

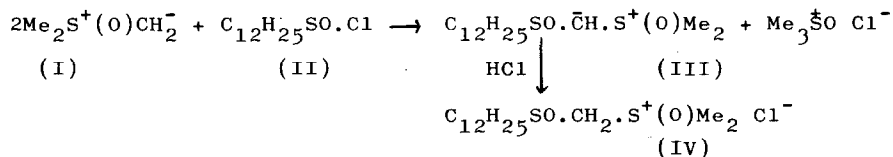
A SULPHINYL-STABILISED SULPHOXONIUM YLID

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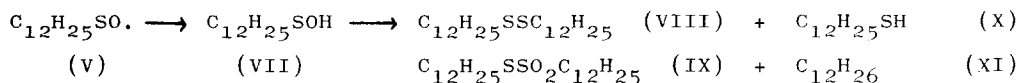
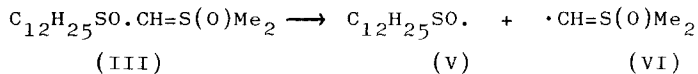
Reactions of dimethylsulphoxonium methylid (I) with acyl and sulphonyl halides yielding keto-sulphoxonium and sulphonyl-sulphoxonium ylids respectively, have been described (1,2). We now report that the reaction of I with an aliphatic sulphonyl chloride has yielded the first example of a new class of compound, a sulphonyl-stabilised sulphoxonium ylid.



Addition of dodecanesulphonyl chloride (II) (3) to a solution of I in tetrahydrofuran at  $-35^\circ$  gave a 22% yield of dimethylsulphoxonium dodecane-sulphonyl-methylid (III) with m.p.  $46-48^\circ$  (from ethanol); a crystalline hydrochloride (IV), m.p.  $94-95^\circ$ , was prepared by mixing solutions of III and hydrogen chloride (1 equiv.) in tetrahydrofuran at  $-40^\circ$  (4).

The ylid may be stored at  $0^\circ$  in the absence of light for at least 24 hr. before decomposition becomes noticeable. Its instability and insolubility precluded measurement of the N.M.R. spectrum. Infrared spectra of III and IV were consistent with the proposed structures, each showing a normal sulphoxide stretching mode, at  $1036$  and  $1049\text{ cm}^{-1}$  respectively, attributable to the  $\text{C}_{12}\text{H}_{25}\text{SO}$  grouping. Peaks at  $1232\text{ cm}^{-1}$  in the spectrum of IV and at  $1160\text{ cm}^{-1}$  in the spectrum of III have been assigned to the sulphoxonium stretching mode (cf. Ref.5). The lower frequency for III reflects the following probable structure:  $-\text{CH}=\text{S}(\text{O})\text{Me}_2 \longleftrightarrow -\bar{\text{C}}\text{H}\cdot\text{S}^+(\text{O})\text{Me}_2$ . The mass spectrum of III did not show a molecular ion; two major peaks at  $m/e$   $230.1705$  ( $\text{C}_{12}\text{H}_{25}\text{SO}\cdot\text{CH}^+$ ) and  $78.01439$  ( $\text{Me}_2\text{SO}^+$ ) were observed.

Thermolysis of III in ethanol (40°) produced didodecyl disulphide (VIII), dodecyl dodecanethiolsulphonate (IX), dodecanethiol (X) and a trace of n-dodecane (XI) (6). Significantly, compounds of types VIII-XI have been described (7) as typical sulphenic acid breakdown products. Thus it seems probable that dodecanesulphenic acid (VII) is formed as an intermediate in the decomposition of III. The mechanism of its formation is still uncertain but may involve homolysis of the ylid as shown:



Hydrogen abstraction from the solvent by dodecanesulphinyl radical (v) would account for the formation of VII. Surprisingly, dimethyl sulphoxide has not been detected among the decomposition products although it would be expected to arise from a fragment such as VI. The fate of this moiety remains to be established.

Although no general theory of ylid decomposition has been established, previous work (1) suggests that carbenes might be formed. However, no products derived from a sulphinyl carbene intermediate ( $\text{C}_{12}\text{H}_{25}\text{SO}\cdot\text{CH}$ ) were detected.

It is apparent that sulphinyl-stabilised sulphoxonium ylids are of marginal stability and it is likely that the short chain members are not isolable.

#### REFERENCES

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2. W.E. Truce and G.D. Madding, Tetrahedron Letters, 3681 (1966).
3. Dodecanesulphinyl chloride (b.p. 122-125/0.1mm) was prepared essentially by the general method of I.B. Douglass and B.S. Farah, J. Org. Chem., **24**, 973 (1959). It was distilled in small portions (< 3g.) to avoid excessive losses by decomposition.
4. Satisfactory analytical data were obtained for all new compounds.
5. F.A. Cotton, R. Francis and W.D. Horrocks, J. Phys. Chem., **64**, 1534 (1960)
6. These compounds were identified by comparison with authentic specimens.
7. N. Kharasch, Organic Sulphur Compounds, Pergamon Press, Vol.1, p.392.