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SULFONE-STABILIZED OXOSULFONIUM YLIDES

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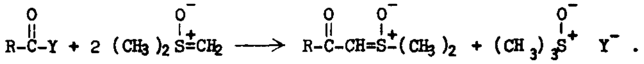
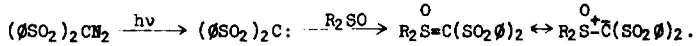
Recently several groups have reported the preparation of stable sulfonium (1-8) and oxosulfonium (9-13) ylides. By analogy to the reaction of two equivalents of dimethyloxosulfonium methylide (I) with an acyl chloride or a phenyl carboxylate ester to give a β-keto oxosulfonium ylide (10), interaction of the simple ylide with a sulfonyl halide should yield a sulfonyl-stabilized ylide. We would like to report the preparation of a series of sulfonyl-stabilized ylides by this process. There has been one other report of an oxosulfonium ylide stabilized by neighboring sulfone groups (11); this is the product resulting from the capture of bis(benzenesulfonyl)-methylene with various sulfides or sulfoxides. However, the ylide in that instance



$$R{-}\overset{\overset{O}{\|}}{C}{-}Y + 2\,(CH_3)_2\overset{\overset{O^-}{|}}{S}{}^{+}{=}CH_2 \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}CH{=}\overset{\overset{O^-}{|}}{S}{}^{+}{-}(CH_3)_2 + (CH_3)_3\overset{\overset{O^-}{|}}{S}{}^{+}\ Y^- .$$



$$(\phi SO_2)_2CN_2 \xrightarrow{h\nu} (\phi SO_2)_2C: \xrightarrow{R_2SO} R_2\overset{O}{S}{=}C(SO_2\phi)_2 \leftrightarrow R_2\overset{O}{S}{}^{+}{-}\bar{C}(SO_2\phi)_2 .$$

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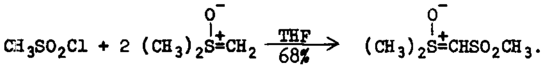
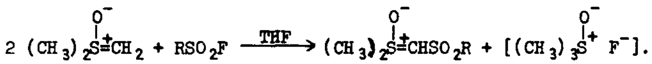
was stabilized by two neighboring sulfonyl groups.

Upon stirring a mixture of methanesulfonyl chloride with two equivalents of dimethyloxosulfonium methylide (I) in THF solution at room temperature for one hour, the sulfone-stabilized ylide, dimethyloxosulfonium methanesulfonylmethylide (II) was produced in 68% yield as a white crystalline solid, m.p. 145.5-148.5°, which is stable indefinitely at room temperature, but which seems to decompose upon heating to approximately 170°. The structure of this ylide has been shown conclusively by its elemental analysis, its infrared spectrum, and its NMR spectrum (see Table 1).



$$CH_3SO_2Cl + 2\ \underset{\text{I}}{(CH_3)_2\overset{O^-}{\overset{|}{S}}\overset{+}{=}CH_2} \xrightarrow[68\%]{THF} \underset{\text{II}}{(CH_3)_2\overset{O^-}{\overset{|}{S}}\overset{+}{=}CHSO_2CH_3}.$$

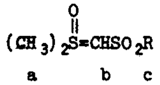
When benzenesulfonyl chloride or α-toluenesulfonyl chloride was treated with two equivalents of dimethyloxosulfonium methylide in THF solution, as above, no crystalline product was obtained, nor could starting material be recovered. It is known that when carbanions interact with sulfonyl chlorides, attack often occurs on chlorine to displace sulfinate, rather than on sulfur to displace chloride (14). It was possible that such might be the case in the interaction of I with sulfonyl chlorides, other than methanesulfonyl chloride. Therefore, the sulfonyl chlorides were converted to the corresponding sulfonyl fluorides (15), wherein displacement on halogen is less likely because of the lower polarizability of fluorine compared to chlorine. Indeed, the interaction of two equivalents of I with one equivalent of alkane- (or arene) sulfonyl fluoride (III) to give the dimethyloxosulfonium alkanesulfonylmethylide (IV) has been shown to be quite a general reaction; the yields of the stable crystalline products ranged from 40 to 90% depending upon the alkyl or aryl substituent. The sulfone-



