Anal. Calcd for $C_9H_9O_2F_3$: C, 52.43; H, 4.40. Found: C, 53.48; H, 4.61.

The *endo* isomer of the trifluoroacetate (**13b**) was obtained by preparative glpc at 52–57° of 25-μl injections of the *exo,endo* mixture on a 10 ft × 0.25 in. 20% diethylene glycol succinate column with Chromosorb P (60–80 mesh) as the solid support.

Anal. Calcd for $C_9H_9O_2F_3$: C, 52.43; H, 4.40. Found: C, 52.94; H, 4.48.

This procedure also gave the *exo* isomer (**17b**).

Anal. Calcd for $C_9H_9O_2F_3$: C, 52.43; H, 4.40. Found: C, 53.03; H, 4.49.

F. ***endo*-2-Hydroxy-*exo*-2-methylbicyclo[2.2.1]hept-5-ene.**—Bicyclo[2.2.1]hept-5-en-2-one was prepared by oxidation of the corresponding carbinol by the method of Toivonen and Kaila[38] and through the hydrolysis of 2-cyano-2-acetoxybicyclo[2.2.1]-hept-5-ene by the method of Bartlett and Tate.[39] The latter precursor was prepared from α-acetoxyacrylonitrile and cyclopentadiene.[39] Addition of methylmagnesium iodide from 2.39 g of Mg (0.983 g-atom) and 5.6 ml of methyl iodide (0.090 mol) to this ketone was carried out by a modification of a method already described.[40] The Grignard reagent in 125 ml of dry diethyl ether was added dropwise with stirring to a solution of 6.03 g of bicyclo[2.2.1]hept-5-en-2-one (0.0558 mol) in 40 ml of anhydrous ether. The reaction mixture was stirred for 3 hr. To the reaction mixture was added 23 ml of saturated ammonium chloride solution. The reaction mixture was stirred an additional 15 min. The ether solution was dried over sodium sulfate, then distilled under reduced pressure using a short-path setup, giving 4.96 g (0.0399 mol, 71.5%) of the desired product, a clear and colorless liquid: bp 69.0° (15 mm); ir (10% CCl_4), 3596 (OH, m, sharp) and 3476 (w, broad) cm^{-1} [lit.[41,42] 3591 and 3610 (shoulder) for 0.005 *M* in CCl_4]; nmr (CCl_4), δ 6.21 (m, 2.00, CH=CH), 2.76 and 2.57 (broad, 2.17), remaining upfield absorptions (m, 8.36, including CH_3) at 1.43 [lit.[43] δ 6.26 (m, CH=CH), 2.82 and 2.63 (broad), 1.49 (s, CH_3)].

G. ***endo*-2-Benzoyloxy-*exo*-2-methylbicyclo[2.2.1]hept-5-ene (13c).**—To a solution of 1.00 g of *endo*-2-hydroxy-*exo*-2-methylbicyclo[2.2.1]hept-5-ene (0.00809 mol) in 20 ml of dry tetrahydrofuran approximately 5 ml of 1.6 *M* *n*-butyllithium (Foote Mineral Co.) (0.008 mol) was added dropwise with stirring. The solution was boiled under a nitrogen atmosphere for 25 hr. To the boiling solution was added dropwise 0.95 ml of freshly distilled benzoyl chloride (0.0083 mol). The reaction mixture was allowed to cool to room temperature and was filtered by suction. The tetrahydrofuran soluble residue was triturated with 20 ml of dry pentane and the resulting mixture filtered by means of suction. The filtrate was washed twice with 20-ml portions of water and dried over sodium sulfate. The pentane soluble residue was purified by chromatography, on silica gel with benzene eluent, to give the desired benzoate (1.16 g, 0.00508 mol, 63%), a pale yellow, clear, viscous liquid: nmr (CCl_4,) δ 7.60 (m, 4.95, aromatic CH), 6.11 (m, 1.95, CH=CH), 3.33 (broad, 1.00, bridgehead CH), 2.82 (broad, 1.03, bridgehead CH), 1.79 (s, 4.76, CH_3 plus some CH_2 absorption), 1.52 (m, 2.38, remaining CH_2 absorption).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 78.92; H, 7.04.

