

Some Reactions of Phenylsulphine and Phenylsulphene

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Phenylsulphine has been prepared in solution from triethylamine and phenylmethanesulphinyl chloride. It slowly decomposes at room temperature to give stilbene, *trans*-4,5-diphenyl-1,2,3-trithiolan 1,1-dioxide, and a 5,6-diphenyl-1,2,3,4-tetrathian dioxide. Phenylsulphine does not react with aldehydes, phenyl isocyanate, benzoyl chloride, or 1,3-dipolar systems. With enamines, electrophilic attack at sulphur to give a dipolar intermediate is followed by proton transfer to form a benzylsulphinyl enamine. Phenylsulphene with enamines gives either thietans or benzylsulphonyl enamines; with the ynamine $\text{PhC}\equiv\text{C}\cdot\text{NEt}_3$ it gives a thieten S,S-dioxide. With the ylid $\text{Ph}_3\text{P}:\text{CH}\cdot\text{CO}_2\text{Et}$, phenylsulphine and phenylsulphene give the stable ylids $\text{Ph}_3\text{P}:\text{C}(\text{SO}\cdot\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{Et}$ and $\text{Ph}_3\text{P}:\text{C}(\text{SO}_2\cdot\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{Et}$, respectively.

SULPHENES, $\text{R}^1\text{R}^2\text{C}:\text{SO}_2$, are well established as reactive intermediates and their chemistry has been extensively investigated.¹ Sulphines, $\text{R}^1\text{R}^2\text{C}:\text{SO}$, on the other hand, have only recently attracted attention.^{2,3} The possibility that sulphines would have nucleophilic carbon and behave as ylids, *i.e.* $\text{R}^1\text{R}^2\text{C}^-\text{SO}^+$ (cf. RNSO^4), prompted the present investigation of the preparation and reactions of phenylsulphine, $\text{PhCH}:\text{SO}$.

Sulphines have been prepared by the oxidation of thio-ketones with monoperoxyphthalic acid⁵ and by the elimination of hydrogen chloride from sulphinyl chlorides by use of triethylamine in anhydrous solvents.^{2,3} The related thioacid chloride S-oxides, $\text{RCCl}:\text{SO}$, have also been obtained from the action of tertiary bases on sul-

phonyl chlorides in cyclohexane.⁶ Treatment of phenylmethanesulphinyl chloride in ether at room temperature with triethylamine gave an immediate precipitate of triethylammonium chloride and a yellow-orange solution containing phenylsulphine. With 2,4-dinitrophenylhydrazine the solution gave hydrogen sulphide and benzaldehyde 2,4-dinitrophenylhydrazine, and u.v. irradiation of the solution gave benzaldehyde. These reactions are held to be characteristic of sulphines.² The solution slowly decomposed at room temperature to give *cis*- and *trans*-stilbenes and two crystalline compounds, *A*, $\text{C}_{14}\text{H}_{12}\text{O}_2\text{S}_3$ and *B*, $\text{C}_{14}\text{H}_{12}\text{O}_2\text{S}_4$. Repeated crystallisation of *A* gave *B* and stilbene. *A* decomposed above its m.p. to give a quantitative yield of *trans*-stilbene while *B* similarly gave an 85% yield of *cis*- and *trans*-stilbenes in the ratio 1:10. Both compounds are

¹ T. J. Wallace, *Quart. Rev.*, 1966, **20**, 67.

² J. Strating, L. Thijs, and B. Zwanenburg, *Rec. Trav. chim.*, 1964, **83**, 631.

³ W. A. Sheppard and J. Dickmann, *J. Amer. Chem. Soc.*, 1964, **86**, 1891.

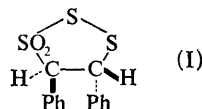
⁴ G. Kresze and R. Albrecht, *Angew. Chem.*, 1962, **74**, 781.

⁵ J. Strating, L. Thijs, and B. Zwanenburg, *Tetrahedron Letters*, 1966, 65.

⁶ J. F. King and T. Durst, *Canad. J. Chem.*, 1966, **44**, 819.

