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TOSYLSULFONIUM IONS AND ACYLSULFONIUM IONS

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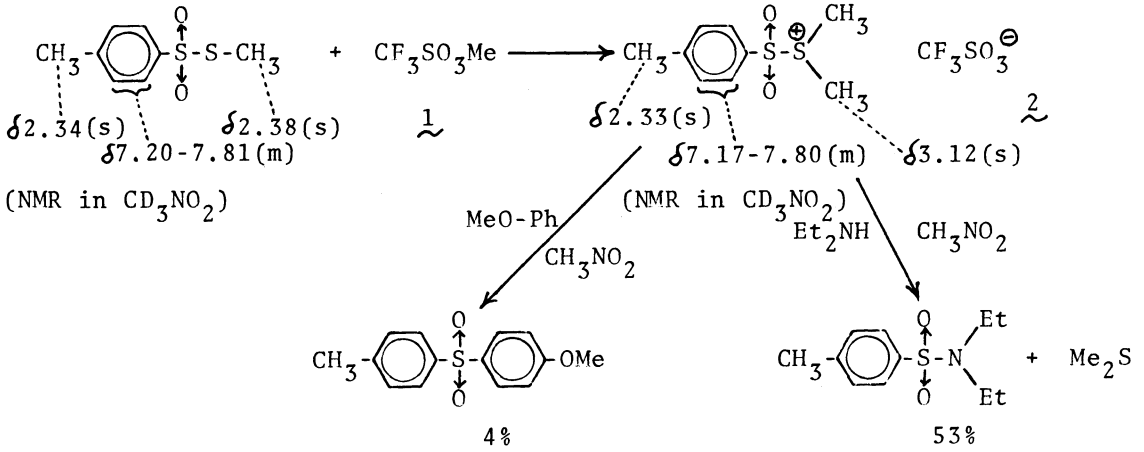
When p-Tol-SO_2-SMe and CF_3SO_3Me were allowed to react in a sealed tube, p-Tol-SO_2-$\overset{\oplus}{S}Me_2$ $CF_3SO_3^{\ominus}$ was isolated as crystals, which upon reaction with Et_2NH yielded p-Tol-SO_2NEt_2. The reaction between p-Tol-SO_2SMe and FSO_3H did not yield p-Tol-$SO_2\overset{\oplus}{S}HMe$ $FSO_3^{\ominus}$ but yielded p-Tol-$\overset{\oplus}{S}O_2H$-SMe $FSO_3^{\ominus}$. From the reaction between $PhCH_2CO$-SMe and CF_3SO_3Me, $PhCH_2CO\overset{\oplus}{S}Me_2$ was not observable, and the products found were $Me_3\overset{\oplus}{S}$ and $PhCH_2CO_2Me$.

Sulfonium ions possessing hetero-atom substituents such as alkoxy and amino groups have been investigated in our laboratories.[1-5] In connection with these studies, sulfonium ions possessing electron-withdrawing tosyl and acyl groups as substituents have been investigated, and the results are described in this communication.

When a mixture of methyl p-toluenethiolsulfonate (2.5 mmol) and methyl trifluoromethanesulfonate (1) (4.4 mmol) was sealed in a pyrex tube (10 mm O. D.) and allowed to stand at room temperature, crystals began to appear after 1 day. After 10 days, the tube was opened and the excess 1 was evaporated under reduced pressure. Colorless crystals were obtained, which were found to be very hygroscopic. The NMR spectrum of the crystals determined in CD_3NO_2 suggested that this compound is dimethyl-p-toluenesulfonylsulfonium trifluoromethanesulfonate (2).

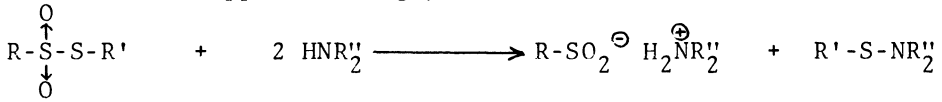


These crystals were dissolved in nitromethane, and diethylamine (25 mmol) was added. The solution became red. The NMR spectrum of the reaction mixture showed that dimethyl sulfide (δ, 2.10 ppm) is present. After it was allowed to stand overnight, the solvent was evaporated under reduced pressure. Some amount of ether was

added to the residue, and diethylammonium triflate crystals were filtered. A column-chromatographic separation (silica gel) of the residue yielded crystals of N,N-diethyl-p-toluenesulfonamide (identified by comparison of its NMR and IR spectra with those of an authentic sample); yield, 1.33 mmol(0.53 mol/mol of TsSMe).

