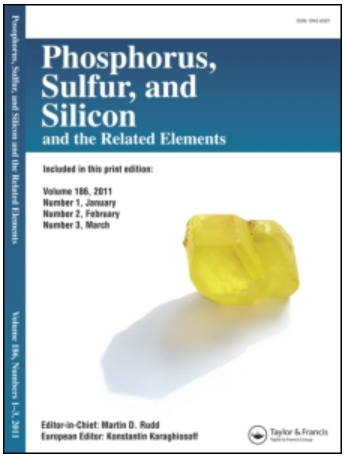

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SULFENAMIDES AND SULFINAMIDES IV. HOMOLYSIS OF SULFENAMIDES IN CYCLOHEXENE

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The photocatalysed decomposition of aromatic sulfenamides in cyclohexene is a rapid reaction at ambient temperature. Products fall into two main groups resulting from recombination of initially formed radicals and from intervention of solvent acting as a radical trap.

Key words: Aromatic sulfenamides; photolysis; homolysis; free-radicals

INTRODUCTION

Although sulfenamides were first described over 60 years ago[1,2] and have been of interest in several different fields, probably their most sustained application has been to the vulcanization of rubber as delayed action accelerators where usage depends on homolysis of the S—N bond at high temperatures. It has been emphasised that sulfenamides and other sulfur-bearing accelerators are virtually inactive below 100°C because of the high thermal stability of the S—N bonds.[3]

However, sulfenamides are very sensitive to light and undergo rapid, quantitative exchange at room temperature according to the expression

$$RSNHR + R'SNHR' \rightleftharpoons RSNHR' + R'SNHR \quad (1)$$

This equilibrium may be approached from either side and is believed to be a four center reaction or a radical chain displacement reaction.[4]

Present work concerns the UV-photocatalysed decomposition of sulfenamides in cyclohexene and is designed as a model of their reactions with polyolefins.

RESULTS AND DISCUSSION

A chromatogram of a typical reaction mixture is shown in Figure 1. The rate of loss of *N*-(phenyl)benzenesulfenamide (**1**) confirms the ease of fission of the S—N bond on exposure to UV radiation (Figure 2). These conditions may be compared with the high temperatures and prolonged heating periods used in previous studies of rearrangement and displacement reactions in aniline.[5–10]

A free radical mechanism for the decomposition is supported by the relatively

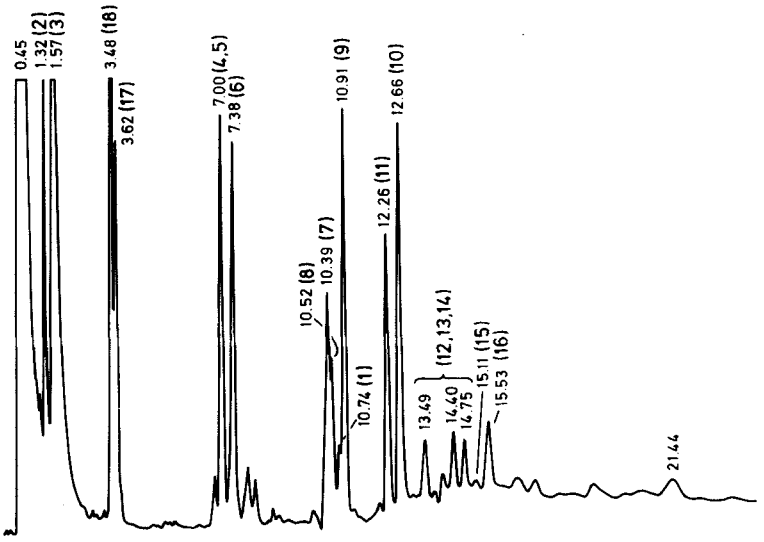


FIGURE 1 Gas chromatographic separation of the products of a typical ultraviolet photolysis of *N*-(phenyl)benzenesulfenamide in cyclohexene. Conditions: OV-17 column (3% on Chromosorb W HP (80–100 mesh; 1.8 m × 3.1 mm), temperature program from 110°C to 250°C at 10°C/min with a final hold time of 15 min. Retention times (min) are at the top of each peak together with the number (boldface) of the compound (see Table II).

slight difference in rate in solvents of widely different dielectric constant–methanol and hexane[11–13] (Table I).