Registry No.—12, 21902-82-9; **13a**, 2890-95-1; **13b**, 21902-83-0; **13c**, 21927-68-4; **16a**, 21902-84-1; **16b**, 21902-85-2; **16c**, 21902-86-3; **17a**, 21902-87-4; **17b**, 21902-88-5.

Acknowledgment.—This work was supported in part by Grant GM-12296 from the U. S. Public Health Service.

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Substituent Effects in the Pyrolysis of Aryl *n*-Propyl Sulfoxides

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The rates of propene formation in the thermal decomposition of phenyl *n*-propyl, *p*-chlorophenyl *n*-propyl, *p*-tolyl *n*-propyl, *p*-methoxyphenyl *n*-propyl, and *p*-nitrophenyl *n*-propyl sulfoxides in phenyl ether solution were measured. Propene formation obeys a first-order rate equation. Activation enthalpies and entropies were in the range of 25 to 28 kcal mol^{-1} and -11.5 to -16 cal deg^{-1} mol^{-1}, respectively. The electron-withdrawing *para* substituents chloro and nitro increased the rate, while methyl and methoxyl decreased the rate. The rates are correlated by a Hammett plot giving $\rho = 0.51$, $r = 0.995$. The results suggest a highly ordered, probably cyclic, transition state with a fractional negative charge developing on the sulfur-containing moiety and a fractional positive charge developing on the propyl group.

Sulfoxides with at least one alkyl group having a hydrogen atom attached to the β-carbon atom suffer thermal decomposition to yield alkenes[1] and sulfenic acids which can be trapped[1m] or which can decompose to form a variety of sulfur containing products.[1e] The mechanistic view that the reaction is a *cis* elimination involving a cyclic quasi five-membered-ring transition state has served to reconcile most of the experimental findings. The observation that unsymmetrical dialkyl sulfoxides preferentially eliminate alkenes derived from the alkyl groups more highly substituted on the α carbon atom[1f] prompted us to explore further aspects of the reaction. In view of the observation that a radical pair may be involved in the decomposition of some sulfoxides,[1a] it was deemed profitable to study the rates of decomposition of members of a series of *para*-substituted phenyl *n*-propyl sulfoxides in which propene was always eliminated so that the effects of substituents on the rates could be assessed. The results of this study are reported herein.

Results and Discussion

Either radical intermediates or a transition state in which the carbon atom becoming separated from sulfur is developing some positive character could account for

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TABLE I
RATE OF FORMATION OF PROPENE IN PYROLYSIS OF ARYL n-PROPYL SULFOXIDES

$\Delta H^\ddagger$	$\Delta S^\ddagger$	Ar in ArS(O)-$CH_2CH_2CH_3$	$k_1 \times 10^4$ sec^{-1} (yield,[a] %) 190.0°	185.0	180.0°	175.0°	170.0°	165.0	160.0°
25.9 ± 1.9	−15.1 ± 6.4	C_6H_5		21.7 ± 0.4[b] (76)	15.6 ± 0.9 (78 ± 4)	11.3 ± 0.8 (75 ± 6)	8.0 ± 0.7 (75 ± 4)		
27.2 ± 2.3	−12.6 ± 7.3	p-$CH_3C_6H_4$	25.1 ± 1.4[b] (80)	18.5 ± 0.3 (81 ± 2)	12.2 ± 0.2 (77 ± 3)	9.2 ± 0.2 (74 ± 5)	6.5[c]		
25.3 ± 2.6	−16.0 ± 8.2	p-ClC_6H_4			17.8 ± 0.5 (77 ± 0.2)	13.4 ± 1.4 (74 ± 6)	9.2 ± 0.5 (75 ± 2)	6.7 ± 0.4 (76)	
25.5 ± 1.5	−14.3 ± 4.8	p-$O_2NC_6H_4$			35.5[c]	26.5 ± 0.4 (86 ± 3)	18.1 ± 1.4 (84 ± 2)	13.1 ± 0.9 (83 ± 1)	9.4 ± 0.3 (79)
27.9 ± 2.1	−11.5 ± 6.7	p-$CH_3OC_6H_4$	20.4 ± 1.3 (69 ± 2)	14.5 ± 1.0 (71 ± 1)	10.1 ± 0.2[b] (71)	7.2 ± 0.5 (72 ± 6)	5.0 ± 0.2[b] (66)		

