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Sulphonyl-stabilised Sulphonium Ylids

By P. Robson, P. R. H. Speakman,* and D. G. Stewart, Basic Research Department, Procter & Gamble Limited, Whitley Road, Longbenton, Newcastle upon Tyne 12

1-Dodecylmethylsulphonium methylsulphonylmethylid and dimethylsulphonium 1-dodecylsulphonyl methylid have been prepared. The ylids are stable crystalline solids but undergo rearrangements in solution at elevated temperatures and under the influence of ultraviolet light. Sulphonyl carbenes are not generated during these reactions.

SULPHONIUM YLIDS have been known since 1930 when Ingold and Jessop isolated 9-dimethylsulphonium fluorenvlid.¹ In recent years there has been renewed activity in this field which was stimulated by the discovery that certain unstable sulphonium ylids would react with aldehydes and ketones to give epoxides,² and with olefinic compounds to give cyclopropanes. This behaviour is exemplified by the simplest of such ylids, dimethylsulphonium methylid (I).^{2c} Although this ylid (I) is known only in solution, relatively stable sulphonium ylids have been isolated,³ and in every case stabilisation has been achieved by the presence of an electron-withdrawing group adjacent to the carbanion [e.g., (II)] where R = alkyl, aryl, alkoxy-]. However, the increase in

$$Me_2 \bar{S} \cdot \bar{C} H_2$$
 (I) $Me_2 \bar{S} \cdot \bar{C} H \cdot COR$ (II)

stability of these ylids (II) is accompanied by a marked decrease in nucleophilicity, and they react extremely slowly ⁴ or not at all 3a, e with aldehydes and ketones. It has been shown ^{3e} that photolysis of dimethylsulphonium phenacylid (II; R = Ph) gives benzoylcarbene.

We have prepared a new type of ylid, the sulphonylstabilised sulphonium ylid (VII), and it was of interest to compare the properties of this class of compound with other sulphur ylids. 1-Dodecylmethylsulphonium methylsulphonylmethylid (VIIa) and dimethylsulphonium 1-dodecylsulphonylmethylid (VIIb) were prepared as shown in the Scheme.

The α -chloro-sulphide (IIIa) was prepared from dimethyl sulphoxide and thionyl chloride,⁵ and (IIIb) was obtained by chloromethylation ⁶ of dodecanethiol.

The ylids were obtained as crystalline solids, insoluble in water, and both were stable in the dark at room temperature for several days. It was interesting that attempts to characterise dimethylsulphonium methylsulphonylmethylid (VIIc) were unsuccessful. The ylid (VIIc) was isolated as a crystalline solid which decomposed rapidly. Thus, the presence of the dodecyl group in ylids (VIIa) and (VIIb) stabilises these materials, and the effect appears to be independent of the position of the long-chain alkyl group in the molecule.

Thermolysis of Ylids.—(a) 1-Dodecylmethylsulphonium methylsulphonylmethylid (VIIa). The ylid was totally

Reagents: 1, H_2O_2 -MeCO₂H; 2, NaSR'; 3, Me₂SO₄; 4, NaOH(aq.) Scheme

decomposed by heating in benzene, under reflux, for 6 hours. Three products, dodec-1-ene, sulphone (IX),

$$\begin{array}{c} \mathsf{MeSO}_2 \cdot \overline{\mathsf{CH}} \cdot \stackrel{+}{\overset{+}{\mathsf{N}}} \mathsf{Me} & \longrightarrow & \mathsf{MeSO}_2 \cdot \mathsf{CH}_2 \cdot \stackrel{+}{\overset{+}{\mathsf{S}}} \stackrel{+}{\overset{-}{\mathsf{C}}} \mathsf{H}_2 \\ (\mathrm{VIIa}) & & & & \mathsf{CH}_2 \\ \downarrow & & & & \mathsf{CH}_2 \\ \mathsf{MeSO}_2 \cdot \mathsf{CH}_2 \cdot \mathsf{SMe} & + & \mathsf{C}_{10}\mathsf{H}_{21} \cdot \mathsf{CH} \cdot \mathsf{CH}_2 & \mathsf{MeSO}_2 \cdot \mathsf{CH}_2 \cdot \mathsf{S} \cdot \mathsf{C}_{12}\mathsf{H}_{25} \\ (\mathrm{IX}) & & & (\mathrm{X}) & + & \mathsf{CH}_2 \\ \end{array}$$