As a basis for discussion of the present reaction an overall view of the origin of products is shown in Scheme 1. Accepting that the first step of decomposition is homolysis of the S—N bond, products result from a series of competing reactions involving (a) hydrogen abstraction (b) homo and hetero recombinations and (c) attack on the solvent.

The yield of aniline (**3**) indicates a preferred hydrogen abstraction by the anilino radical with either **1** itself or solvent cyclohexene acting as hydrogen donor (Table II). In the former case the sequence would be

$$\underset{\mathbf{1}}{\mathrm{RSNHR}} \rightarrow \mathrm{RS}^{\cdot} + {}^{\cdot}\mathrm{NHR} \qquad (2)$$

$$\mathrm{RSNHR} + {}^{\cdot}\mathrm{NHR} \rightarrow \underset{\mathbf{3}}{\mathrm{RS\dot{N}R}} + \mathrm{H_2NR} \qquad (3)$$

This requires a ratio of 2:1 for **1** lost/**3** formed and inspection of Figure 2 at the point of intersection of the respective curves shows that the loss of **1** is more than sufficient to account for this sequence.

Formation of diphenyl disulfide (**7**) and 2- and 4-aminodiphenyl sulfides (**9** and **10**), which *in toto* represent a major fraction of the sulfur available, are expected recombination products and appear early in the photolysis. The formation of **9** and **10** represents a diversion of anilino radicals from other reactions. It is significant that no evidence was obtained for dimerization to hydrazobenzene and

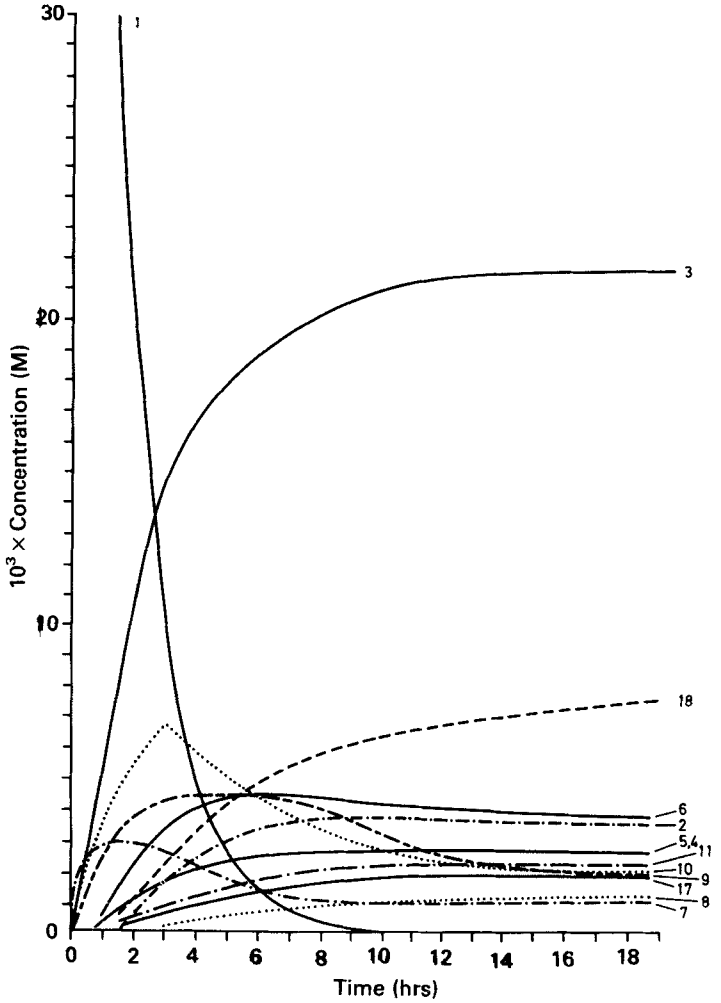
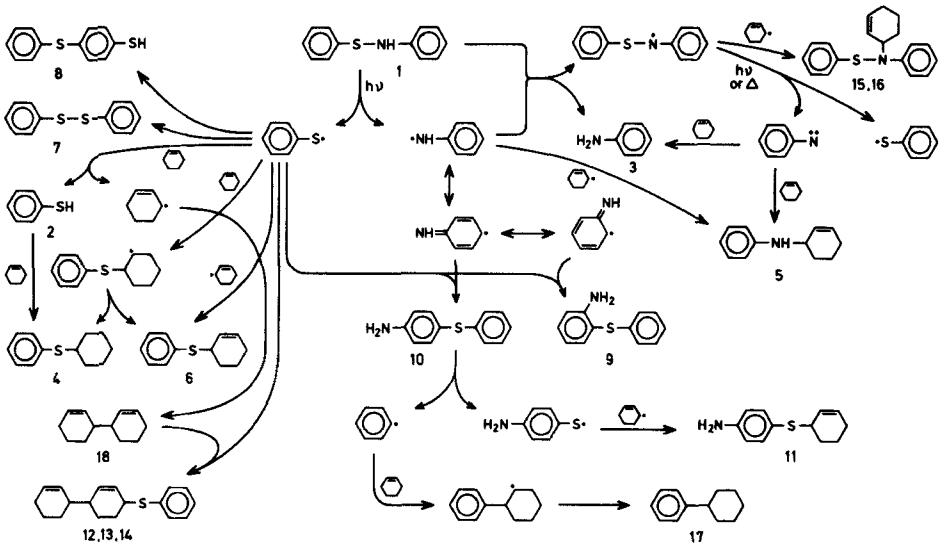


