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REACTIONS OF SULFINATES AND SULFOXYLATES WITH METHYL HALOSULFONATES AND TRIFLUOROMETHANESULFONATE. EVIDENCE FOR THE FORMATION OF DIALKOXYSULFONIUM IONS

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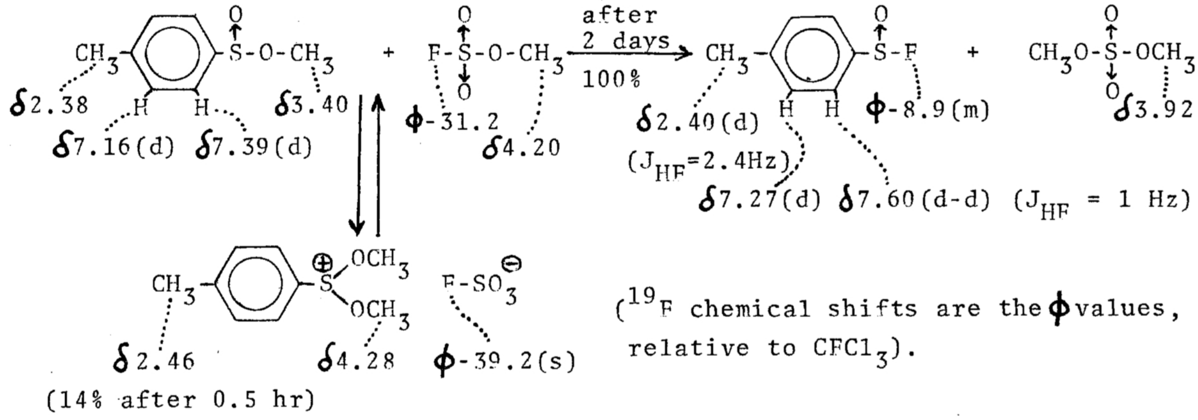
Dialkoxysulfonium ions were prepared by methylation of sulfinates and sulfoxylates.

Alkoxysulfonium ions, $R_1R_2\overset{\oplus}{S}\text{-}OR_3$, were prepared and studied,[1] but the formation of dialkoxysulfonium ions and trialkoxysulfonium ions has not been reported in the literature. Methylations of sulfinates, sulfoxylates and sulfites were attempted in nmr tubes with methyl fluorosulfonate (1), methyl chlorosulfonate (2) and methyl trifluoromethanesulfonate (3).

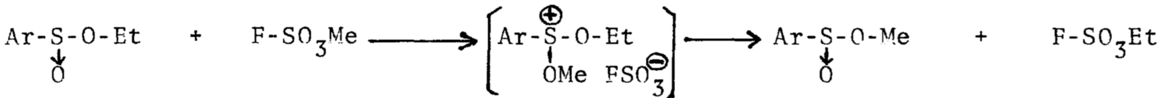
When a mixture of methyl p-toluenesulfinate (0.59 mmol) and 1 (3.1 mmol) in an nmr tube was allowed to stand at 34°C, the absorptions attributable to dimethoxy-p-tolylsulfonium fluorosulfonate were present (0.14 mol/mol of the ester) after 0.5 hr, but the amount of the sulfonium ion did not increase further. After 2 days, the reactants were converted almost quantitatively to p-toluenesulfinyl fluoride and methyl sulfate.



(^{19}F chemical shifts are the φ values, relative to $CFCl_3$).

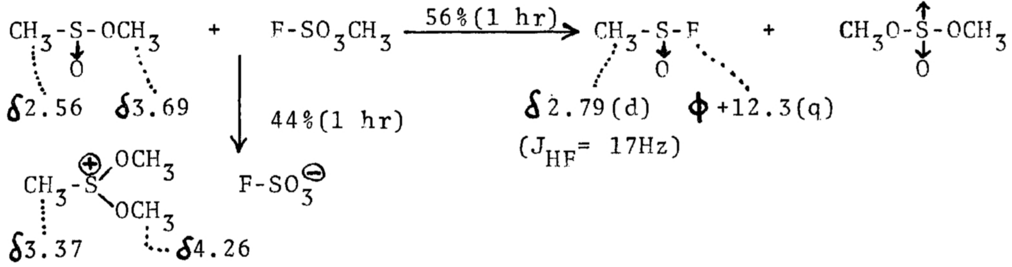
One should note the fairly large J_{HF} value for the coupling through seven bonds between the F and the methyl H's in p-$CH_3C_6H_4S(O)F$. The J_{HF}'s for the methyl H's and F in p-$CH_3C_6H_4SO_2$-F and p-$CH_3C_6H_4F$ were 0 and 1.5 Hz, respectively.[2]