and a small amount of sulphone (Va) were obtained. A likely mechanism for this reaction involves an ylid intermediate (VIII), tautomeric with the original ylid. Breakdown of the intermediate can occur by release of methylene to give sulphone (Va) (route A), and by $\alpha'\beta$ -elimination ⁷ to give sulphone (IX) and dodec-1ene (X) (route B). It is also possible that part, if not all, of the elimination products (IX) and (X) is formed directly from the original ylid (VIIa) by $\alpha'\beta$ -elimination (route C).

Rearrangement of sulphonium ylids to less stable tautomers [e.g. (VIIa) \rightarrow (VIII)] is not without precedent. Treatment of dimethylsulphonium fluorenylid (XI) with alcoholic alkali or with liquid ammonia resulted⁸ in the formation of 1-methylthiomethylfluorene (XIII), and it was proposed⁹ that the reaction proceeded through a less stable tautomer (XII).

4 A. W. Johnson and R. T. Amel, Tetrahedron Letters, 1966, 819.

⁵ F. G. Bordwell and B. M. Pitt, J. Amer. Chem. Soc., 1955,

77, 572.
⁶ H. Böhme, Ber., 1936, 69, 1610.
⁷ G. Wittig and R. Polster, Annalen, 1956, 599, 13.
⁷ A. Dinck and G. E. Hilbert, J. Amer. Chem. S. ⁸ L. A. Pinck and G. E. Hilbert, J. Amer. Chem. Soc., 1938, **60**, 494.

⁹ C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, N.Y., 1953, p. 643.

¹ C. K. Ingold and J. A. Jessop, J. Chem. Soc., 1930, 713. ² (a) A. W. Johnson and R. B. LaCount, J. Amer. Chem. Soc., 1961, 83, 417; (b) A. W. Johnson, V. J. Hruby, and J. L. Williams, *ibid.*, 1964, 86, 918; (c) E. J. Corey and M. Chaykovsky, *ibid.*, 1965, 87, 1353; (d) V. Franzen and H. E. Driessen, Chem. Ber., 1963 96 1881 1963, 96, 1881.

<sup>1903, 90, 1831.
&</sup>lt;sup>3</sup> (a) H. Nozaki, K. Kondo, and M. Takaku, Tetrahedron Letters, 1965, 251; (b) W. J. Middleton, E. L. Buhle, J. G. McNally, and M. Zanger, J. Org. Chem., 1965, 30, 2384; (c) A. Hochrainer, Monatsh., 1966, 97, 823; (d) K. W. Ratts and A. N. Yao, J. Org. Chem., 1966, 31, 1185; (e) B. M. Trost, J. Amer. Chem. Soc., 1967, 89, 138.

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The decomposition of 1-dodecylmethylsulphonium methylsulphonylmethylid provides the first example, as far as we are aware, of a Hofmann elimination of a sulphonium ylid performed under neutral conditions, and this lends support to the view ¹⁰ that ylids may be intermediates in the Hofmann eliminations of certain sulphonium salts.

(b) Dimethylsulphonium 1-dodecylsulphonylmethylid (VIIb). By analogy with ylid (VIIa), dimethylsulphonium dodecylsulphonylmethylid (VIIb) was expected to yield a single sulphone (Vb) on thermal decomposition in benzene, with a tautomeric ylid (XIV) as an intermediate. Although sulphone (Vb) was obtained from the reaction, a second, liquid product was

$$\begin{array}{ccc} C_{12}H_{25}\cdot SO_2\cdot \bar{C}H\cdot \bar{S}\cdot Me & \Longrightarrow & C_{12}H_{25}\cdot SO_2\cdot CH_2\cdot S^{+} \bar{C}H_2 \longrightarrow \\ (VIIb) & & & & (XIV) & & \\ & Me & & Me & \\ & & & C_{12}H_{25}\cdot SO_2\cdot CH_2\cdot S\cdot Me + [CH_2] \\ & & & (Vb) \end{array}$$

isolated in approximately equal yield. The i.r. and n.m.r. spectra suggested that it was 1-(1-dodecyl-sulphonyl)-1-methylthioethane (XV), and this was confirmed by oxidising it to a crystalline disulphone (XVI).