FIGURE 2 Photolysis of *N*-(phenyl)benzenesulfenamide in cyclohexene under ultraviolet light. Rate of formation of products (numbers as in Table II).

TABLE I

Effect of solvent and lighting on the decomposition (%) of *N*-(phenyl)benzenesulfenamide

		Solvent		
Lighting	Time	*n*-Hexane	Cyclohexene	Methanol
Dark	100 h	3.3	3.4	6.0
Sunlight	10 h	13.5	19.6	41.5
	40 h	26.5	58.4	74.3
Ultraviolet	8 h	—	95	—



SCHEME 1

its dehydrogenated product, azobenzene as reported in the thermal decompositions in aniline.

This difference in course of reaction between thermal and photolytic decompositions may be attributed to solvent and concentration effects. The high temperature decompositions to **7**, azobenzene and **9** and **10** have been classed as disproportionation and rearrangement reactions following homolysis of the S—N bond.[10] However heating of sulfenamides in aniline under these conditions would favor stabilization of the anilino radical by exchange with the solvent, so that, in the absence of other substrates for attack, recombination products are observed. The influence of aniline on the photolysis of *N,N*-bis(4-methoxyphenyl)benzenesulfenamide has been demonstrated[14]

$$PhSN(C_6H_4OMe)_2 + H_2NPh \rightarrow PhSNHPh + PhSSPh + MeOC_6H_4NHC_6H_4OMe \quad (4)$$

In the absence of aniline only disulfide and a substituted amino sulfide are obtained.

In the present work low concentration and hetero recombination reactions inhibit the self recombination of anilino radicals to hydrazobenzene. Possibly the most interesting reactions concern cyclohexene, products from which reflect the free radical environment of the system. Radicals from the solvent may be generated by removal of a hydrogen atom from an α-methylene group or by attack at the double bond. For example decomposition of benzoyl peroxide in cyclohexene at 140°C gives a mixture of saturated and unsaturated derivatives indicative of attack at α-methylenic positions rather than at carbon–carbon double bonds. Formation of dicyclohexenyl products occurs.[15] However when carbon tetrachloride is also present, attack occurs at the double bond. A