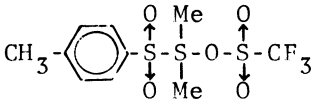
The reaction of 2 with anisole was also investigated. In purified nitromethane (10 ml), 2 (2.5 mmol) was allowed to react with anisole (5 mmol) for 1 week in a closed tube at room temperature. Then the nitromethane was evaporated under a reduced pressure, and the residue was separated by thin layer chromatography. A fraction was found to be p-tolyl p-anisyl sulfone (identified by comparison of its NMR and IR spectra with those of an authentic sample); yield, 0.095 mmol (0.04 mol/mol of TsSMe).

Colorless crystals of 2 readily decomposed by a trace amount of moisture, and neither its elemental analysis nor anion exchange was possible. However, its NMR data and the results of the reactions with diethylamine and anisole described above show that it is a dimethyl-p-toluenesulfonylsulfonium salt. The results reported by Dunbar and Rogers[6] that the reactions between thiolsulfonates and amines yield sulfenamides and sulfinic acids support strongly our conclusion.

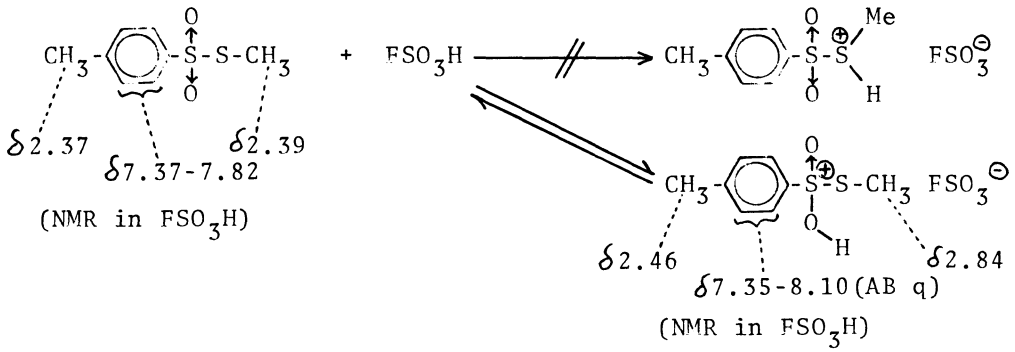


It is of interest that tosylsulfonium salts have lifetime long enough for isolation at room temperature. It is also worth noting that the attack of diethylamine takes place on the sulfonyl sulfur atom of 2, and very little, if any, on the methyl groups.

It is possible that 2 is a sulfurane (shown below) rather than a salt. However, its ^{19}F-NMR spectrum excludes the possibility. The ^{19}F in 2 absorbs at Φ80.15 ppm, while $CF_3SO_3^{\ominus}$ absorbs at Φ80.15 and CF_3SO_3Me absorbs at Φ76.50 ppm.

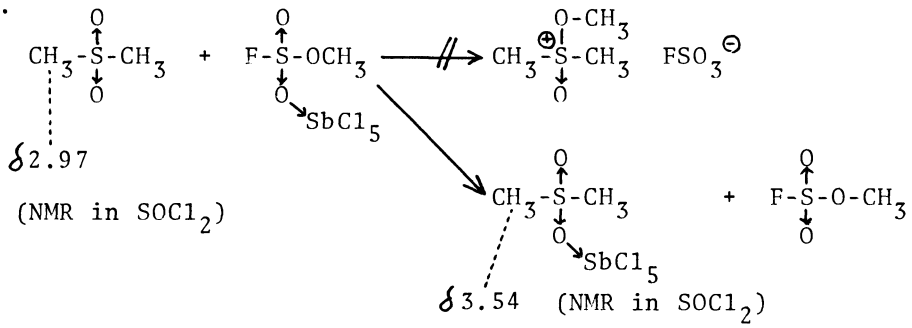


The synthesis of methyl-p-tosylsulfonium ion was attempted by protonation of p-Ts-SMe by magic acid. When p-TsSMe was dissolved in magic acid at -40°C, the NMR spectrum of the solution showed that the sulfonium ion formed is not methyl-p-tosylsulfonium ion but hydroxy(methylthio)oxo(p-tolyl)sulfonium ion shown below. Apparently the sulfonyl oxygen is more basic than the sulfide sulfur atom of p-TsSMe.