[a] Mole per cent basis sulfoxide. [b] One run. [c] Extrapolated.

rate enhancement when the sulfoxide is one in which the α-carbon atom is branched by one or more alkyl groups. The approach of varying the substituent on the phenyl group of *para*-substituted phenyl n-propyl sulfoxides should give needed insight into this reaction as it has in the case of the pyrolysis of alkyl benzoates.[2] Those studies showed that electron-attracting substituents increased the rate, and electron-releasing substituents decreased the rate of olefin formation suggesting some degree of ionic character in the transition state. The effect of substituents on reactions involving radical intermediates is less clear-cut. For example, in the decomposition of *para*-substituted benzoyl peroxides, electron-donating groups increased the rate while electron-withdrawing groups produced little change in the rate compared with benzoyl peroxide itself.[3a,b] In the decomposition of t-butyl phenylperacetates, electron-donating *para* substituents accelerated the reaction and electron-withdrawing *para* substituents slowed the reaction.[3c]

The results of the present investigation are given in Table I. The sulfoxides, in phenyl ether solution, were allowed to decompose and the progress of the reaction was followed by measuring the quantity of propene produced. The reaction is first order in the appearance of propene and the rate constant does not vary appreciably with concentration (Table II). The effect of the substituents was not large but was in the direction of increased rates with the electron-withdrawing substituents, chloro and nitro, and decreased rates with the electron-withdrawing substituents, methyl and methoxyl. The effects of this group of *para* substituents on the rate of propene formation from the substituted phenyl n-propyl sulfoxides is seen to resemble the effects that the substituents have on the acidities of benzoic acids[4] and the rate of thermal decomposition of alkyl benzoates.[2] The same substituents produced quite different effects on the rates of decomposition of benzoyl peroxides,[3b] for which a satisfactory Hammett plot was not obtained, or the decomposition of t-butyl phenylperacetates[3c] for which the Hammett plot gave a negative ρ. A plot of log k_1 *vs.* σ[5] for our data gives a reasonable correlation (Figure 1) with $\rho = 0.51$, $r = 0.995$. A slightly better correlation is obtained ($\rho = 0.29$, $r = 0.999$) using σ^+ for methyl and methoxyl, σ for chloro, and σ^- for nitro.[6]

TABLE II
RATES OF PROPENE FORMATION AT DIFFERENT CONCENTRATIONS[a]

Ar in ArS(O)-$CH_2CH_2CH_3$	Concn, mol l.$^{-1}$	$k_1 \times 10^4$ sec^{-1} 185.0°	180.0°	175.0°	170.0°	Yield,[b] %
C_6H_5	0.187		15.0			77
	0.214		16.2			82
	0.416		15.9			78
	0.725		15.5			76
p-$CH_3C_6H_4$	0.178	18.4				83
	0.224	18.5				80
	0.785	18.7				79
p-ClC_6H_4	0.164			13.1		78
	0.209			14.2		68
	0.420			13.4		78
	0.712			12.3		77
p-$O_2NC_6H_4$	0.155				18.9	85
	0.205				17.9	83
	0.448				18.5	83
	0.694				17.0	84
p-$CH_3OC_6H_4$	0.187	13.9				70
	0.273	13.8				72
	0.792	15.9				72

[a] $k_1 \times 10^4$ sec^{-1}. [b] Mole per cent basis sulfoxide.