TABLE II

Photolysis products of *N*-(phenyl)benzenesulfenamide in cyclohexane

Products	No.	GC retention time (min)	Maximum level detected %	Compared with standard	Cl (methane) mass spectral data–main peaks; *m/z* (relative intensity)
Thiophenol	**2**	1.32	7	*	
Aniline	**3**	1.57	41	*	
Phenylcyclohexyl-sulfide	**4**	7.00	5	#	193$[M+1]^+$ of C_6H_{11}-S-Ph (96), 111$[M+1]^+$ of Ph-SH(54)
Phenylcyclohexenyl-amine	**5**			#	174$[M+1]^+$ of C_6H_9-NH-Ph (100), 94$[M+1]^+$ of Ph-NH_2 (79),81$[C_6H_9]$ (56)
Phenylcyclohexenyl-sulfide	**6**	7.38	8	#	191$[M+1]^+$ of C_6H_9-S-Ph (75), 111$[M+1]^+$ of Ph-SH (100), 113$[C_6H_9$-S] (53), 82 (52), 80$[C_6H_9]$ (90)
Diphenyl disulfide	**7**	10.39	12	*	219$[M+1]^+$ of $(Ph\text{-}S)_2$ (58), 141[Ph-S-S] (100), 111$[M+1]^+$ of Ph-SH] (51)
Mercaptodiphenyl-sulfide	**8**	10.52	2		219 (56), 141 (74), 111 (37)
2-Aminodiphenyl-sulfide	**9**	10.91	9		202$[M+1]^+$ of Ph-S-C_6H_4-NH_2 (65), 124[S-C_6H_4-NH_2] (24), 111 (14), 110[Ph-SH] (10), 94 (93), 93[Ph-NH_2] (100)
4-Aminodiphenyl-sulfide	**10**	12.66	13	#	202$[M+1]^+$ of Ph-S-C_6H_4-NH_2 (100), 124[S-C_6H_4-NH_2], (77), 93[Ph-NH_2] (35)
4-Aminophenyl-cyclohexenylsulfide	**11**	12.26	4	#	206$[M+1]^+$ of C_6H_9-S-C_6H_4-NH_2] (39), 126 (71), 125 (44), 124[S-C_6H_4-NH_2] (74), 113$[C_6H_9S]$ (53), 81$[C_6H_9]$ (100)
Dicyclohexenyl-phenylsulfide	**12**	13.49			271$[M+1]^+$ of C_6H_9-C_6H_8-S-Ph (13), 189$[C_6H_8$-S-Ph] (16), 161$[C_6H_9$-$C_6H_8]$ (88), 111$[M+1]^+$ of Ph-SH (42), 81$[C_6H_9]$
Isomer of **12**	**13**	14.40			271 (3), 189 (8), 161 (100), 111 (63)
Isomer of **12**	**14**	14.75			271 (4), 189 (9), 161 (100), 111 (55)
N-(Phenyl)-*N*-((cyclo-hexenyl) benzene-sulfenamide or isomer	**15**	15.11			282$[M+1]^+$ of Ph-S-N(C_6H_9)-Ph or isomer] (6), 202 (14), 201[Ph-S-NH-Ph] (6) 126 (51), 125 (50), 124[S-NH-Ph] (71), 111$[Ph\text{-}SH_2]^+$ (100), 94 (17), 93[Ph-NH_2] (65)
Isomer of **15**	**16**	15.53			282 (43), 202 (100), 173 (19), 81 (86)
Phenylcyclohexane	**17**	3.62			161$[M+1]^+$ of Ph-C_6H_{11}] (19), 159[M − 1 of Ph-C_6H_{11}] (14), 83$[C_6H_{11}]$ (100)
Dicyclohexene	**18**	3.48			163$[M+1]^+$ of $(C_6H_9)_2$ (23), 161$[M-1]^+$ of $(C_6H_9)_2$] (100), 82 (77), 80$[C_6H_9]$

* Standard materials obtained commercially
\# Standard materials prepared by synthesis

continuing attack of a cyclohexenyl radical on cyclohexene is proposed in this reaction.[16]

The reactivity of the phenylthiyl radical is shown by the fact that products containing sulfur provide a greater range of derivatives than those containing nitrogen. Indeed most of the latter type derivatives also contain sulfur.