When the above reactants were diluted with dichloromethane, the dialkoxysulfonium ion was not observed by nmr, but its formation was suggested from the finding that ethyl p-toluenesulfinate was converted to its methyl ester in a mixture with 1 and dichloromethane.


$$\mathrm{Ar{-}\underset{\downarrow O}{S}{-}O{-}Et} + \mathrm{F{-}SO_3Me} \longrightarrow \left[\mathrm{Ar{-}\overset{\oplus}{S}{-}O{-}Et}\ \ \mathrm{OMe}\ \ \mathrm{FSO_3^{\ominus}}\right] \longrightarrow \mathrm{Ar{-}\underset{\downarrow O}{S}{-}O{-}Me} + \mathrm{F{-}SO_3Et}$$

When methyl p-methoxybenzenesulfinate(0.81 mmol) was treated with 1(6.6 mmol), 26% of the ester was converted to the corresponding dimethoxysulfonium ion in 1.3 hr. After 50 hr, the reactants were quantitatively converted to methyl sulfate and p-methoxybenzenesulfinyl fluoride (MeO, δ 3.84(s); F, ϕ -12.3 ppm(m)).

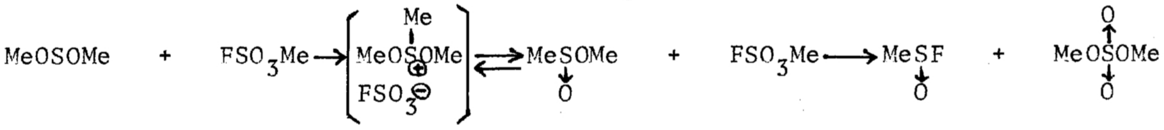
When a mixture of methyl methanesulfinate(3.2 mmol) and 1(6.4 mmol) was allowed to stand at 34°C for 1 hr, its nmr spectrum suggested the formation of dimethoxymethylsulfonium ion in 44% yield and methanesulfinyl fluoride and methyl sulfate in 56% yield.



Methanesulfinyl fluoride has not been described in the literature. Since it is unstable and reacts with glass, it was not possible to isolate it. Its structural assignment is based on the analogy to the reactions between methyl p-toluenesulfinate and 1 and between methyl sulfite and 1 (vide infra) and the nmr data: H absorptions; $\mathrm{MeO\underset{O}{S}Cl}$, δ, 4.04; $\mathrm{MeS(O_2){-}Cl}$, 3.66; $\mathrm{Me\underset{O}{S}Cl}$,3.32; $\mathrm{MeO\underset{O}{S}F}$, 3.87(d); $\mathrm{MeS(O_2){-}F}$, 3.27; $\mathrm{Me\underset{O}{S}F}$, 2.79(d).

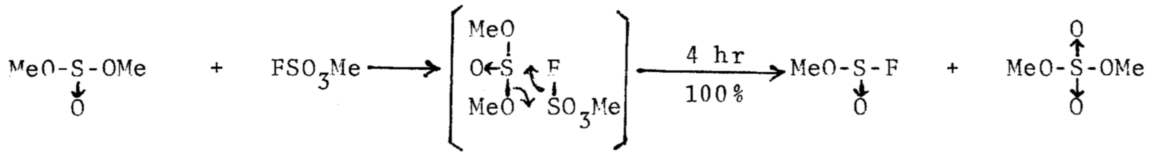
The methanesulfinyl fluoride in a sealed nmr tube gradually decomposed, and after 3 days only one strong absorption observed was that of methyl sulfate.

When a mixture of methyl sulfoxylate(1.1 mmol) and 1(2.3 mmol) was allowed to stand in an nmr tube, dimethoxymethylsulfonium ion (47%), methanesulfinyl fluoride (9%) and methyl sulfate (9%) were present after 2.5 hr. A plausible reaction path is shown below. Methanesulfinyl fluoride is formed probably not from $\mathrm{Me\overset{\oplus}{S}(OMe)_2}$ but directly from MeS(O)OMe and 1, since in the case of MeOSOMe, much less MeS(O)F and much more $\mathrm{Me\overset{\oplus}{S}(OMe)_2}$ are formed than in the case of MeS(O)OMe.