Its NMR spectrum did not change when the mixture was kept at -20 -40°C, but the salt decomposed when its isolation was attempted.

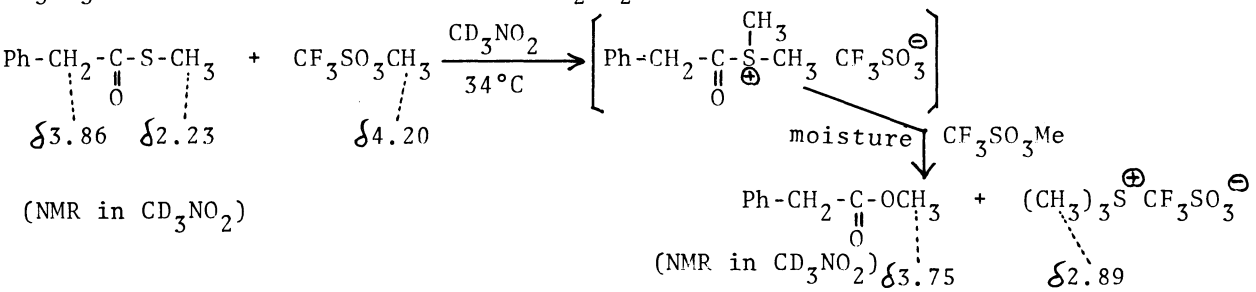
Since this oxohydroxysulfonium ion appears to be interesting, synthesis of an analogous oxomethoxysulfonium ion was attempted by methylation of a sulfone. When methyl sulfone and $FSO_3Me \cdot SbCl_5$ (1 : 1) were mixed in SO_2ClF at -70°C, colorless needles precipitated. They were filtered, and the NMR spectrum of the crystals was determined in $SOCl_2$ at room temperature. This compound was found to be a complex between methyl sulfone and $SbCl_5$. When phenyl sulfone and methyl p-tolyl sulfone were mixed with $FSO_3Me \cdot SbCl_5$ (1:1), $Ph_2SO_2 \cdot SbCl_5$ and $p\text{-TolMeSO}_2 \cdot SbCl_5$ precipitated, respectively.



Use of other methylating agents did not yield methylated sulfones either. Thus, protonation of sulfones is possible, but alkylation of sulfones seems to be very difficult, if not impossible.

It has been suggested that a FSO_3Me-Lewis acid complex is a methylating agent more powerful than magic methyl (FSO_3Me) itself.[7,8] However, we found that the $J_{^{13}C\text{-}H}$ and δ_H of $FSO_3Me \cdot SbCl_5$ are the same as those of free FSO_3Me (153 Hz and 4.20 ppm, respectively). These data show that the positive character of the methyl carbon of $FSO_3Me \cdot SbCl_5$ is equal to that of free FSO_3Me, and hence the methylating power of $FSO_3Me \cdot SbCl_5$ is expected not to be greater than magic methyl itself.

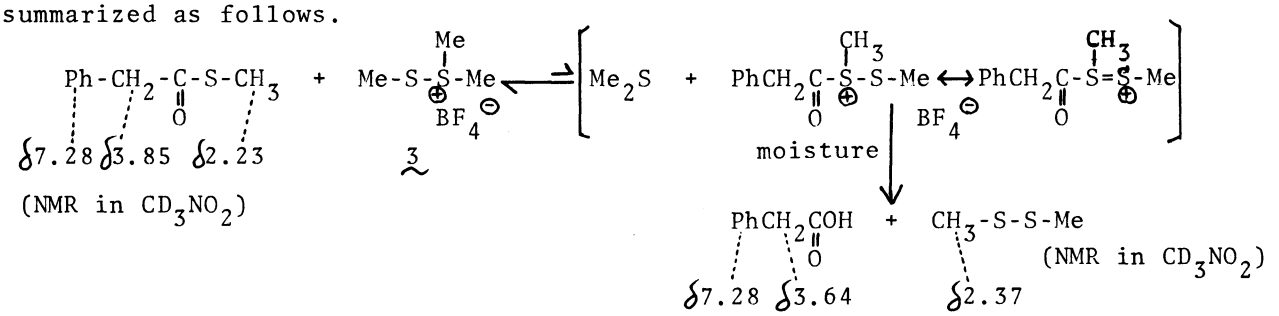
Methylations of thiolesters with triethyloxonium tetrafluoroborate and diethoxycarbonium hexachloroantimonate were reported in the literature,[9] but acylsulfonium salts were not isolated. Therefore, methylations of thiolesters with 1 were examined. A mixture of $PhCH_2CO\text{-}SMe$ (0.48 mmol), 1 (3.64 mmol), and CD_3NO_2 (0.3 ml) was allowed to stand at 34°C in a sealed NMR tube and its NMR spectrum was determined occasionally. After 4 h, 0.23 mmol(48 mol%) of trimethylsulfonium triflate was present. After 2 days, the NMR spectrum showed that the mixture contains $Me_3S^{\oplus}$ $CF_3SO_3^{\ominus}$ (0.46 mmol; 96 mol%) and $PhCH_2CO_2Me$ (0.46 mmol; 96 mol%).



