reflux for 90 min. The solvent was then distilled off and the residue was extracted with ether. The neutral portion of this extract amounted to 2.5 g and according to its thin layer chromatogram contained many compounds. After attempted purification by thick layer chromatography, the remaining material (1.7 g) was subjected to column chromatography on neutral alumina, activity II. Elution with 600 ml of petroleum ether (bp 30–60°) gave 100 mg of carbonyl compounds. Then, using petroleum ether containing 10% benzene, the next 200 ml of eluate gave 50 mg of a solid, whose infrared, nmr, and mass spectra were identical with those obtained from **2** produced by photolysis of **1**.

Thermal Stability of 2.—A sealed capillary containing 30 mg of **2** was heated at 220–225° for 6 hr; at the end of this period, the melting point, infrared spectrum, and ultraviolet spectrum of the solid were unchanged.

Synthesis of 1-Methyl-3,5-diphenyl-1,2,4-triazole (4).—The triazole **4** was prepared by the methylation[18] of 3,5-diphenyl-1,2,4-triazole.[21] The product was a solid, mp 83–85°, whose ultraviolet spectrum had λ_{max} 247 mμ (ε 18,700). The nmr spectrum of **4** in deuterochloroform showed multiplets centered at τ 1.85 (2H) and 2.51 (8 H) and a sharp singlet at τ 6.10 (3 H).

Photolysis of 4.—A 0.1 *M* solution of **4** in dioxane was photolyzed for 3 hr. The triazole **4** was then recovered unchanged in 90% yield.

Attempted Synthesis of 3.—The synthesis of **3** *via* oxidation of benzil bismethylhydrazone gave a complex mixture of products from which no **3** could be obtained. Benzaldehyde methyl hydrazone was converted by an oxidative coupling[22] to 1,2-diphenyl-1,2-bismethylazoethane, but this compound also failed to yield **3** on oxidation with a variety of reagents. The difficulty is believed to be a result of the sensitivity of **3** to both base and acid. All attempts to reduce **3** to its hexahydro derivative, either catalytically, with diimide, or with tin or zinc, gave intractable mixtures. Lithium aluminum hydride reduction of **3** failed to give a dihydro derivative.[16]

Registry No.—**1**, 20743-49-1; **2**, 21690-97-1; **3**, 21690-98-2.

Acknowledgment.—The authors thank the National Research Council of Canada for their financial support. The technical assistance of Mrs. E. Sano is appreciated. We are also grateful for some very constructive comments by both referees.

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[16] D. Y. Curtin, R. J. Crawford, and D. K. Wedegaertner, *J. Org. Chem.*, **27**, 4300 (1962).

[17] All melting points are corrected. Infrared spectra were measured on a Beckman IR-8 spectrometer. Ultraviolet and visible spectra were measured on a Perkin-Elmer ultraviolet–visible spectrophotometer, Model 202. Nmr spectra were measured on either an HA-60 or an HA-100 spectrometer, using internal tetramethylsilane as reference. Mass spectra were recorded using an Hitachi Perkin-Elmer RMU-6D instrument with an ionization voltage of 70 eV.

[18] M. R. Atkinson, J. B. Polya, and E. A. Parkes, *J. Chem. Soc.*, 4257 (1954).

[19] D. Cardwell and M. O. Forster, *ibid.*, 868 (1913).

[20] Prepared as reported by H. E. Khadem, *ibid.*, 3155 (1962).

[21] H. Wolchowe, *Monatsch. Chem.*, **37**, 475 (1916).

[22] T. W. Mulligan and B. C. Minor, *J. Org. Chem.*, **27**, 4663 (1962).