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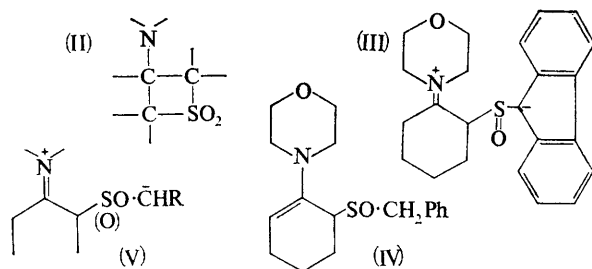
sulphones (ν_{\max} , 1130 cm^{-1}) and in both the two non-aromatic protons constitute an AB system in the n.m.r. spectrum. Compound *A* is therefore formulated as *trans*-4,5-diphenyl-1,2,3-trithiolan 1,1-dioxide (I), while *B* is either the 1,1- or 2,2-dioxide of the corresponding 5,6-diphenyltetraethian.



The additional sulphur atoms in *A* and *B* must come from the sulphur monoxide produced in the formation of stilbenes from phenylsulphine but the mechanisms of the formation of *A* and *B* are obscure.

Although phenylsulphine with chlorine gives chloro-(phenyl)methanesulphinyl chloride,⁷ it did not react at room temperature with benzaldehyde, chloral, phenyl isocyanate, or benzoyl chloride, nor was any reaction observed with the 1,3-dipolar systems phenyl azide and the nitrile imine, $\text{PhC:N}\cdot\text{NPh}$. More vigorous conditions could not be used because of the thermal instability of the sulphine. However, phenylsulphine is an electrophile and we have studied its reactions with enamines and with phosphorus ylids.

Enamines react with sulphines to give the thietans (II).¹ However, Sheppard and Dickmann³ obtained a 1:1-adduct from the sulphine thiofluorenone S-oxide and 1-morpholinocyclohexene to which they assigned the dipolar structure (III). Phenylsulphine with 1-morpholinocyclohexene gave a 1:1-adduct which contained both sulfoxide (ν_{\max} , 1020 cm^{-1}) and enamine (1640 cm^{-1}) groups. The n.m.r. spectrum showed one olefinic proton at τ 4.8 and an AB system (2H) at 5.72 and 6.07 due to the magnetically non-equivalent protons of the $\text{SO}\cdot\text{CH}_2\text{Ph}$ group. The adduct is therefore the enamine (IV). A similar experiment with phenylsulphine and



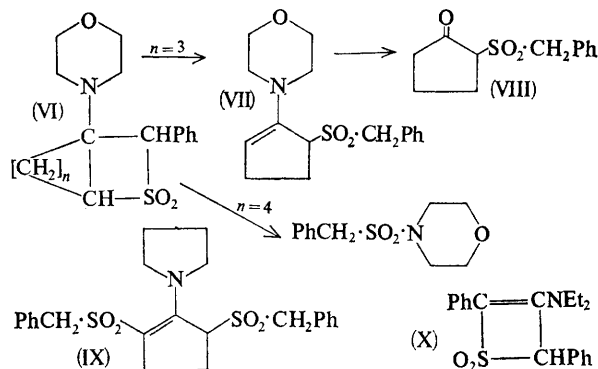
1-pyrrolidinocyclohexene gave only 2-benzylsulphinylcyclohexanone, presumably formed during isolation by hydrolysis of the enamine analogous to (IV).

The reactions of sulphines and sulphenes with enamines are probably two-step processes *via* the dipolar intermediates (V). With phenylsulphine ($R = \text{Ph}$), proton transfer completes the reaction rather than the cyclisation hitherto considered to be characteristic of sulphenes. It seemed possible that this difference arose

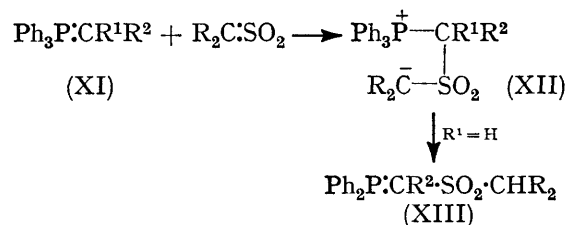
from the greater stability of the carbanion in (V) due to the phenyl group, and the corresponding reactions of phenylsulphene were therefore investigated.