No evidence for the presence of the dimethylacylsulfonium ion was obtained from the NMR spectra during the reaction. Apparently the dimethylacylsulfonium ion formed were decomposed by trace amount of moisture in the solvent, and cannot be isolated as

such. The reaction of S-methyl thiobenzoate with 1 gave similar results and the yield of $Me_3S^{\oplus}\ CF_3SO_3^{\ominus}$ was 57% after 4 h and 100% after 48 h.

Then the reaction between $PhCH_2CO$-SMe and dimethylmethylthiosulfonium tetrafluoroborate (3) was examined. The acylsulfonium ion formed from these two has a methylthio group capable of 3p-3d resonance stabilization of the sulfonium ion. When $PhCH_2CO$-SMe (1.69 mmol) and 3 (1.58 mmol) were mixed in CD_3NO_2 (2 ml; dried with molecular sieve), no change was observed in the NMR spectrum. Apparently the initial reaction between these two is reversible, and the equilibrium of the reversible reaction lies far to the left.[10] When the mixture was heated at 80°C for 6 h, irreversible change occurred. Vacuum distillation of the mixture gave methyl disulfide (0.66 mol/mol 3). From the residue, phenylacetic acid was obtained (identified from its NMR and IR spectra); yield, 0.76 mol/mol 3. The reaction can be summarized as follows.



Thus, a tosylsulfonium salt is isolable as crystals at room temperature, while an acylsulfonium salt is not. In view of the stronger electron-withdrawing power of the tosyl group in comparison with that of an acyl group, this fact is puzzling. This difference in the reactivity with nucleophiles is probably ascribable to a steric factor; the tosyl sulfur atom of 2 is sterically blocked by the four substituents and the access of nucleophiles is very difficult, whereas the carbonyl carbon atom of an acylsulfonium ion is easily accessible. It is also worth noting that both the tosyldimethylsulfonium ion and acyldimethylsulfonium ion appeared to act as tosylating and acylating agents rather than methylating agents toward nucleophiles.

REFERENCES

1. H. Minato, K. Yamaguchi, and M. Kobayashi, Chem. Lett., 307 (1975).
2. H. Minato, T. Miura, and M. Kobayashi, Chem. Lett., 701 (1975).
3. H. Minato, K. Yamaguchi, and M. Kobayashi, Chem. Lett., 991 (1975).
4. H. Minato, T. Miura, and M. Kobayashi, Chem. Lett., 1055 (1975).
5. H. Minato, K. Okuma, and M. Kobayashi, Chem. Commun., 868 (1975).
6. J. E. Dunbar and J. H. Rogers, J. Org. Chem., 31, 2842 (1966).
7. M. G. Ahmed, R. W. Alder, G. H. James, M. L. Sinnott, and M. C. Whiting, Chem. Commun., 1533 (1968).
8. R. W. Alder, Chem. Ind., 20, 783 (1973).
9. M. Mori, M. Shiozawa, Y. Ban, and T. Oishi, Chem. Pharm. Bull., 19, 2033 (1971).
10. H. Minato, T. Miura, F. Takagi, and M. Kobayashi, Chem. Lett., 211 (1975); J. K. Kim and M. C. Caserio, J. Amer. Chem. Soc., 96, 1930 (1974); S. H. Smallcombe and M. C. Caserio, ibid., 93, 5826 (1971).

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