# Reactions and Mass Spectra of Some Aryl-alkyl Sulphoxides

By **I. D. Entwistle,** Medical Research Council Unit, Exeter University
**R. A. W. Johnstone,** The Robert Robinson Laboratories, Liverpool University
**B. J. Millard,** College of Technology, Liverpool 3

The sulphoxides $Ph\cdot[CH_2]_n\cdot SO\cdot Me$ ($n$ = 0—4) were compared in pyrolytic and mass spectrometric behaviour. On pyrolysis either β-elimination or rearrangement occurred, but similar effects were not observed in the mass spectra. The attempted preparation of one of the sulphoxides actually yielded the next higher homologue by a complex series of reactions.

THE aryl-alkyl sulphoxides, $Ph\cdot[CH_2]_n\cdot SO\cdot Me$ (I; $n$ = 0—4) were prepared, and pyrolysed at 160—220°. The preparation of the sulphoxides (I; $n$ = 1—4) was attempted by treatment of the corresponding halide, $Ph\cdot[CH_2]_{n-1}X$ (X = Cl or Br) with dimethyl sulphoxide anion (dimsyl sodium) as has been described with alkyl halides.[1] A good yield of 4-phenylbutyl methyl sulphoxide (I; $n$ = 4) was obtained from 3-phenylpropyl bromide and dimsyl sodium, but the reaction was no longer useful when the alkyl chain was shortened.

---

[1] I. D. Entwistle and R. A. W. Johnstone, *Chem. Comm.*, 1965, 29.

Thus, under similar conditions, phenethyl bromide afforded a complex mixture separable by thin-layer chromatography into three main sulphoxides, including the required 3-phenylpropyl methyl sulphoxide (I; $n = 3$). The other two major components, 1-phenethyl-3-phenylpropyl methyl sulphoxide and bis-3-phenylpropyl sulphoxide, identified by infrared, nuclear magnetic resonance, and mass spectrometry, were formed by substitution of the initially produced 3-phenylpropyl methyl sulphoxide. The reaction of benzyl chloride with dimsyl sodium was still more complex, as has been noted by other workers,[2] and yielded none of the required phenethyl methyl sulphoxide (I; $n = 2$). The reaction product was first chromatographed on alumina to give *trans*-stilbene and a mixture of sulphoxides, and the latter were separated by preparative thin-layer chromatography into three major components and many minor ones. One of the components was shown to be 3-phenylpropyl methyl sulphoxide (I; $n = 3$) by comparison with an authentic specimen, and because it afforded allylbenzene on pyrolysis. The formation of this sulphoxide and not the expected phenethyl methyl sulphoxide showed that a lengthening of the alkyl chain by one methylene unit had occurred. The other two components of the sulphoxide mixture were shown to be the diastereoisomers of 1,2-diphenylethyl methyl sulphoxide (II) and each yielded the same sulphone on oxidation. The diastereoisomers (II) had bands in the infrared region corresponding to sulphoxides, and each gave *trans*-stilbene on heating to about 150°. However, on standing in the air for only a few minutes, the sulphoxides (II) were oxidised so rapidly to the sulphone that the latter was used to elucidate their structures. The nuclear magnetic resonance spectrum showed a clearly defined ABX system, indicating considerably restricted rotation about the central carbon–carbon bond. The mass spectrum of the sulphone showed a loss of a $CH_3SO_2$ radical to give a fragment ion at *m/e* 181, which then fragmented further like the 1,2-diphenylethyl ion.[3] Probable reactions leading to the formation of the above sulphoxides are shown:

(i) $\mathrm{Ph{\cdot}CH_2Cl + Na^+\,\bar{C}H_2{\cdot}SO{\cdot}CH_3 \longrightarrow Ph{\cdot}CH_2{\cdot}CH_2{\cdot}SO{\cdot}CH_3 + NaCl}$

(ii) $\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}SO{\cdot}CH_3 + Na^+\,\bar{C}H_2{\cdot}SO{\cdot}CH_3 \rightleftharpoons Ph{\cdot}CH{=}CH_2 + CH_3SO^-\,Na^+ + CH_3{\cdot}SO{\cdot}CH_3}$