The disulphone (XVI) was independently prepared from 1-dodecylthiomethylsulphonylmethane (Va) by oxidation to (XVII) followed by methylation with methyl iodide.

¹⁰ (a) S. J. Cristol and F. R. Stermitz, J. Amer. Chem. Soc., 1960, **82**, 4692; (b) F. Weygand and H. Daniel, Chem. Ber., 1961, **94**, 3145; (c) V. Franzen and H. J. Schmidt, *ibid.*, p. 2937; (d) V. Franzen and C. Mertz, *ibid.*, 1960, **93**, 2819. The formation of this second product (XV) is an example of a Stevens rearrangement of a sulphonium ylid, and is unusual now that the original report ^{11a} of the rearrangement of benzylmethylphenacyl sulphonium bromide (XVIII) has been shown ^{11b} to be incorrect. Thus, the sulphonium bromide (XVIII) rearranges, under basic conditions, to give an enol ether (XIX) by an electrocyclic rearrangement mechanism,^{11c} and the Stevens rearrangement does not occur.



In the thermal decompositions of the ylids (VIIa) and (VIIb), methylene is believed to be liberated. However, attempts to trap the carbene by thermolysing (VIIb) in the presence of cyclohexene or 2,3-dimethylbut-2-ene were not successful. Indirect evidence for the reaction sequence (VIIb) \longrightarrow (XIV) \longrightarrow (Vb) was obtained through thermolysis of (VIIb) in pyridine solution. The presence of a base should catalyse prototropic shifts of the type (VIIb) \rightarrow (XIV), and, as expected, and in contrast to thermolyses in neutral solution, the only isolable product of the reaction was sulphone (Vb) obtained in higher yield than by thermal decomposition of (VIIb) in benzene. In this connection, the high-resolution mass spectra of the ylids (VIIa) and (VIIb) were helpful. Both ylids showed molecular ions (measured mass 308.1841; theoretical 308.1840), and the primary fragmentation process in each case was initial loss of CH₂ to give ions with m/e 294. Loss of methylene is an unusual occurrence in mass spectrometry, and the readiness with which it occurs in these cases is strong evidence for the intermediate formation of methylene ylids (VIII) and (XIV). Alternatively, the spectra might be explained by loss of a methyl group from the molecular ion, followed by hydrogen capture (which is effectively loss of CH₂). This, however, seems unlikely because no fragment was observed at m/e 293, which would represent loss of methyl alone.

Photolysis of Ylids (VIIa) and (VIIb).—Ultraviolet irradiation of the ylids in benzene gave essentially the same products as were obtained from the corresponding thermolyses. In general, the photolytic reactions also gave several trace products not observed in thermal reactions, but these were not investigated since pure samples could not be isolated. Also, the photolysis of 1-dodecylmethylsulphonium methylsulphonylmethylid (VIIa) yielded a higher proportion of sulphone (Va) than

¹¹ (a) T. Thomson and T. S. Stevens, J. Chem. Soc., 1932, 69;
(b) E. B. Ruiz, Acta Salmenticensi Ser. Cience, 1958, 2, 64;
(c) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, Chem. Comm., 1968, 538.

did the thermal decomposition, indicating that reaction by route A is of greater importance in the photolytic reaction.

To summarise, the sulphonyl-sulphonium ylids (VIIa) and (VIIb) undergo rearrangements under thermal and photolytic conditions. No evidence of cleavage of these ylids into sulphonyl carbenes and alkyl methyl sulphides $[RSO_2 \cdot CH^{-} + S(Me)R' \longrightarrow RSO_2 \cdot CH + MeS \cdot R']$ was observed, and this contrasts with the photolytic behaviour of keto-sulphonium ylids ^{3e} (e.g., PhCO · CH⁻ + SMe₂) and keto-sulphoxonium ylids ¹² [e.g., PhCO · CH⁻ + S(\rightarrow O)Me₂]. The ylids (VIIa) and (VIIb) are far less stable (both thermally and photolytically) than the sulphonylsulphoxonium type ¹³ (RSO₂ · CH⁻ + S(\rightarrow O)Me₂), which is a reflection of the general increase in stability on moving from sulphonium to the corresponding sulphoxonium ylids.