$$\underset{\text{I}}{2\ (CH_3)_2\overset{O^-}{\overset{|}{S}}\overset{+}{=}CH_2} + \underset{\text{III}}{RSO_2F} \xrightarrow{THF} \underset{\text{IV}}{(CH_3)_2\overset{O^-}{\overset{|}{S}}\overset{+}{=}CHSO_2R} + \underset{\text{VI}}{[(CH_3)_3\overset{O^-}{\overset{|}{S}}{}^{+}\ F^-]}.$$

stabilized ylides prepared to date are summarized in Table 1.

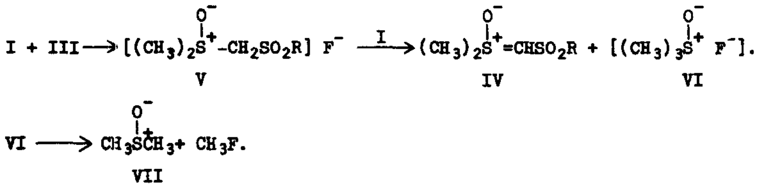
TABLE 1



$$\underset{a}{(CH_3)_2}\overset{O}{\overset{\|}{S}}{=}\underset{b}{CH}SO_2\underset{c}{R}$$

R or Ar	X	%	m.p.°	NMR (δ) a	 b	 c
CH_3	Cl	68.0	145.5-148.5	3.48	4.40	2.96 (CH_3)
CH_3CH_2	F	74.5	99-101	3.53	4.29	1.43 (CH_3) 3.17 (CH_2)
$C_6H_5CH_2$	F	42.0	137.5-140	3.30	3.95	4.35 (CH_2) 7.5 (Ar)
p-$CH_3OC_6H_4$	F	(91.5	127-128	3.53	4.29	3.91 (CH_3) 7.5 (Ar)
p-$CH_3C_6H_4$	F	45.0	144-146	3.46	4.35	2.38 (CH_3) 7.5 (Ar)

Presumably, this reaction involves the initial dispalcement of fluoride by one equivalent of I to give a dimethylalkanesulfonylmethyloxosulfonium fluoride (V), and the stable ylide (IV) is generated by loss of a proton to the second equivalent of I. A molecule of trimethyloxosulfonium fluoride (VI) would also be formed in the reaction. Another white solid is actually formed, but it decomposes quite rapidly to give dimethylsulfoxide. That the oxosulfonium salt V could be an



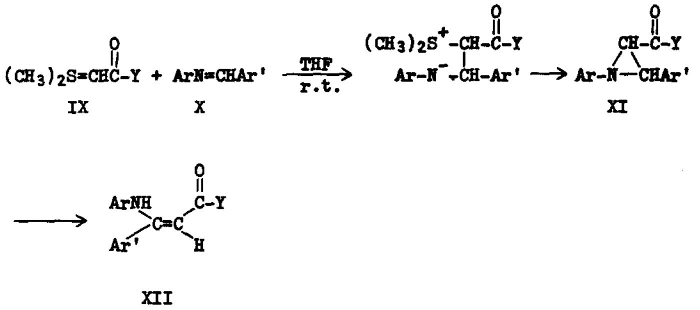
$$\mathrm{I} + \mathrm{III} \longrightarrow \underset{\mathrm{V}}{[(\mathrm{CH_3})_2\overset{\mathrm{O}^-}{\overset{|}{\mathrm{S}^+}}\mathrm{-CH_2SO_2R}]\ \mathrm{F}^-} \xrightarrow{\mathrm{I}} \underset{\mathrm{IV}}{(\mathrm{CH_3})_2\overset{\mathrm{O}^-}{\overset{|}{\mathrm{S}^+}}\mathrm{=CHSO_2R}} + \underset{\mathrm{VI}}{[(\mathrm{CH_3})_3\overset{\mathrm{O}^-}{\overset{|}{\mathrm{S}^+}}\ \mathrm{F}^-]}.$$