The yield of thiophenol (**2**) is somewhat surprising in view of the potential for an addition reaction with the solvent to give phenyl cyclohexyl sulfide (**4**). With the abundance of olefin available the survival of less **2** might have been expected. Compound **4** is formed but in relatively small amount.

With the diversion of thiyl radicals to formation of **9** and **10** it is probable that replenishment of the thiyl radical comes from **7**. This is important in providing thiyl radicals for other tertiary reactions. The product mixture contains a number of unsaturated, solvent-derived materials indicative of attack at the α-methylenic group. Clearest evidence of this is provided by identification of dicyclohexene (**18**) and the dicyclohexenyl phenylsulfide isomers (**12**, **13**, **14**) as products of further reaction similar to that giving the simpler phenyl cyclohexenyl sulfide (**6**).

Identification of the species attacking the α-methylenic groups of the solvent presents problems. Although reaction of the phenylthiyl radical at the double bond is favored, attention may be directed to its hydrogen abstracting activity. Thus photolysis of di-isobutyl disulfide in cumene gives isobutyl mercaptan and dicumene.[17] Similarly hydrogen abstraction occurs in the photolysis of dimethyl sulfide with dihydroanthracene[18] and dimethyl disulfide with cyclopentene.[19]

Phenyl nitrene derived from the photolysis or α-elimination of the sulfenamido radical (Equation 3) may insert into the α-methylenic C—H bond to form phenyl cyclohexenyl amine (**5**).[20] Phenyl nitrene may also abstract hydrogen from the solvent to form the anilino radical and subsequently aniline. Anilino radicals from this reaction or from the initial fission of **1** may combine with the cyclohexenyl radical to form **5**. Addition reactions of nitrenes are well established and could be the source of **5** through rearrangement of an intermediate aziridine.

It seems that decomposition of **10** gives rise to 4-aminophenyl cyclohexenyl sulfide (**11**) and both compounds are present in similar concentration in the later stages of the reaction. The mass spectrum of **10** shows that fragmentation between the unsubstituted benzene ring and S leading to the $SC_6H_4NH_2$ ion is very favored and the equivalent radical is also apparently formed under conditions of photolysis together with the phenyl radical. Clearly $SC_6H_4NH_2$ reacts readily with cyclohexenyl radicals. Although the dissociation energy of the allyl-S bond is some 35 kcal/mol less than that of the Ph—S bond,[21,22] and therefore it would be predicted that **10** would be stable, formation of **11** probably occurs at the expense of **10** because of the overwhelming abundance of cyclohexenyl radicals in the reaction mixture.

Formation of products with m/z 282 $[M+1]^+$ and 281 $[M]^+$ suggests the reaction of PhSNPh or of the radicals of **9** and **10** with the cyclohexenyl radical. However no products were observed which indicated that **1** could add to a double bond in the manner of a sulfenyl chloride or sulfenate ester. The mechanism of the formation of phenyl cyclohexane (**17**) must be open to conjecture. It is probably the result of attack by a phenyl radical, generated by scission of a Ph—S bond, at the double bond of the solvent to form a phenyl cyclohexyl radical and subsequent H abstraction by this species. Thermal scission of the Ph—S bond

accounts for formation of diphenyl in dehydrogenations of phenylcyclohexane and phenylcyclohexene by **7**.[23]

Figure 2 shows that secondary reactions appear very soon in the photolysis, are important in the overall reaction and emphasize the radical generating potential of the cyclohexene. Finally the combined weight of identifiable products decreases as the irradiation is continued, presumably due to formation of high molecular weight products not eluted in the analysis.