The 1:1-adducts of phenylsulphene with 1-morpholinocyclohexene and 1-morpholinocyclopentene showed no intense absorption in the i.r. around 1640 cm^{-1} and their n.m.r. spectra were consistent with formulation as thietans (VI). The adducts were very sensitive to hydroxylic solvents. Crystallisation of the adduct (VI; $n = 4$) from ethanol gave *N*-benzylsulphonylmorpholine; the adduct (VI; $n = 3$) in ethanol under reflux gave first the corresponding enamine (VII) and then the ketone (VIII). These reactions establish the reversibility of both stages of the reaction between sulphenes and enamines. Paquette and Rosen⁸ have recently described the reactions of phenylsulphene with 1,3-bis-dimethylaminoalk-1-enes, which they interpreted in terms of a non-concerted addition.

Phenylsulphene and 1-pyrrolidinocyclopentene gave a 2:1-adduct which showed absorption at 1600 cm^{-1} and was formulated as the enamine (IX). With 1-pyrrolidinocyclohexene the enamine 1:1-adduct corresponding to (VII) was isolated; with an excess of phenylsulphene this gave a 2:1-adduct corresponding to (IX). With the ynamine PhC:CNEt_2 , phenylsulphene gave the thieten SS-dioxide (X), which showed enamine absorption at 1615 cm^{-1} but was resistant to hydrolysis. No crystalline adduct was obtained from this ynamine and phenylsulphene.



Ito, Okano, and Oda⁹ have shown that sulphenes react with stable phosphorus ylids to give initially the



betaines (XII) which, if $\text{R}^1 = \text{H}$, transfer a proton to give the ylids (XIII). Phenylsulphene with the ylid

⁷ J. Strating, L. Thijs, and B. Zwanenburg, *Rec. Trav. chim.*, 1967, **86**, 641.

⁸ L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, 1967, **89**, 4102.

⁹ Y. Ito, M. Okano, and R. Oda, *Tetrahedron*, 1967, **23**, 2137.

(XI; $R^1 = H$, $R^2 = CO_2Et$) gave the ylid (XIII; $R = Ph$, H ; $R^2 = CO_2Et$). Phenylsulphine with the same ylid gave the ylid $Ph_3P:C(CO_2Et) \cdot SO \cdot CH_2Ph$. No crystalline compounds could be isolated from the reaction of phenylsulphine with the ylid (XI; $R^1 = Me$, $R^2 = CO_2Et$).

EXPERIMENTAL

1H N.m.r. spectra were recorded for solutions in deuteriochloroform with a Varian A-60 spectrometer. Mass spectra were determined with an A.E.I. MS 9 instrument; in each case the mass peak is given first and is followed by those of structural significance.

Phenylsulphine.—Triethylamine (2.1 g.) was added slowly to a stirred solution of phenylmethanesulphinyl chloride (3.6 g.) in ether (25 ml.) cooled in ice, triethylammonium chloride was filtered off, and the filtrate was set aside at room temperature. The first crystalline material to separate was usually the dimer *A*, trans-4,5-diphenyl-1,2,3-trithiolan 1,2-dioxide (I), m.p. 114–115° (decomp.), ν_{max} 1130 cm^{-1} , τ 2.7 (10H, m) and 5.1 (2H, centre of AB system, J_{HH} 10 c./sec.) [Found: C, 54.8; H, 3.8; S, 31.2%; *M* (vapour pressure osmometer), 308. $C_{14}H_{12}O_2S_3$ requires C, 54.6; H, 3.9; S, 31.2%; *M*, 308]. Repeated crystallisation from chloroform–ether gave the dimer *B*, m.p. 135° (decomp.), which sometimes also separated directly from the original solution; ν_{max} 1135 cm^{-1} , τ 2.7 (10H, m) and 4.05 and 4.8 (2H, AB system, J_{HH} 11 c./sec.) [Found: C, 49.3; H, 3.6; S, 36.9%; *M* (vapour pressure osmometer), 337. $C_{14}H_{12}O_2S_4$ requires C, 49.4; H, 3.6; S, 37.6%; *M*, 340].