$$\mathrm{VI} \longrightarrow \underset{\mathrm{VII}}{\mathrm{CH_3}\overset{\mathrm{O}^-}{\overset{|}{\mathrm{S}^+}}\mathrm{CH_3}} + \mathrm{CH_3F}.$$

intermediate in the reaction is shown by the fact that dimethyloxosulfonium methanesulfonylmethylide (II) yields dimethylmethanesulfonylmethyloxosulfonium chloride (VIII) upon treatment with dilute hydrochloric acid, and the ylide can be regenerated by treatment of the salt with aqueous sodium hydroxide.

A number of experiments have been conducted to determine the potential reactivity of the sulfone-stabilized ylides, and it has become obvious that the most significant feature of these compounds, not unlike the dimethylsulfonium dicyanomethylides (3), is their exceptional stability.

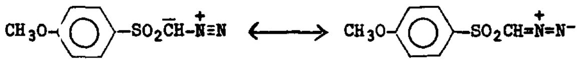
It has been shown that certain carbonyl-stabilized ylides (IX) react with Schiff's bases (X) to give α-aminocinnamic acid derivatives (XII) (1). These workers feel that the reaction proceeds through aziridine (XI) formation, followed by ring opening. Similar reactions were



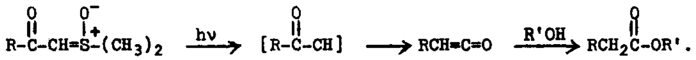
attempted using the sulfone-stabilized ylides. For example, stirring IV (R=CH_3 or p-$CH_3OC_6H_4$) with benzalaniline (X, Ar=Ar'=C_6H_5) in THF at room temperature or at reflux for as much as 24 hours gives nearly quantitative recovery of both starting materials. To the extent that the ylides partake of the charge separated form, $R_2\overset{\overset{O}{\|}}{S}{}^{+}\text{-}\bar{C}HSO_2R$, the reaction should be influenced by the nature of the solvent. In particular, it is generally agreed that dimethylsulfoxide and dimethylformamide promote anion reactions. Therefore, the reactions above were attempted in DMSO at room temperature, and at 60°, and in DMF at room temperature, 60°, and at reflux. No cleam reaction was observed in any case; in refluxing DMF there seemed to be some decompostion leading to a small amount of gummy material.

p-Nitrobenzaldehyde is normally reactive toward nucleophiles, but it gave no reaction with IV (R=CH_3 or p-$CH_3OC_6H_4$) when experiments were conducted under the various conditions described above, except in the case of refluxing DMF solvent, wherein a small amount of unidentified gummy material was obtained.

Another interesting possibility was investigated. The preparation of p-methoxybenzenesulfonylcarbene (XIII) has been accomplished by the photolysis of p-methoxybenzenesulfonyldiazomethane (XIV) (16); the α-diazosulfone is somewhat analogous to an ylide as shown by the resonance form XIV. Furthermore, a number of β-keto-oxosulfonium ylides (XVI) have been decomposed photolytically to carbonylcarbenes (XVII), which rearrange to ketenes (XVIII) (10, 17). By analogy to these examples it seemed that the sulfone-stabilized ylides might decompose photolytically (or pyrolytically) to give a sulfonyl carbene. Therefore, IV ($R{=}p\ CH_3OC_6H_4$) was heated with cyclohexene in a sealed tube at 170° for one hour. The ylide was partially recovered; the rest of the material was a dark tar which could not be purified or identified. Next, IV ($R{=}\ \underline{p}\text{-}CH_3OC_6H_5$) was irridiated in methanol at approximately 260 mμ for periods up to 24 hours, and the starting ylide was recovered each time.



XIV XV



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH{=}\overset{\overset{O^-}{|}}{S^+}\text{-}(CH_3)_2 \xrightarrow{h\nu} [R\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH] \longrightarrow RCH{=}C{=}O \xrightarrow{R'OH} RCH_2\overset{\overset{O}{\|}}{C}\text{-}OR'.$$

XVI XVII XVIII

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