EXPERIMENTAL

IR spectra were determined on a Pye Unicam SP1000 spectrometer, UV spectra on a Pye Unicam SP1800 spectrophotometer. ^{1}HNMR spectra were taken in $CDCl_3$ on a JEOL FX100 spectrometer. Electron impact mass spectra were recorded on an A.E.I. MS 12 or an A.E.I. MS 902 mass spectrometer. GC-mass spectra were obtained using a Finnigan 3200 quadrupole GC-MS system interfaced to an Incos 2300 data system. Gas chromatography was performed on a Hewlett Packard 5840 A instrument equipped with a flame ionization detector. Products were separated on an OV-17 column (3% on Chromosorb W HP (80–100 mesh; 1.8 m × 3.1 mm), temperature programming from 110°C to 250°C at 10°C/min with a final hold time of 15 min.

All chemicals were of analytical reagent grade and were used as commercially obtained without further purification, unless otherwise stated. Cyclohexene was washed with ferrous sulfate solution, dried, distilled and stored in sealed glass ampoules.

N-(Phenyl)benzenesulfenamide (**1**),[24] phenyl cyclohexyl sulfide (**4**),[25] 3-bromocyclohexene,[26] phenyl-2-cyclohexenyl sulfide (**6**),[27] 4-aminodiphenyl sufilde (**10**)[28] were prepared by standard methods and gave satisfactory elemental analyses.

Phenyl-2-cyclohexenylamine (**5**) To a well stirred solution of aniline (35 g, 0.38 mol) in carbon tetrachloride (100 ml) at room temperature was added dropwise 3-bromocyclohexene (20 g, 0.13 mol) in carbon tetrachloride (20 ml). Aniline hydrobromide which separated was filtered off and the solvent removed in vacuo. Compound **5** was isolated by distillation (b.p. 126–129°C/3 mm Hg) as a light yellow liquid. Calcd. for $C_{12}H_{15}N$: C, 83.23; H, 8.67; N, 8.09. Found: C, 83.05; H, 8.31; N, 8.13.

4-*Aminophenyl cyclohexenyl sulfide* (**11**) To sodium (0.37 g, 0.016 A) in absolute ethanol (30 ml) was added 4-aminothiophenol (2 g, 0.016 mol) to form the thiophenolate. 3-Bromocyclohexene (2.58 g, 0.016 mol) was added dropwise at room temperature and the reaction mixture then heated under reflux for 15 min on a boiling water bath. Sodium bromide which separated was filtered off and the solvent removed *in vacuo* to give **11** as a heavy oil. The EI mass spectrum was as follows (relative intensities of the ions in brackets) m/z 207 $[M+2]^+$ (1); 206 $[M+1]^+$ (2); 205 $[M]^+$ (16); 125 $[HS\text{-}C_6H_4\text{-}NH_2]^+$ (100); 81 $[C_6H_9]^+$ (30). Calcd. for $C_{12}H_{15}NS$: C, 70.24; H, 7.32; N, 6.83. Found: C, 70.44; H, 7.37; N, 7.07.

Photolyses

(a) *Solvent influence on rate of decomposition*: Solutions of **1** (1.0 g) in either *n*-hexane (100 ml), cyclohexene (100 ml) or methanol (100 ml) were transferred into quartz ampoules, sparged with nitrogen and stoppered. One set of solutions in each solvent was kept in the dark (control), another set exposed to sunlight and a third set exposed to ultraviolet light. Decomposition of **1** in each solution was analysed periodically by gas chromatography (Table I).

(b) **1** *in cyclohexene*: Compound **1** (1.0 g) was dissolved in cyclohexene (100 ml), aliquots (7 ml) transferred into quartz ampoules, frozen (dry ice/acetone), evacuated to 1 mm Hg and sealed. The solutions were allowed to thaw and the ampoules arranged in a circular array in a motor-driven carousel placed inside an Oliphant ultraviolet reaction cabinet (Adelaide, South Australia) with fan cooling. The carousel rotated at 35 rpm during the photolysis, ensuring uniform radiation dosage for all ampoules. At intervals, 0.5, 1, 2, 3, 4, 5, 8, 10, 12, 14, 18 and 22 h ampoules were removed and frozen (dry ice/acetone) for analysis. Products were identified by GC-MS (CI methane) and, where possible, confirmed by comparison of retention times and mass spectral data with those of commercially available or synthetic material.