The enthalpies of activation are in the range of 25 to 28 kcal mol^{-1} and the entropies of activation range from −11.5 to −16 cal deg^{-1} mol^{-1}. The enthalpies are too small to suggest ionic intermediates and the entropies suggest a highly ordered, probably cyclic, transition state. The pK_a's of the conjugate acids of several aryl methyl sulfoxides have been measured and substantial differences in the basicities of the sulfoxide oxygens were seen to exist.[7] These differences in oxygen basicities do not serve to explain our results, however. If the reasonable assumption were made that the more basic oxygens would more readily abstract β hydrogens from the propyl group, just the opposite rate effects would be seen.

Recent studies of the racemization of optically active sulfoxides have shown[8] that a radical mechanism intervenes when one of the groups attached to sulfur can form a benzylic radical. Otherwise, pyramidal inversion occurs, but at higher temperatures (180–210°) for rates which are at least an order of magnitude smaller than those at which the phenyl n-propyl sulfoxides decomposed. The apparently authentic cases of thermolysis of sulfoxides to yield alkenes proceeding by way

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[2] (a) G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, **28**, 403 (1963). (b) G. G. Smith and D. A. K. Jones, *ibid.*, **28**, 3496 (1963).

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[6] The use of σ^+ and σ^- to correlate a body of data has been employed: H. H. Jaffé, *J. Org. Chem.*, **23**, 1790 (1958).

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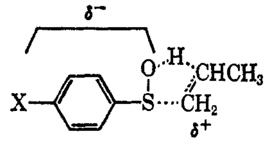
[8] (a) D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4854 (1968). (b) E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *ibid.*, **90**, 4861 (1968).

of radical-pair intermediates were those involving the diastereomeric 1,2-diphenyl-1-propyl sulfoxides in which a substituted benzyl radical could readily be formed.[1a] In the absence of special structural features of this sort, sulfoxides appear to decompose by a concerted cyclic pathway as previously asserted,[1a] and I appears as a reasonable depiction of the transition state.



I

Experimental Section

Materials Used.—Benzenethiol (Eastman), *p*-toluenethiol (Eastman, mp 41–43°), *p*-chlorobenzenethiol (Aldrich, mp 51–53°), and *p*-nitrobenzenethiol (Aldrich) were used as received. *p*-Methoxybenzenethiol was prepared from *p*-methoxybenzenesulfonyl chloride (mp 38.6°, lit.[9] 41–42°) using an adaptation of the method of Gilman and Broadbent.[10] The thiol was obtained in 36% yield basis anisole, bp 74.5–75° (1.9 mm), lit.[11] 88–90° (5 mm). *n*-Propyl bromide (Mallinkrodt) was distilled using an 18-cm column packed with glass helices and the fraction boiling at 70.5° (749 mm) was retained. *n*-Hexane (Phillips 99%) was used as received. Phenyl ether (Eastman) was dried over calcium hydride and distilled through an 18-cm column packed with glass helices. A heart cut of bp 70° (0.15 mm) was retained.

Preparation of the Sulfides.—The sulfides were prepared by mixing, in 95% ethanol, equimolar portions of the appropriate thiol, 50% sodium hydroxide, and *n*-propyl bromide. The reaction mixtures were diluted with water; the sulfides were extracted with hexane, dried ($CaCl_2$), and distilled through an 18-cm column packed with glass helices. No attempt was made to distill *p*-nitrophenyl *n*-propyl sulfide. The pertinent data for the sulfides are reported in Table III.