Reaction with Electrophiles.—Neither ylid (VIIa) or (VIIb) reacted with p-nitrobenzaldehyde in refluxing tetrahydrofuran. Only the normal products of thermolysis resulted. However, the ylid (VIIb) was readily benzoylated using benzoyl chloride in the presence of an excess of triethylamine.

$$\begin{array}{c} C_{12}H_{25} \cdot SO_2 \cdot \bar{C}H \cdot \bar{S}Me_2 \longrightarrow C_{12}H_{25} \cdot SO_2 \cdot \bar{C} \cdot \bar{S}Me_2 \\ (VIIb) & (XX) & \downarrow \\ COPh \end{array}$$

The benzoyl ylid (XX) showed i.r. absorption at 1562 cm.⁻¹, typical for the >C⁻-CO system and indicative of electron delocalisation through the carbonyl group. The sulphonyl-stabilised sulphonium ylids thus exhibit a low degree of nucleophilicity which is comparable to that of other stabilised sulphonium ylids.

EXPERIMENTAL

Light petroleum had b.p. 60-80° except where stated.

Spectra.—Infrared spectra were recorded with a Perkin-Elmer Infracord spectrophotometer as Nujol mulls, and ¹H n.m.r. spectra of materials in deuteriochloroform solution were recorded using a Varian HA-60 spectrometer with tetramethylsilane as internal reference. High-resolution mass spectra were obtained using an A.E.I MS9 spectrometer.

Chromatography.—Silica gel (Hopkin and Williams) was used for column chromatography, and Silica Gel G (Merck) for analytical thin-layer chromatography (t.l.c.). For preparative t.l.c., Silica Gel H (Merck) was used. Chromatograms were developed with iodine.

Irradiations.—A Hanovia 1-1. photochemical reactor with low-pressure mercury source emitting at 180 and 254 m μ was used.

Chloromethyl 1-Dodecyl Sulphide (IIIb).—Dry hydrogen chloride was passed into a mixture of paraformaldehyde (12 g.) and n-dodecanethiol (80.4 g.) in light petroleum (b.p. 40—60°), kept at 0°. After stirring for 2 hr. a cloudy solution was obtained which was clarified at intervals by addition of small amounts of dichloromethane. The passage of hydrogen chloride was continued for a further 2 hr. The solution was then dried (Na_2SO_4) and distilled, to give

¹² E. J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 1964, 86, 1640.

chloromethyl 1-dodecyl sulphide (61·2 g.), b.p. $120-122^{\circ}/0.2$ mm. (Found: C, 62·2; H, 10·6. $C_{13}H_{27}ClS$ requires C, 62·3; H, 10·8%).

Chloromethyl 1-Dodecyl Sulphone (IVb).—Hydrogen peroxide (17 ml.; 85%) was added, with stirring, to glacial acetic acid (160 ml.) at 15°. The resulting solution was cooled to 5°, and chloromethyl dodecyl sulphide (60 g.) was added dropwise with vigorous stirring. On completion of the addition, the solution was heated on a steam-bath for 30 min. and left for 16 hr. at room temperature. Filtration gave chloromethyl 1-dodecyl sulphone (55 g.), m.p. 77— 78° (from light petroleum) (Found: C, 55·1; H, 9·7. C₁₃H₂₇ClO₂S requires C, 55·2; H, 9·6%), ν_{max} . 1130, 1317 (SO₂), and 715 cm.⁻¹.

Prepared from chloromethyl methyl sulphide ⁵ in the same way, chloromethyl methyl sulphone (IVa) had m.p. 55–57° (from ethanol) (Found: C, 18.7; H, 3.9. Calc. for $C_2H_5ClO_2S$: C, 18.7; H, 3.8%), ν_{max} 1120, 1150, 1317 (SO₂), and 760 cm.⁻¹.

1-Dodecylsulphonylmethylthiomethane (Vb).— Methanethiol (25 ml.) was added to ice-cold ethanolic sodium ethoxide (250 ml.; from 4.9 g. of sodium). Chloromethyl 1-dodecyl sulphone (55 g.) in ethanol (300 ml.) was added in several portions, and the solution was stirred at 0° for 2 hr. and then heated under reflux for 3 hr. Addition of a large volume of water precipitated 1-dodecylsulphonylmethylthiomethane (47 g.), m.p. 57—59° (from aqueous ethanol). In subsequent experiments, another crystalline form, m.p. 65—66°, was obtained. Mixtures of the two crystalline modifications melted at the lower temperature (57—59°) (Found: C, 57.2; H, 10.1. $C_{14}H_{30}O_2S_2$ requires C, 57.15; H, 10.2%), v_{max} . 1155, 1268, 1284, and 1316 cm.⁻¹.