(iii) $\mathrm{Ph{\cdot}CH{=}CH_2 + Na^+\,\bar{C}H_2{\cdot}SO{\cdot}CH_3 \longrightarrow Ph{\cdot}\bar{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}SO{\cdot}CH_3\,Na^+}$

(iv) $\mathrm{2Ph{\cdot}CH_2Cl \longrightarrow Ph{\cdot}CH{=}CH{\cdot}Ph}$

(v) $\mathrm{Ph{\cdot}CH{=}CH{\cdot}Ph + CH_3SO^-\,Na^+ \longrightarrow Ph{\cdot}\bar{C}H{\cdot}CH(SOCH_3)Ph\,Na^+}$

The expected reaction (i) occurs first and is then followed by the well-known reactions (ii) and (iii)[4] to give 3-phenylpropyl methyl sulphoxide and liberate sodium methylsulphenate. In the presence of strong base benzyl chloride yields *trans*-stilbene,[5] which can add on sodium methylsulphenate to give the diastereoisomeric sulphoxides (II). In a separate experiment, it was found that *trans*-stilbene did not add a molecule of dimsyl sodium under the above reaction conditions. The products of the reaction of benzyl chloride with dimsyl sodium can thus be accounted for satisfactorily by reactions (i)—(v), given suitable overall reaction rates. As a test of the proposed reaction sequence, a mixture of *trans*-stilbene and phenethyl methyl sulphoxide was treated with dimsyl sodium, when again 3-phenylpropyl methyl sulphoxide and the diastereoisomers (II) were formed.

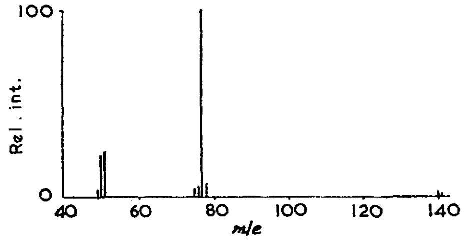


FIGURE 1 Mass spectrum of $Ph{\cdot}SO{\cdot}CH_3$

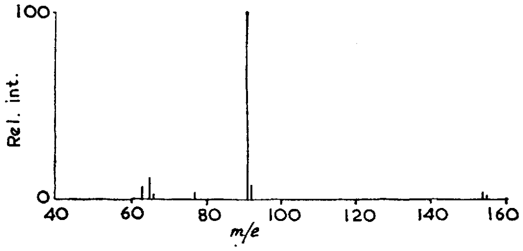


FIGURE 2 Mass spectrum of $Ph{\cdot}CH_2{\cdot}SO{\cdot}CH_3$

The sulphoxides (I; $n = 0$—$2$), which could not be prepared by the action of dimsyl sodium on the corresponding halide, were obtained by oxidation of phenylalkyl methyl sulphides with hydrogen peroxide. The preparation of benzhydryl methyl sulphide from benzhydryl bromide and methanethiol in the presence of base gave very poor yields. Good yields of the sulphide were obtained by treatment of diphenyldiazomethane with methanethiol and toluene-*p*-sulphonic acid in acetonitrile.

On mass spectrometry, the sulphoxides (I; $n = 0$—$4$; Figures 1—5) and the corresponding sulphones rarely showed a parent ion. Commonly, a hydrocarbon fragment ion was formed by cleavage at the α-position to the sulphoxide or sulphone group.

$$\mathrm{Ph{\cdot}[CH_2]_n{\cdot}\overset{+\bullet}{S}O{\cdot}CH_3 \longrightarrow Ph{\cdot}[CH_2]_n^{\,+} + CH_3S\dot{O}}$$

Even at a mass spectrometer source temperature of 100° there was an indication of β-elimination of methylsulphenic acid from the relatively volatile sulphoxides

---

[2] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1345.

[3] R. A. W. Johnstone and B. J. Millard, *Z. Naturforsch.*, 1966, **21***a*, 604.

[4] C. Walling and L. Bollyky, *J. Org. Chem.*, 1964, **29**, 2699.