Table III

Properties of $ArSCH_2CH_2CH_3$ and $ArS(O)CH_2CH_2CH_3$

Sulfide, Ar	Bp, °C[a] (mm) Lit.	Bp, °C[a] (mm) Found	$n^{25}D$ Lit.	$n^{25}D$ Found	Yield, mol %	Ref
C_6H_5	117–118 (15)	61.8 (1.2)	1.5526	1.5516	83	*b,c*
p-$CH_3C_6H_4$	55.6 (0.8)	73.6 (1.1)		1.5452	79	*d*
p-ClC_6H_4	108–109 (7)	87–88 (1.3)	1.5701 (20)	1.5663	84	*e*
p-$O_2NC_6H_4$	Dec			1.6249	63	*f*
p-$CH_3OC_6H_4$	110–111 (5)	81–82 (0.3)	1.5545	1.5509	75	*g*

Sulfoxide, Ar	Bp, °C (mm), or mp[a] Lit.	Bp, °C (mm), or mp[a] Found	$n^{25}D$	Yield, mol %
C_6H_5	102–103[h] (0.01)	90 (0.1)	1.5581	68
p-$CH_3C_6H_4$			1.5488	66
p-ClC_6H_4			1.5673	54
p-$O_2NC_6H_4$		47–48.5		12
p-$CH_3OC_6H_4$			1.5569	45

[a] Boiling points are uncorrected, melting points are corrected. [b] G. Modena, *Gazz. Chim. Ital.*, **89**, 834 (1959). [c] R. D. Obolentsev, N. G. Marina, and L. V. Vafina, *Khim. Seraorgan. Soedin, Soderzhásch, v Neft, i Nefteprod., Akad. Nauk SSSR, Bashkirsk. Filial*, 6, 220 (1964). [d] J. Gasparič, M. Večeřa, and M. Jureček, *Chem. Listy*, **52**, 1720 (1958). [e] A. M. Kuliev and F. I. Gasanov, *Azerb. Khim. Zh.*, 48 (1967). [f] W. R. Waldron and E. E. Reid, *J. Amer. Chem. Soc.*, **45**, 2399 (1923). [g] Reference 11. [h] A. Cerniani, G. Modena, and P. E. Todesco, *Gazz. Chim. Ital.*, **90**, 3 (1960).

Preparation of the Sulfoxides.—Equimolar portions of the sulfides and 30% hydrogen peroxide were mixed in *t*-butyl alcohol and the mixtures were allowed to stand for several days.[1b] The solvent was then evaporated in a stream of air. Phenyl *n*-propyl sulfoxide was distilled. *p*-Nitrophenyl *n*-propyl sulfoxide was recrystallized from a mixture of cyclohexane and ethyl acetate. The other sulfoxides were treated with anhydrous cupric chloride or anhydrous cobaltous chloride, in the ratio of 0.5 mol of metal salt/1 mol of sulfoxide. Semisolid complexes formed[12] which were washed repeatedly with benzene–hexane or ether–hexane mixtures. The complexes were decomposed by stirring them with water. The sulfoxides were then extracted with methylene chloride or ether and the extracts were decolorized (carbon) and dried (Na_2SO_4). The solvent was removed by evaporation at 0.7–0.35 mm for 16 hr. The sulfoxides were mixed with 2 g of Grade I 60/80 mesh chromatographic alumina (Fisher), filtered in a dry atmosphere, and stored in a desiccator. The properties of the sulfoxides are given in Table III. Satisfactory analyses for carbon, hydrogen, and heteroatoms (±0.3%) were obtained.[13]

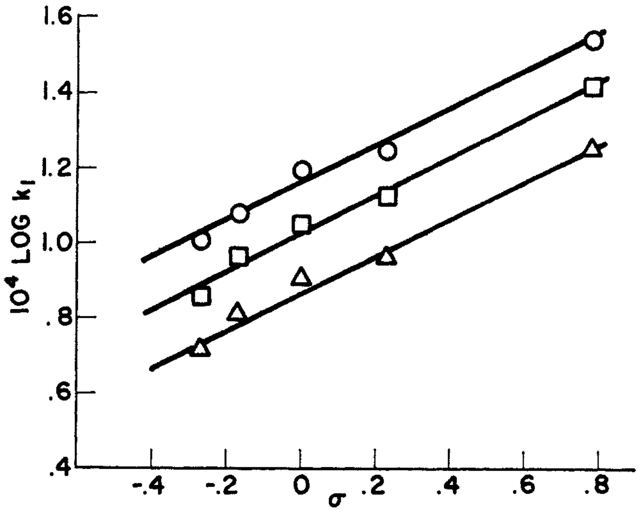


Figure 1.—Propene formation from *p*-$XC_6H_4S(O)CH_2CH_2CH_3$. Correlation of rate constants with substituent constants: ○, 180°; □, 175°; △, 170°.