The following compounds were identified by their CI mass spectra, 4-mercaptodiphenylsulfide (**8**), 3 isomers of phenyl dicyclohexenyl sulfide (**12**, **13**, **14**), 2 isomers of *N*-phenyl-*N*-cyclohexenyl benzene sulfenamide (**15**, **16**), phenyl cyclohexane (**17**), dicyclohexene (**18**).

The products were quantitated by gas chromatography as above using external standards. Compounds **17** and **18** were estimated using biphenyl as standard, while the unresolved peak (t_r 7.0 min) of **4** and **5** was estimated using an equimolar mixture of those two compounds as standard. Compound **9** was estimated using the response factor of **10** and **8** using that of its isomer **7**.

REFERENCES

1. C. W. Bedford and L. B. Sebrele, *Ind. Eng. Chem.*, **13,** 1034 (1921).
2. G. Bruni and B. Romani, *Giorn. Chim. Ind. Applicata,* **3,** 196 (1921).
3. M. W. Philpott, *Proc. Rubber Technol. Conf.* 4th London, 39 (1962).
4. R. Bayfield and E. R. Cole, *Phosphorus and Sulfur,* **1,** 19 (1976).
5. M. L. Moore and T. B. Johnson, *J. Am. Chem. Soc.*, **57,** 1517 (1935).
6. M. L. Moore and T. B. Johnson, *J. Am. Chem. Soc.*, **58,** 1091 (1936).
7. F. A. Davis, S. Divald and A. H. Confer, *J. Chem. Soc., Chem. Commun.* 294 (1971).
8. F. A. Davis and R. P. Johnson, *J. Org. Chem.*, **37,** 859 (1972).
9. F. A. Davis, C. J. Horner, E. R. Fretz and J. F. Stackhouse, *J. Org. Chem.*, **38,** 695 (1973).
10. F. A. Davis, E. R. Fretz and C. J. Horner, *J. Org. Chem.*, **38,** 690 (1973).
11. E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai and Y. J. Pocker, *J. Chem. Soc.*, 220 (1957).
12. G. M. Burnett, "*Mechanism of Polymer Reactions*", Interscience Publishers, N.Y. p. 236 (1954).
13. A. V. Tobolsky and R. B. Mesrobian, "*Organic Peroxides*", Interscience Publishers, N.Y. p. 60 (1954).
14. T. Ando, M. Nojima and N. Tokina, *J. Chem. Soc., Perkin* I, 2227, (1977).
15. E. H. Farmer, *J. Chem. Soc.*, 1519, (1947).
16. E. C. Kooyman and E. Farenhorst, *Rec. Trav. Chim.*, **70,** 867 (1971).
17. C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81,** 1137 (1959).
18. Y. Schaafsma, A. F. Bickel and E. C. Kooyman, *Tetrahedron,* **16,** 76 (1960).
19. L. Lunazzi and G. Placucci, *J. Chem. Soc., Chem. Commun.*, 533 (1979).
20. T. W. Gilchrist and C. W. Rees, "*Carbenes, Nitrenes and Arynes*", Ch. 7, Nelson, London (1969).
21. W. A. Pryor, "*Mechanism of Sulfur Reactions*", McGraw Hill, p. 17 (1962).
22. S. W. Benson, *Chem. Rev.*, **78,** 23 (1978).
23. M. Nakazaki, *J. Inst. Polytech. Osaka City Univ.*, Ser. C, 2, no. 1, 19 (1951); *Chem. Abs.* **46,** 7067g (1952).
24. T. Zincke and Baeumer, *Annalen,* **416,** 86 (1918).
25. J. I. Cunneen, *J. Chem. Soc.*, 36 (1947).
26. C. Djerassi, *Chem. Rev.*, **43,** 271 (1948).
27. L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 1596 (1955).
28. S. Krisna and H. Singh, *J. Am. Chem. Soc.*, **50,** 792 (1928).