[5] F. W. Bergstrom and W. C. Fernelius, *Chem. Rev.*, 1947, **20**, 435.

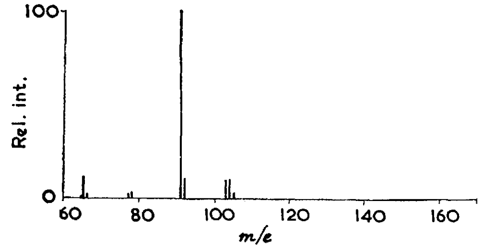


FIGURE 3 Mass spectrum of Ph·[$CH_2$]$_2$·SO·$CH_3$

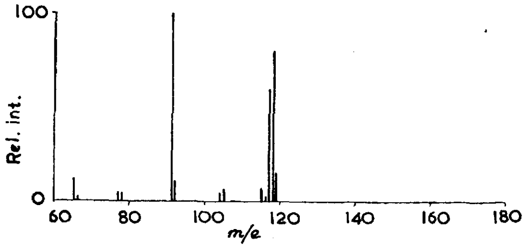


FIGURE 4 Mass spectrum of Ph·[$CH_2$]$_3$·SO·$CH_3$

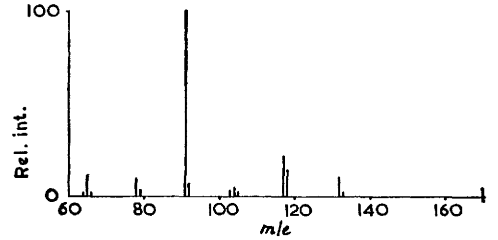
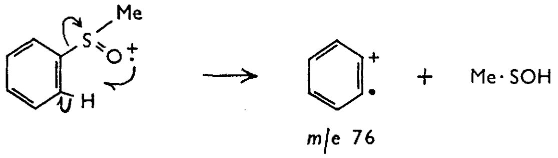


FIGURE 5 Mass spectrum of Ph·[$CH_2$]$_4$·SO·$CH_3$

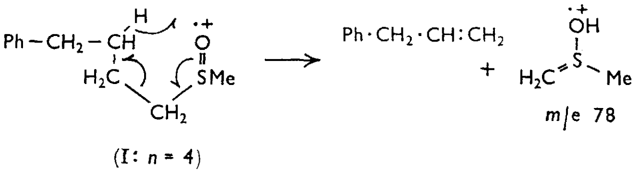
(I; $n = 2$—4), but the sulphoxide (I; $n = 1$) did not show any rearrangement to benzaldehyde as occurs thermally. Methylsulphenic acid was eliminated even from the sulphoxide (I; $n = 0$) to yield the benzyne ion-radical at *m/e* 76,



The hydrocarbon ions at $M - 64$ arising through β-elimination of methylsulphenic acid did not change significantly in intensity at the higher source temperature of 200°, indicating the probable ionic and not thermal nature of the mechanism.

The base peak in all the spectra (except Figure 1) was formed by a β-cleavage reaction common to many alkylbenzenes[6] to give the tropylium ion at *m/e* 91, which then loses a molecule of acetylene to give the ion at *m/e* 65. The phenyl ion at *m/e* 77 was also commonly formed by a type of α-cleavage, which in the case of the sulphoxides (I; $n = 1$) also gave a significant amount of the ion at *m/e* 63 ($CH_3SO$).

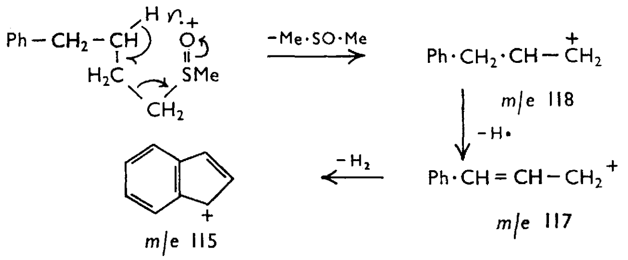
Apart from the simple cleavage and elimination reactions discussed above, there was evidence of a McLafferty type rearrangement[7] in the odd-electron system[8] formed by initial ionisation of the sulphoxides (I; $n = 3$, 4). This previously unreported rearrangement reaction of the sulphoxides is of a type, proceeding through a six-membered transition state as shown, which is fairly common in mass spectrometry.[7]