General Procedure for the Decomposition of Sulfoxides.—The reaction vessel was a round-bottomed Pyrex flask of approximately 15-ml capacity, 14 cm long, topped by the socket of a 18/9 ball and socket joint. The ball part of the joint was connected to a section of 12-mm glass tubing packed with a mixture of anhydrous calcium sulfate and Ascarite to absorb water vapor and acidic gases, respectively. This tube was connected to the gas collecting and measuring part of the apparatus.[1f] During runs the bulb and about two-thirds of the neck of the reaction flask was immersed in a vigorously stirred, thermostated oil bath controlled to ±0.1°. Temperature was monitored using a copper–constantan thermocouple immersed in the bath and connected to a potentiometer. Time was measured with an electric timer. The bulb of the reactor was charged with 10.2 g of either 3-mm or 4-mm KiMAX beads (the bead size had no influence on the rate) and an appropriate quantity of phenyl ether. Pure grade propene was bubbled through the phenyl ether in the reactor at room temperature to insure saturation of the solvent with propene. The water in the gas collecting bottle was also saturated with propene prior to making runs. The ball and socket joint was connected and the reactor was placed in the oil bath to equilibrate for 15 min. Runs were initiated by opening the ball joint, adding the sulfoxide with a hypodermic syringe, shaking the reactor to mix the sulfoxide and solvent, placing a small wad of cotton in the neck of the reactor at the oil bath level, reconnecting the ball joint, and reading the water level in the 50-ml graduated cylinder of the gas measuring part of the apparatus. The quantity of sulfoxide introduced was measured by weighing the syringe before and after addition of the sulfoxide. *p*-Nitrophenyl *n*-propyl sulfoxide was introduced as a 50% by weight solution in phenyl ether. Readings of gas volume as a function of time were started after 4–7 ml of gas had been collected, a sufficient time for the reactor contents to come to bath temperature. Readings were continued for 6–8 half-lives, longer times

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(9) M. S. Morgan and L. H. Cretcher, *J. Amer. Chem. Soc.*, **70**, 375 (1948).

(10) H. Gilman and H. S. Broadbent, *ibid.*, **69**, 2053 (1947).

(11) C. M. Suter and H. L. Hansen, *ibid.*, **54**, 4100 (1932).

(12) F. A. Cotton and R. Francis, *ibid.*, **82**, 2986 (1960).

(13) Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

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.

Acknowledgments.—We are indebted to Professor R. A. Potts for advice on purification of sulfoxides by complexation, to Professor A. R. Emery for advice on various aspects of computing, to The University of Michigan Dearborn Campus for funds to pay for materials and microanalyses, to The University of Michigan Computing Center for computer time, and to Professor M. Stiles for a penetrating and stimulating discussion.

The Photolysis of 2-Methyl-5-Phenyltetrazole

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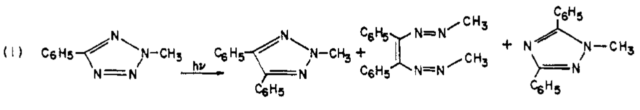
The photolysis of 2-methyl-5-phenyltetrazole has been found to produce 2-methyl-4,5-diphenyl-1,2,3-triazole (**2**) in 22–27% yield and 1,2-di(methylazo)-1,2-diphenylethylene (**3**) in 6–10% yield. In contrast to previous studies on the photolytic behavior of tetrazoles, no evidence of production of 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 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).