A solution of phenylsulphine, prepared from triethylamine (1.0 g.) and phenylmethanesulphinyl chloride (1.74 g.) in ether, was concentrated under reduced pressure and the residue was heated under reflux in methanolic sulphuric acid containing 2,4-dinitrophenylhydrazine (1.98 g.) for 3 hr. Hydrogen sulphide was evolved. Benzaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 236–237°, was filtered off.

Reaction of Phenylsulphine with 1-Morpholinocyclohexene.—Phenylmethanesulphinyl chloride (5.22 g.) was added slowly to a stirred solution of triethylamine (3.0 g.) and 1-morpholinocyclohexene (5.0 g.) in ether (150 ml.) and the suspension was set aside at room temperature for 5 days. Water (100 ml.) was added and the product was filtered off to give 3-benzylsulphinyl-2-morpholinocyclohexene (1.5 g.), m.p. 152–153° (from methanol), ν_{max} 1640, 1120, and 1020 cm^{-1} , τ 2.7 (5H, s), 4.8 (1H, t, J_{HH} 4 c./sec.), 5.72 and 6.07 (2H, AB system, J_{HH} 13 c./sec.), 6.2–6.7 (4H, m), and 7.2–8.6 (11H, m) (Found: C, 66.6; H, 7.5; N, 4.6. $C_{17}H_{12}NO_2S$ requires C, 66.8; H, 7.6; N, 4.6%). The ethereal filtrate was washed with 2N-hydrochloric acid and with water and dried. Removal of solvent and crystallisation of the residue from ether–light petroleum gave 2-benzylsulphinylcyclohexanone, m.p. 120°, ν_{max} 1700 and 1030 cm^{-1} , τ 2.7 (5H, s), 5.8 and 6.1 (2H, AB system, J_{HH} 13 c./sec.), 6.8 (1H, m), and 7.4–8.5 (8H, m), *m/e* 236, 218, 178, 140, and 91 (Found: C, 66.1; H, 6.6; S, 13.7. $C_{13}H_{16}O_2S$ requires C, 66.1; H, 6.8; S, 13.6%). The same compound was obtained when 6-benzylsulphinyl-1-morpholinocyclohexene (0.1 g.) was hydrolysed in ethanol (5 ml.) containing 12N-hydrochloric acid (0.05 ml.) at room temperature for 1 hr.

The corresponding experiment with 1-pyrrolidinocyclo-

hexene gave only 2-benzylsulphinylcyclohexanone, m.p. and mixed m.p. 120°.

Reaction of Phenylsulphene with 1-Morpholinocyclohexene.—Phenylmethanesulphonyl chloride (5.7 g.) in ether (200 ml.) was added slowly to a stirred solution of triethylamine (3.0 g.) and 1-morpholinocyclohexene (5.0 g.) in ether (150 ml.) and the suspension was set aside at room temperature for 4 days. Water (100 ml.) was added and the product filtered off to give 1-morpholino-3-thiabicyclo[4.2.0]octane 3,3-dioxide (VI; $n = 4$) (8.5 g.), m.p. 139–140° (from chloroform–ethyl acetate), ν_{max} 1310 and 1150 cm^{-1} , τ 2.7 (5H, s), 5.1 (1H, s), and 5.6 (1H, m), *m/e* 321, 256, 176, and 167 (Found: C, 63.7; H, 7.4; N, 4.4. $C_{17}H_{23}NO_3S$ requires C, 63.6; H, 7.2; N, 4.4%). This compound (0.2 g.) was heated under reflux in ethanol (10 ml.) containing morpholine (50 mg.) for 3 hr. and cooled. N-Benzylsulphonylmorpholine was filtered off; m.p. and mixed m.p. with an authentic sample prepared from phenylmethanesulphonyl chloride and morpholine 177–178° (Found: C, 54.7; H, 6.3; N, 5.7. $C_{11}H_{15}NO_3S$ requires C, 54.8; H, 6.2; N, 5.8%).