(I: *n* = 4)

A closely similar reaction was noted as the major fragmentation path in the mass spectra of some 1,2-oxaza ring systems.[9]

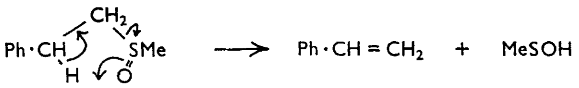
Hydrocarbon fragment ions were also produced by the same reaction, but with the charge appearing on the hydrocarbon fragment, as indicated.



The fragment ion at *m/e* 118 decomposed further by loss of first an atom and then a molecule of hydrogen to give the indenyl ion at *m/e* 115.

The sulphoxides (I; $n = 0$—4) did not show the loss of sulphur monoxide reported for some sulphoxides.[10]

On heating to 160—180°, the sulphoxides suffered the normal β-elimination of methylsulphenic acid observed in alkyl sulphoxides,[1]



The phenylalkenes produced were identified by infrared, nuclear magnetic resonance, and mass spectrometry. In contrast to the observed formation of aldehydes in the pyrolysis of di-*n*-alkyl sulphoxides,[11] no carbonyl compounds were formed. The formation of such carbonyl compounds has been ascribed to the unstable nature of the alkyl-sulphenic acids produced by β-elimin-

---

[6] J. H. Beynon, " Mass Spectrometry and its Applications to Organic Chemistry," Elsevier, 1960, p. 340.

[7] F. W. McLafferty, " Mass Spectrometry of Organic Ions," Academic Press, 1963, p. 336.

[8] C. Djerassi, M. Fischer, and J. B. Thomson, *Chem. Comm.*, 1966, 12.

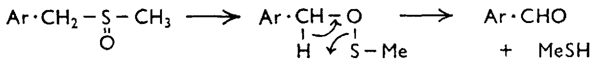
[9] R. A. W. Johnstone, B. J. Millard, E. J. Wise, and W. Carruthers, following Paper.

[10] J. Ø. Madsen, C. Nolde, S.-O. Lawesson, G. Schroll, J. H. Bowie, and D. H. Williams, *Tetrahedron Letters*, 1965, 4377.

[11] D. G. Barnard-Smith and J. F. Ford, *Chem. Comm.*, 1965, 120.

ation,[12] and in this series of sulphoxides this elimination reaction can occur in only one direction to give methylsulphenic acid. Formaldehyde and hydrogen sulphide were identified in the pyrolysates from the phenylalkyl methyl sulphoxides, but on prolonged heating dimethyl sulphoxide (in which β-elimination cannot occur but rearrangement might) showed no indication of any decomposition.

A rearrangement of sulphoxides similar to the Meisenheimer rearrangement of *N*-oxides has been reported briefly by us.[12] Benzyl methyl sulphoxide rearranges to give benzaldehyde in high yield, but the temperature required (210—230°) is significantly higher than for β-elimination.



$$\mathrm{Ar{\cdot}CH_2{-}\overset{\displaystyle S}{\underset{O}{\|}}{-}CH_3} \longrightarrow \mathrm{Ar{\cdot}CH{-}O,\ H,\ S{-}Me} \longrightarrow \mathrm{Ar{\cdot}CHO + MeSH}$$

TABLE

| RR′SOCH$_3$: | R′ = H; R = C$_6$H$_5$, | $p$-O$_2$N·C$_6$H$_4$, | $p$-BrC$_6$H$_4$, | $o$-CH$_3$·C$_6$H$_4$, | $p$-CH$_3$OC$_6$H$_4$; | R′ = R = C$_6$H$_5$ |
|---|---|---|---|---|---|---|
| Percentage yield of aldehyde, RR′CO: | 87 | 75 | 30 | 56 | 25 | 12 |

Several similar sulphoxides were pyrolysed and the aldehydes produced were identified by comparison with authentic specimens and the formation of 2,4-dinitrophenylhydrazones. The rearrangement of *p*-nitrobenzyl methyl sulphoxide to give *p*-nitrobenzaldehyde provided additional evidence for the formation of methanethiol, since 15% of the product was isolated as the methanethioketal of *p*-nitrobenzaldehyde.