1-Dodecylthiomethylsulphonylmethane (Va).—Dodecanethiol (58·7 g.) was added to ethanolic sodium ethoxide (150 ml.; from 6·7 g. of sodium). Chloromethyl methyl sulphone (37 g.) in warm ethanol (100 ml.) was added, and the solution was boiled under reflux for 1 hr. Addition of water (500 ml.) gave 1-dodecylthiomethylsulphonylmethane (56·9 g.), m.p. 66—67° (from light petroleum) (Found: C, 57·0; H, 10·1%), v_{max} . 1108, 1157, 1214, 1292, and 1310 cm.⁻¹, n.m.r., τ 9·10 (CH₃[CH₂]_n), 8·73 (10CH₂), 7·09 ([CH₂]_nCH₂S), 6·96 (SO₂CH₃), and 6·7 (SCH₂SO₂).

Methylsulphonylmethylthiomethane (IX).—Chloromethyl methyl sulphone (1.3 g.) was treated with methanethiol (5 ml.) and ethanolic sodium ethoxide (20 ml.; from 0.3 g. of sodium). The resulting solution was boiled for 1 hr., poured into water, and then extracted with chloroform, to give methylsulphonylmethylthiomethane (0.6 g.), m.p. 50—51° (lit.,¹⁴ 50—51°) (from chloroform–light petroleum) (Found: C, 26.0; H, 5.8. Calc. for C₃H₈O₂S₂: C, 25.7; H, 5.7%), v_{max} . 1120, 1160, 1220, 1280, and 1308 cm.⁻¹, n.m.r. τ 7.60 (SCH₃), 6.97 (SO₂CH₃), and 6.15 (SCH₂SO₂).

Preparation of Methosulphates (VIa) and (VIb).—Alkylthiosulphones (Va) and (Vb) were heated at 50—60° for 16 hr., with an excess of dimethyl sulphate (5—10 mol.). The cooled solutions were poured into large volumes of ether, and the flasks were vigorously scratched to assist crystallisation. The methosulphates were recrystallised from acetone to give overall yields of about 70%. 1-Dodecylmethyl(methylsulphonylmethyl)sulphonium methosulphate (VIa) had m.p. 66—68° (Found: C, 45·8; H, 8·7. C₁₆H₃₆O₆S₃ requires C, 45·7; H, 8·6%), ν_{max} 1020, 1118, ¹³ W. E. Truce and G. D. Madding, Tetrahedron Letters, 1966, 3681.

¹⁴ H. Böhme and P. Heller, Chem. Ber., 1953, 86, 785.

1153, 1295, and 1308 cm.⁻¹. Dimethyl-(1-dodecylsulphonylmethyl)sulphonium methosulphate (VIb) had m.p. $69-70^{\circ}$ (Found: C, 45.8; H, 8.8%), ν_{max} 1010, 1140, and 1318 cm.⁻¹.

Preparation of Ylids (VIIa) and (VIIb).—Methosulphates (VIa) and (VIb) (1 equiv.) in water (20 ml. per g.) were stirred with aqueous sodium hydroxide (2 equiv.). The solutions became cloudy, and after 5—10 min. the ylids were completely precipitated. Yields of 75—80% were obtained. 1-Dodecylmethylsulphonium methylsulphonylmethylid (VIIa) had m.p. 64—65° (Found: C, 58·2; H, 10·3%; M, 308·1841. C₁₅H₃₂O₂S₂ requires C, 58·4; H, 10·4%; M, 308·1840), v_{max}. 948, 1088, 1250, and 1300 cm.⁻¹. Dimethylsulphonium 1-dodecylsulphonylmethylid (VIIb) had m.p. 74—75° (Found: C, 58·5; H, 10·15%; M, 308·1841), v_{max}. 955, 1091, and 1255 cm.⁻¹. Dimethylsulphonium Benzoyl-1-dodecylsulphonylmethylid