$$\mathrm{MeOSOMe} + \mathrm{FSO_3Me} \rightarrow \left[\mathrm{MeO\overset{Me}{\underset{\oplus}{S}}OMe}\ \ \mathrm{FSO_3^{\ominus}}\right] \rightleftarrows \mathrm{Me\underset{\downarrow O}{S}OMe} + \mathrm{FSO_3Me} \longrightarrow \mathrm{Me\underset{\downarrow O}{S}F} + \mathrm{MeO\overset{O\uparrow}{\underset{\downarrow O}{S}}OMe}$$

(47% after 2.5 hr)

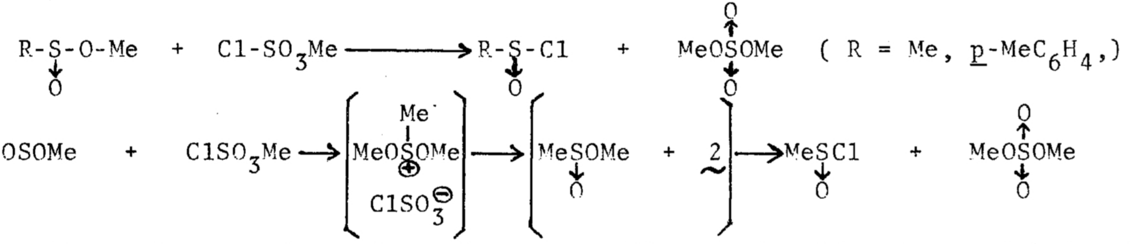
When a mixture of methyl sulfite and 1 was allowed to stand in an nmr tube, trimethoxysulfonium ion was not detected. After 4 hr, the reactants were converted almost quantitatively to methyl fluorosulfinate and methyl sulfate.



The displacement of F in 1 with OMe is a rather unusual reaction of 1. A plausible mechanism for this reaction is the 4-centered displacement shown above. A similar 4-centered mechanism is plausible for the reaction between MeS(O)OMe and 1, forming RS(O)F and Me_2SO_4.

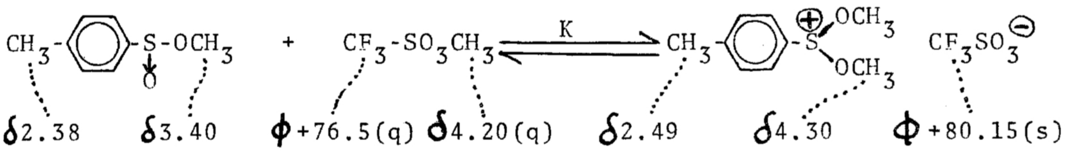
The method described in the literature for the preparation of FS(O)OMe is the reaction of ClS(O)OMe and KSO_2F.[3] However, its preparation from methyl sulfite and 1 is quick and quantitative, and seems to be a better method.

The reactions of sulfinates and sulfoxylates with methyl chlorosulfonate (2) proceeded faster than those with 1; the reactions were almost instantaneous at room temperature and no sulfonium ions were detected by nmr. The results can be represented as follows.

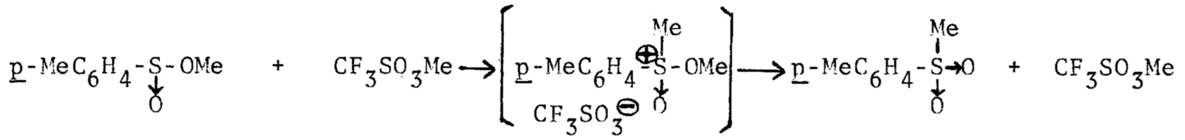


Since the reactions of sulfinates, sulfites and sulfoxylates with 1 and 2 always involve the rupture of the S-F and S-Cl bonds, use of methyl trifluoromethanesulfonate (3) was examined.

When a mixture of methyl p-toluenesulfinate (0.58 mmol) and 3 (3.3 mmol) was allowed to stand in a sealed nmr tube for 2 hr, its nmr spectrum showed the presence of dimethoxy-p-tolylsulfonium trifluoromethanesulfonate. No further change was observed with elapse of time, and the equilibrium constant was calculated; $K = 2.2 \times 10^{-3}$. The dimethoxysulfonium ion was stable and did not decompose in 3.