Pyrolysis of benzhydryl methyl sulphoxide gave a poor yield of benzophenone, and the major product was tetraphenylethane. The formation of the latter suggests a decomposition of the sulphoxide into radicals first, but when the reaction was repeated in mesitylene no diphenylmethane was formed as might have been expected with benzhydryl radical intermediates. In the presence of air, benzhydryl radicals could give benzophenone, but the yield of the latter was undiminished in the absence of air, showing that some rearrangement had occurred.

## EXPERIMENTAL

Molecular weights were obtained by mass spectrometry. Mass spectra were determined on an A.E.I. M.S./9 mass spectrometer at 70 ev and source temperature up to 200°, using a direct inlet system.

*Thin-layer Chromatography*.—The sulphoxides and sulphones were chromatographed on silica gel with either ethyl acetate or benzene–acetone (3 : 1 to 1 : 1).

*Pyrolyses*.—The sulphoxides (I; $n = 2$—4) were heated to 160—180° to afford a distillate from which the phenylalkene was isolated by chromatography on neutral alumina (Woelm, Grade I) with light petroleum (b. p. 40—60°). The sulphoxides (I; $n = 1$), and benzhydryl methyl sulphoxide were heated to 210—230° for 10—15 min. and the carbonyl compounds purified by chromatography on silica gel with benzene. Benzhydryl methyl sulphoxide afforded 48% of the tetraphenylethane, m. p. 218°, *M* 334, besides benzophenone. Benzhydryl methyl sulphoxide (200 mg.) in mesitylene (2 ml.) again gave 48% of tetraphenylethane and 12% of benzophenone. Gas chromatography showed that no diphenylmethane had been formed.

The pyrolysis of 3-phenylpropyl methyl sulphoxide was carried out under a slow stream of nitrogen which was then bubbled into a solution of 2,4-dinitrophenylhydrazine hydrochloride. The precipitate was crystallised from ethanol to yield formaldehyde 2,4-dinitrophenylhydrazone, m. p. 167°, alone or admixed with an authentic specimen.

Pyrolysis of *p*-nitrobenzyl methyl sulphoxide afforded *p*-nitrobenzaldehyde and its methanethioketal, m. p. 75° [ethanol–light petroleum (b. p. 60—80°)], $\tau$ 7·9 (CH$_3$S); 5·2 (CH); 2·5, 2·3, 1·9, 1·7 (C$_6$H$_4$) (Found: C, 47·3; H, 5·0; S, 27·7. $C_9H_{11}NO_2S_2$ requires C, 47·1; H, 4·8; S, 28·0%). The thioketal gave *p*-nitrobenzaldehyde on mild acid hydrolysis.

*Action of heat on dimethyl sulphoxide*. The sulphoxide was heated to 200° for 1 hr. in a sealed tube. Tests for carbonyl material by infrared spectroscopy and 2,4-dinitrophenylhydrazine hydrochloride solution were negative.

*Action of Dimsyl Sodium on Phenylalkyl Halides*.—(i) A solution of 3-phenylpropyl bromide (1 mol.) was added slowly, with stirring, to a solution of dimsyl sodium * (1 mol.) at room temperature. The mixture was set aside overnight, poured into water, and extracted with ether to yield 4-phenylbutyl methyl sulphoxide (40%), m. p. 30—31°, from ether (Found: C, 67·1; H, 8·3; S, 16·2. $C_{11}H_{16}OS$ requires C, 67·3; H, 8·2; S, 16·3%).