Dimethylsulphonium Benzoyl-1-dodecylsulphonylmethylid (XX).—Benzoyl chloride (0·2 g.) in tetrahydrofuran (1 ml.) was added to an ice-cold solution of dimethylsulphonium 1-dodecylsulphonylmethylid (0·4 g.) and triethylamine (0·6 g.) in tetrahydrofuran (5 ml.). When the addition was complete, the temperature was raised to 20° and the mixture was stirred for 2 hr. Triethylamine hydrochloride was removed by filtration, 1 drop of water was added to the filtrate to hydrolyse any residual benzoyl chloride, and after dilution with chloroform the solution was washed with aqueous sodium hydrogen carbonate and dried (Na₂SO₄). Removal of solvent yielded the *acylated ylid* (XX) (0·25 g.), m.p. 119—120° (from aqueous ethanol) (Found: C, 62·4; H, 9·3. $C_{22}H_{36}O_{3}S_{2}$ requires C, 62·2; H, 9·2°/), ν_{max} . 1562 cm.⁻¹ (CO), n.m.r. τ 9·12 ($CH_{3}[CH_{2}]_{n}$), 8·73 ($[CH_{2}]_{n}$), 8·20 ($CH_{2}CH_{2}SO_{2}$), 6·97 (+SMe₂), 6·72 ($CH_{2}SO_{2}$), and 2·62 (COPh).

Attempted Preparation of Dimethylsulphonium Methylsulphonylmethylid (VIIc).—Methylsulphonylmethylthiomethane (IX) (1.4 g.) was heated for 15 hr. at 60° with dimethyl sulphate (12.6 g.). The cooled solution was poured into ether, and an oil, which would not crystallise, separated. Without further purification, the oil was dissolved in 0.25N-sodium hydroxide (50 ml.), and after 15 min. the solution was extracted with chloroform. The extracts yielded a crystalline solid whose i.r. spectrum (v_{max} . 962, 1095, and 1250 cm.⁻¹) was very similar to that of ylid (VIIb). Within 10 min., the product liquefied and radical differences in the i.r. spectrum indicated that decomposition had occurred.

Thermal Decomposition of 1-Dodecylmethylsulphonium Methylsulphonylmethylid (VIIa).—The ylid (VIIa) (1.35 g.) was heated under reflux in benzene (30 ml.) for 6 hr. The product (1.32 g.) contained three components (t.l.c.). Chromatography on silica gel (60 g.) and elution with benzene gave dodec-1-ene (0.45 g.) identified by comparison with an authentic sample. Elution with benzene-ether (92:8) gave (a) 1-dodecylthiomethylsulphonylmethane (Va) (44 mg.), m.p. and mixed m.p. 65° (from light petroleum), n.m.r. spectrum identical with that of an authentic sample (Found: C, 57.4; H, 10.0. Calc. for $C_{14}H_{30}O_2S_2$: C, 57.15; H, 10.2%), and (b) methylsulphonylmethylthiomethane (IX) (0.65 g.), m.p. and mixed m.p. 50-51° (from chloroform-light petroleum), n.m.r. spectrum identical with that of an authentic sample (Found: C, 26.0; H, 5.9. Calc. for C₃H₈O₂S₂: C, 25.7; H, 5.7%).

Thermal Decomposition of Dimethylsulphonium 1-Dodecylsulphonylmethylid (VIIb).—(a) In benzene. A solution of the ylid (VIIb) (1·1 g.) in benzene (30 ml.) was heated under reflux for 4 hr. T.1.c. of the product revealed two major 2183

components, one of which had the same $R_{\rm F}$ value as dodecylsulphonylmethylthiomethane, and a trace of a third component. Column chromatography of the products (0.95 g.) on silica gel did not resolve the mixture. A portion (100 mg.) was resolved by preparative t.l.c. using light petroleum-acetone (9:1) as eluant. Two distinct bands were obtained. These were, in order of elution: (A) 1-(1-dodecylsulphonyl)-1-methylthioethane (XV) as a chromatographically homogeneous liquid (29 mg.), $v_{\rm max}$ 1125 and 1317 cm.⁻¹, n.m.r. τ 9·12 (CH₃[CH₂]_n), 8·72 (10CH₂), 8·30 [doublet; SO₂CH(CH₃)S], 7·65 (SCH₃), 6·82 (CH₂CH₂SO₂), and 6·22 [quartet; SO₂CH(CH₃)S]; (B) dodecylsulphonylmethylthiomethane (Vb) (32 mg.), m.p. and mixed m.p. 65—66° (Found: C, 57·1; H, 9·9%).