Reaction of Phenylsulphene with 1-Morpholinocyclopentene.—Phenylmethanesulphonyl chloride (5.7 g.) in ether (200 ml.) was added slowly to a stirred solution of triethylamine (3.0 g.) and 1-morpholinocyclopentene (4.6 g.) in ether (100 ml.) and the suspension was set aside at room temperature for 5 days, then washed with water, dried, and evaporated. Crystallisation of the residue from ether–light petroleum gave 1-morpholino-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (VI; $n = 3$) (9.0 g.), m.p. 134–135°, ν_{max} 1320 and 1115 cm^{-1} , τ 2.5 (5H, s), 4.3 (1H, s), 5.4br (1H, s), and 6.26 (4H, t), *m/e* 307, 243, and 152 (Found: C, 62.6; H, 6.9; N, 4.7; S, 10.3. $C_{16}H_{21}NO_3S$ requires C, 62.5; H, 6.8; N, 4.6; S, 10.4%).

The dioxide, when heated under reflux in ethanol for 15 min., gave 3-benzylsulphonyl-2-morpholinocyclopentene, m.p. 106–108°, ν_{max} 1635, 1305, and 1120 cm^{-1} , τ 5.1br (1H, s), 5.8 (2H, s), 6.3 (4H, t), and 6.7–7.8 (9H, m). When either this or the original dioxide was heated under reflux in ethanol for 3 hr. the product was 2-benzylsulphonylcyclopentanone, m.p. 91–92° (from ethanol), ν_{max} 1740, 1305, and 1115 cm^{-1} , τ 2.3–2.8 (5H, m), 5.23 and 5.75 (AB system, J_{HH} 14 c./sec.), 6.5 (1 H, m) 7.2–8.0 (6H, m), *m/e* 238, 174, 156, 146, 106, and 91 (Found: C, 60.25; H, 5.7; S, 13.7; $C_{12}H_{14}O_3S$ requires C, 60.5; H, 5.9; S, 13.45%).

Reaction of Phenylsulphene with 1-Pyrrolidinocyclopentene.—Phenylmethanesulphonyl chloride (5.7 g.) in ether (250 ml.) was added slowly to a stirred solution of triethylamine (3.0 g.) and the enamine (5.0 g.) in ether (100 ml.), and the suspension was set aside at room temperature for 5 days and filtered. The solid was washed with water and crystallised from chloroform–ether to give 1,3-di(benzylsulphonyl)-2-pyrrolidinocyclopentene (0.7 g.), m.p. 216–217°, ν_{max} 1600, 1300, and 1120 cm^{-1} , *m/e* 445, 354, 338, 290, 226, 199, 134, and 91 (Found: C, 61.7; H, 6.2; N, 3.1. $C_{23}H_{27}NO_4S_2$ requires C, 62.0; H, 6.1; N, 3.15%). The ethereal filtrate was washed with water, dried, and evaporated. The residue gave 2-benzylsulphonylcyclopentanone, m.p. and mixed m.p. 91–92° (from ethyl acetate–light petroleum).

Reaction of Phenylsulphene with 1-Pyrrolidinocyclohexene.—Phenylmethanesulphonyl chloride (5.7 g.) in ether (200 ml.) was added slowly to a stirred solution of triethylamine (3.0 g.) and the enamine (4.6 g.) in ether (100 ml.), and the suspension was set aside at room temperature for 5 hr. Water (150 ml.) was then added and the ethereal solution

was dried and evaporated. The residue gave **3-benzylsulphonyl-2-pyrrolidinocyclohexene** (2.5 g.), m.p. 118–120° (from ether–light petroleum), ν_{max} . 1650, 1300, and 1125 cm^{-1} , τ 5.04 (1H, t, J_{HH} 4 c./sec.), 5.62 (2H, s), and 6.06br (1H, s) (Found: C, 66.5; H, 7.5; N, 4.5. $\text{C}_{17}\text{H}_{23}\text{NO}_2\text{S}$ requires C, 66.9; H, 7.6; N, 4.6%). Hydrolysis of this compound at room temperature in ethanol containing hydrochloric acid gave **2-benzylsulphonylcyclohexanone**, m.p. 101–102° (from ethyl acetate–light petroleum), ν_{max} . 1720, 1315, and 1125 cm^{-1} , τ 2.6 (5H, s), 5.42 and 5.77 (2H, AB system, J_{HH} 14 c./sec.), 6.4 (1H, t, J_{HH} 6 c./sec.), and 7.1–8.4 (8H, m), m/e 252, 188, and 91 (Found: C, 62.1; H, 6.5; S, 12.8. $\text{C}_{13}\text{H}_{16}\text{O}_3\text{S}$ requires C, 61.9; H, 6.4; S, 12.7%).