(ii) A mixture of phenethyl bromide (1 mol.) and dimsyl sodium (1 mol.) was prepared and worked up as in reaction (i) to afford a mixture of sulphoxides (33%). The mixture was separated by thin-layer chromatography into three main components present in approximately equal amounts: (*a*) 3-phenylpropyl methyl sulphoxide (see below), m. p. 41°; (*b*) 1-phenethyl-3-phenylpropyl methyl sulphoxide, liquid (decomposes on attempted distillation), *M*, 286; $\nu_{\text{max.}}$ 700, 755, 1045 cm.$^{-1}$; oxidised to sulphone, b. p. 210°/0·05 mm. (Found: C, 71·7; H, 7·2; S, 10·8. $C_{18}H_{22}O_2S$ requires C, 71·5; H, 7·3; S, 10·6%); (*c*) bis-3-phenylpropyl sulphoxide, liquid, *M*, 286, $\nu_{\text{max.}}$ 685, 700, 750, 1040 cm.$^{-1}$; oxidised to sulphone, m. p. 113—115° from ether (Found: C, 71·4; H, 7·1; S, 10·7. $C_{18}H_{22}O_2S$ requires C, 71·5; H, 7·3; S, 10·6%).

(iii) A mixture of benzyl chloride (1 mol.) and dimsyl sodium (1 mol.) was set aside for 18 hr. at room temperature and worked up as in reaction (i) above to yield an oil which was chromatographed on neutral alumina (Woelm, Grade I). Elution with benzene afforded *trans*-stilbene (20% yield), and further elution with ether gave a mixture of sulphoxides (30% yield). The sulphoxides were separated on silica gel to give three main components (*a*) 3-phenylpropyl methyl sulphoxide, m. p. 41° (see below), and (*b*) the two closely separated diastereoisomers of 1,2-diphenylethyl methyl sulphoxide, $\nu_{\text{max.}}$ 700, 750, 1020 cm.$^{-1}$; each

---

* Prepared from sodium hydride and dimethyl sulphoxide (ref. 2).

[12] W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. and Ind.*, 1966, 342.

was oxidised to 1,2-diphenylethyl methyl sulphone, m. p. 121° (ethanol–ether), $\nu_{max.}$ 1120, 1280 cm.$^{-1}$; $\tau$ 7·43 ($C_6H_5$); ABX system where $H_A = 6{\cdot}22$, $H_B = 6{\cdot}76$, $H_C = 5{\cdot}74$ with $J_{AX} = 3$, $J_{BX} = 11$, $J_{AB} = 14$ c./sec. and $\delta_{AB} = 27{\cdot}7$ c./sec. (Found: C, 69·4; H, 6·0; S, 12·4. $C_{15}H_{14}O_2S$ requires C, 69·2; H, 6·1; S, 12·3%).

*Action of Dimsyl Sodium on Phenethyl Methyl Sulphoxide.*—A mixture of the sulphoxide (1 mol.), *trans*-stilbene (1 mol.), and dimsyl sodium (1 mol.) was kept at room temperature for 12 hr. The mixture was poured into water, extracted with ether, and chromatographed on alumina. Elution with benzene afforded some *trans*-stilbene and further elution with ether gave a mixture of sulphoxides, which was separated by thin-layer chromatography into the main components, namely 3-phenylpropyl methyl sulphoxide and the diastereoisomers of 1,2-diphenylethyl methyl sulphoxide.

*Action of Dimsyl Sodium on* trans-*Stilbene.*—A mixture of *trans*-stilbene (1 mol.) and dimsyl sodium (1 mol.) was set aside at room temperature for 18 hr. On working up in the usual way, only dimethyl sulphoxide and *trans*-stilbene were obtained.

*Phenyl Alkyl Methyl Sulphides.*—The corresponding bromide or chloride (1 mol.) in methanol was added to a solution of methanethiol (1·2 mol.) in methanol containing sodium methoxide (1 mol.), and the mixture was set aside for 18 hr. at room temperature to yield the phenylalkyl methyl sulphide. Thus were prepared benzyl methyl sulphide, b. p. 195°/760 mm.,[13] p-*methoxybenzyl methyl sulphide*, b. p. 138°/17 mm. (Found: C, 64·1; H, 7·0; S, 19·0. $C_9H_{12}OS$ requires C, 64·3; H, 7·1; S, 19·0%), *p*-nitrobenzyl methyl sulphide,[14] m. p. 23°, p-*bromobenzyl methyl sulphide*, b. p. 89°/0·4 mm. (Found: C, 44·6; H, 4·0; S, 15·0. $C_8H_9BrS$ requires C, 44·2; H, 4·1; S, 14·8%), *o*-xylyl methyl sulphide, b. p. 123°/27 mm.[15]