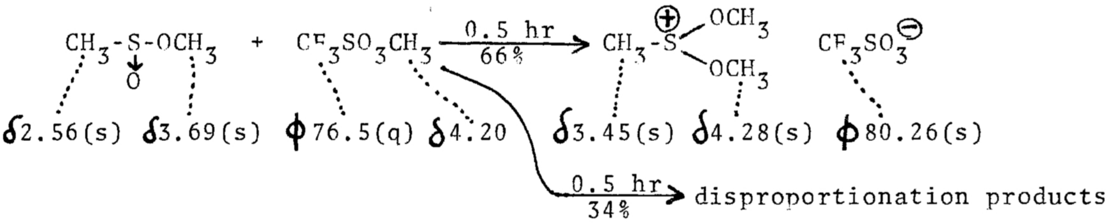
When the equilibrium mixture of methyl p-toluenesulfinate and 3 containing the dimethoxysulfonium ion was heated at 100°C for 5 hr, 47% of the ester was converted to methyl p-tolyl sulfone. This finding suggests the following pathway, which involves S-methylation of the ester forming an alkoxyoxosulfonium ion.



$$p\text{-}MeC_6H_4\text{-}\underset{\underset{O}{\downarrow}}{S}\text{-}OMe + CF_3SO_3Me \longrightarrow \left[\begin{matrix} p\text{-}MeC_6H_4\text{-}\overset{\overset{Me}{|}}{\underset{\underset{O}{\downarrow}}{\overset{\oplus}{S}}}\text{-}OMe \\ CF_3SO_3^{\ominus} \end{matrix}\right] \longrightarrow p\text{-}MeC_6H_4\text{-}\overset{\overset{Me}{|}}{\underset{\underset{O}{\downarrow}}{S}}\rightarrow O + CF_3SO_3Me$$

When a mixture of methyl p-methoxybenzenesulfinate (0.83 mmol) and **3** (3.4 mmol) was allowed to stand, 21% of the ester was converted to the corresponding dimethoxysulfonium ion after 1 hr, 26% after 23.5 hr and 26% after 50 hr. The equilibrium constant was calculated; $K = 2.4 \times 10^{-2}$.

When a mixture of methyl methanesulfinate (0.91 mmol) and **3** (2.8 mmol) was allowed to stand for 0.5 hr, 66% of the ester was converted to dimethoxymethylsulfonium ion and 34% yielded various disproportionation products. This dimethoxysulfonium ion was stable for several days at room temperature, and for 2 weeks at -20°C.

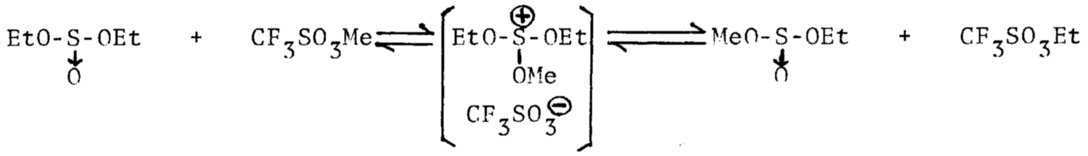


$$CH_3\text{-}\underset{\underset{O}{\downarrow}}{S}\text{-}OCH_3 + CF_3SO_3CH_3 \xrightarrow[66\%]{0.5\ hr} CH_3\text{-}\overset{\oplus}{S}(OCH_3)_2 \quad CF_3SO_3^{\ominus}$$

$$\xrightarrow[34\%]{0.5\ hr} \text{disproportionation products}$$

The dimethoxysulfonium ion was found to be a powerful methylating agent. When methyl sulfide was added, it reacted exothermically, forming trimethylsulfonium ion and methyl methanesulfinate.

When methyl sulfite was treated with **3**, formation of trimethoxysulfonium ion was not detected by nmr. However, when ethyl sulfite was allowed to stand in **3**, methyl ethyl exchange occurred (7% in 24 hr, 16% in 50 hr). This suggests the formation of $MeO\text{-}\overset{\oplus}{S}(OEt)_2$ in small concentration as a pathway of the methyl ethyl exchange.



$$EtO\text{-}\underset{\underset{O}{\downarrow}}{S}\text{-}OEt + CF_3SO_3Me \rightleftharpoons \left[\begin{matrix} EtO\text{-}\underset{\underset{OMe}{|}}{\overset{\oplus}{S}}\text{-}OEt \\ CF_3SO_3^{\ominus} \end{matrix}\right] \rightleftharpoons MeO\text{-}\underset{\underset{O}{\downarrow}}{S}\text{-}OEt + CF_3SO_3Et$$

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