Phenylmethanesulphonyl chloride (0.64 g.) in ether (15 ml.) was added slowly to triethylamine (0.4 g.) and **3-benzylsulphonyl-2-pyrrolidinocyclohexene** (1 g.) in ether (25 ml.). After 3 hr. the solution was washed with water, dried, and evaporated. The residue gave **1,3-di(benzylsulphonyl)-2-pyrrolidinocyclohexene** (0.9 g.), m.p. 149–150° (decomp.) (from chloroform–ether), ν_{max} . 1570, 1280, 1130, and 1110 cm^{-1} , τ 2.6–2.75 (10H, m), 5.68 (2H, s), and 5.76 (2H, s with fine structure), m/e 459, 395, 368, 303, and 91 (Found: C, 62.7; H, 6.4; N, 2.95. $\text{C}_{24}\text{H}_{29}\text{NO}_4\text{S}_3$ requires C, 62.7; H, 6.3; N, 3.05%).

Reaction of Phenylsulphine with Diethylphenylethynylamine.—Phenylmethanesulphonyl chloride (0.95 g.) in ether (20 ml.) was added slowly to a stirred solution of triethylamine (0.5 g.) and diethylphenylethynylamine (0.86 g.) in ether (10 ml.) at 0° and the suspension was set aside at room temperature for 1 hr. Water (20 ml.) was added and the solid was filtered off and gave **3-diethylamino-2,4-di-**

phenylthieten 1,1-dioxide (X) (1.4 g.), m.p. 142° (from chloroform–ether), ν_{max} . 1615, 1260, 1150, and 1090 cm^{-1} , τ 2.56 (10H, s) 4.32 (1H, s), 6.95 (4H, q, J_{HH} 7.5 c./sec.), and 9.13 (6H, t, J_{HH} 7.5 c./sec.), m/e 327, 263, 248, 234, 206, 191, and 178 (Found: C, 69.6; H, 6.5; N, 4.2. $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{S}$ requires C, 69.7; H, 6.4; N, 4.3%). The compound (0.3 g.) was recovered unchanged after 15 hr. under reflux in ethanol (20 ml.) containing 2N-hydrochloric acid (1 ml.).

Reaction of Phenylsulphine with Ethoxycarbonylmethylene-triphenylphosphorane.—Phenylmethanesulphonyl chloride (1.9 g.) in benzene (10 ml.) was added slowly to the phosphorane (3.5 g.) and triethylamine (1.1 g.) in benzene (20 ml.) and the suspension was set aside at room temperature for 2 hr. Water (50 ml.) was then added. **Benzylsulphonyl-(ethoxycarbonylmethylene)triphenylphosphorane** (4.6 g.) was filtered off; m.p. 205–206° (from ethanol), ν_{max} . 1655, 1290, 1245, and 1110 cm^{-1} , τ 2.5–2.7 (20H, m), 5.41 (2H, s), 6.11 (2H, q, J_{HH} 7 c./sec.), and 9.26 (3H, t, 7 c./sec.) (Found: C, 68.7; H, 5.6; S, 6.4. $\text{C}_{28}\text{H}_{27}\text{O}_4\text{PS}$ requires C, 68.6; H, 5.5; S, 6.5%).

Reaction of Phenylsulphine with Ethoxycarbonylmethylene-triphenylphosphorane.—Reaction as above, with phenylmethanesulphonyl chloride (1.95 g.), gave **benzylsulphonyl-(ethoxycarbonylmethylene)triphenylphosphorane** (3.5 g.), m.p. 191–192° (from ethanol), ν_{max} . 1655, 1240, and 1020 cm^{-1} , τ 2.4–2.8 (20H, m), 4.5 and 5.8 (2H, AB system), 5.96 (2H, q, J_{HH} 7 c./sec.), and 9.13 (3H, t, J_{HH} 7 c./sec.) (Found: C, 71.0; H, 5.7; S, 6.7. $\text{C}_{28}\text{H}_{27}\text{O}_3\text{PS}$ requires C, 70.9; H, 5.7; S, 6.75%).

We thank the S.R.C. for a Senior Research Assistantship.

[8/098 Received, January 25th, 1968]