*Benzhydryl Methyl Sulphide.*—Benzophenone hydrazone (20 g.) and dry mercuric oxide (50 g.) were stirred in light petroleum (b. p. 40—60°) at room temperature for 4 hr. The solution was decanted from the residue, cooled to −60° for 10 min., and filtered to yield diphenyldiazomethane. Without removing all the solvent, the diphenyldiazomethane was dissolved in acetonitrile (200 ml.) and treated with an excess of methanethiol, and a little toluene-*p*-sulphonic acid (*ca.* 100 mg.) at room temperature. Nitrogen was evolved, and when the solution became colourless it was poured into water and extracted with ether to give *benzhydryl methyl sulphide* (40%), b. p. 155°/2 mm., m. p. 35—36° (Found: C, 78·3; H, 6·4; S, 15·0. $C_{12}H_{14}S$ requires C, 78·5; H, 6·6; S, 14·9%).

*Sulphoxides.*—The corresponding sulphide was treated with an equal weight of hydrogen peroxide (30%; 100 vol.) in sufficient acetone to make an homogeneous solution. The mixture was kept overnight, poured into water, and extracted with ether to yield the following aryl methyl sulphoxides, $RSO{\cdot}CH_3$: phenyl,[16] b. p. 89°/4 mm.; benzyl, m. p. 55°;[17] *phenethyl*, b. p. 120°/0·05 mm. (Found: C, 64·1; H, 7·0; S, 19·2. $C_9H_{12}OS$ requires C, 64·3; H, 7·1; S, 19·1%); 3-*phenylpropyl*, m. p. 41° (Found: C, 65·8; H, 7·6; S, 17·6. $C_{10}H_{14}OS$ requires C, 65·9; H, 7·7; S, 17·6%); 4-*methoxybenzyl*, m. p. 52—53° (Found: C, 58·3; H, 6·3; S, 17·0. $C_9H_{12}O_2S$ requires C, 58·7; H, 6·5; S, 17·4%); 4-*nitrobenzyl*, m. p. 108° (Found: C, 48·5; H, 4·8; S, 16·0. $C_8H_9NO_3S$ requires C, 48·2; H, 4·5; S, 16·1%); 4-*bromobenzyl*, m. p. 103° (Found: C, 41·4; H, 3·8; S, 13·9. $C_8H_9BrOS$ requires C, 41·2; H, 3·9; S, 13·7%); 2-*methylbenzyl*, m. p. 42° (Found: C, 64·4; H, 7·2; S, 19·3. $C_9H_{12}OS$ requires C, 64·3; H, 7·2; S, 19·1%); *benzhydryl*, m. p. 112—114° (Found: C, 73·0; H, 6·0; S, 14·2. $C_{14}H_{14}OS$ requires C, 73·0; H, 6·1; S, 13·9%). The sulphoxides were crystallised from light petroleum (b. p. 40—60°)–ethanol.

*Sulphones.*—These were prepared by heating the corresponding sulphoxide with potassium permanganate in glacial acetic acid to 100°.

The authors thank Dr. D. Whittaker for the valuable suggested synthesis of benzhydryl methyl sulphide, and the S.R.C. for a Fellowship (B. J. M.).

[6/1016 *Received, August* 11*th*, 1966]

---

[13] I. J. Buchi, M. Prost, H. Eichenberger, and R. Lieberherr, *Helv. Chim. Acta*, 1952, **35**, 1527.

[14] H. Hellmann and D. Eberle, *Annalen*, 1963, **662**, 201.

[15] R. Oda and K. Yamamoto, *J. Org. Chem.*, 1961, **26**, 4679.

[16] H. Böhme, H. Fischer, and R. Frank, *Annalen*, 1949, **563**, 54.

[17] S. Hünig and O. Boes, *Annalen*, 1953, **579**, 23.