Fraction A (29 mg.) was heated at 100° for 30 min. with glacial acetic acid (0.2 ml.) containing hydrogen peroxide (0.02 ml.; 85%). Removal of volatile material gave 1-(1-dodecylsulphonyl)-1-methylsulphonylethane (XVI), m.p. and mixed m.p. $81.5-83^{\circ}$ (Found: C, 53.05; H, 9.4. Calc. for $C_{15}H_{32}O_4S_2$: C, 52.9; H, 9.4%).

(b) In pyridine. A solution of the ylid (VIIb) (0.5 g.) in pyridine (5 ml.) was kept at 60° for 6 hr. The dark solution was poured into water and extracted with chloroform. Evaporation of the extracts gave a dark semi-solid residue (0.21 g.) containing one main component (t.l.c.). Chromatography on silica gel (10 g.), eluting with benzeneether (95:5), gave dodecylsulphonylmethylthiomethane (Vb) (120 mg.), m.p. and mixed m.p. $64-65^{\circ}$. No other product was eluted.

1-(1-Dodecylsulphonyl)-1-methylsulphonylethane (XVI). Dodecylthiomethylsulphonylmethane (Va) (2 g.) was oxidised using glacial acetic acid (10 ml.) containing hydrogen peroxide (0.6 ml.; 85%) at 100° for 1 hr. Water was then added to precipitate 1-dodecylsulphonylmethylsulphonylmethane (XVII) (1.65 g.), m.p. 106—107° (from ethanol) (Found: C, 51.8; H, 9.4. $C_{14}H_{30}O_4S_2$ requires C, 51.5; H, 9.2%), ν_{max} . 1130, 1300, and 1325 cm.⁻¹, n.m.r. τ 9.13 (CH₃[CH₂]_n), 8.72 (10CH₂), 6.75 (CH₃SO₂), 6.58 (CH₂CH₂SO₂), and 5.56 (SO₂CH₂SO₂).

The above disulphone (XVII) (1.15 g.) was added to ethanol (20 ml.) containing sodium ethoxide (from 0.085 g. of sodium). The solution was heated under reflux for 15 min., and then cooled to 55°. Methyl iodide (0.53 g.) in ethanol (10 ml.) was added, and the solution kept at 55° for 4 hr., and then at 70° for 1 hr. Dilution with water precipitated 1-(1-dodecylsulphonyl)-1-methylsulphonylethane (XVI) (0.95 g.), m.p. 82—82.5° (from ethanol) (Found: C, 53.1; H, 9.25. $C_{15}H_{32}O_4S_2$ requires C, 52.9; H, 9.4%), v_{max} . 1125 and 1300 cm.⁻¹, n.m.r. τ 9.12 ($CH_3[CH_2]_n$), 8.72 ($10CH_2$), 8.15 [doublet; SO₂CH(CH_3)SO₂], 6.81 (CH_3SO_2), 6.65 ($CH_2CH_2SO_2$), and 5.80 [quartet; SO₂CH(CH_3)SO₂].

Photolysis of Ylids.—1-Dodecylmethylsulphonium methylsulphonylmethylid (VIIa) (1.55 g.) was irradiated in benzene (400 ml.) for 6 hr. in a nitrogen atmosphere. The crude product (1.4 g.) was chromatographed on silica gel (70 g.), to give dodec-1-ene (0.41 g.), dodecylthiomethylsulphonylmethane (Va) (0.26 g.), m.p. and mixed m.p. 65°, and methylsulphonylmethylthiomethane (IX) (0.27 g.), m.p. and mixed m.p. 50°. Traces of two other compounds were isolated but could not be purified.

Dimethylsulphonium 1-dodecylsulphonylmethylid (VIIb) (1.7 g.) was irradiated in similar fashion, to give 1-(1-dodecylsulphonyl)-1-methylthioethane (XV) (0.29 g.) and dodecylsulphonylmethylthiomethane (Vb) (0.33 g.).

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