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METHYLSULFONIUM SALTS OF 1,3,5-TRITHIANE

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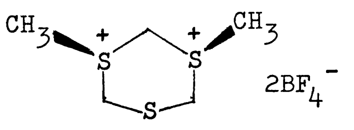
Mono-S-methylation of 1,3,5-trithiane (1) is effected smoothly by heating 1 in dimethyl sulfate or in methyl p-toluenesulfonate. A mixture of cis- and trans-1,3-dimethylbissulfonium salts of 1 is obtained by methylation with the Meerwein or Borch reagents. With all attempts no trimethylation of 1 is successful. Nucleophilicity of the last sulfur atom is suppressed to a considerable extent by the two sulfur atoms already methylated.

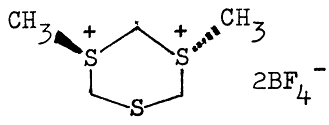
The reaction of methyl iodide with 1,3,5-trithiane (1) in methanol has been reported to give trimethylsulfonium iodide.1) Since iodide ion is an effective nucleophile, displacement reaction takes place. We have carried out the methylation of 1 under alternate conditions and have found that mono-S-methylation of 1 is effected smoothly, dimethylation takes place sluggishly, and trimethylation is never accomplished.

When 1 was heated at 80°C for 10 min in dimethyl sulfate and the cooled solution was diluted with ether, the mono-S-methylsulfonium salt of 1 is obtained in high yield. The oily product was treated with aqueous sodium tetraphenylborate to give 1-methyl-1,3,5-trithianium tetraphenylborate: mp 150 ~ 151°C decomp; nmr (CD_3CN):a singlet at δ 3.00 (3H, CH_3-S^+), two AB quartets centered at 4.14 (2H, S-CH_2-S, $\Delta\nu_{AB}$= 18.2 Hz, J_{AB}= 15.2 Hz) and 4.75 (4H, S-CH_2-S^+, $\Delta\nu_{AB}$= 32.1 Hz, J_{AB} = 14.4 Hz), and a multiplet at 6.6 ~ 7.4 (20H, Ph).2) Prolonged heating afforded trimethylsulfonium hydrogen sulfate and polyoxymethylene. No 1,3-dimethylbissulfonium salt of 1 is obtained under these conditions.3)

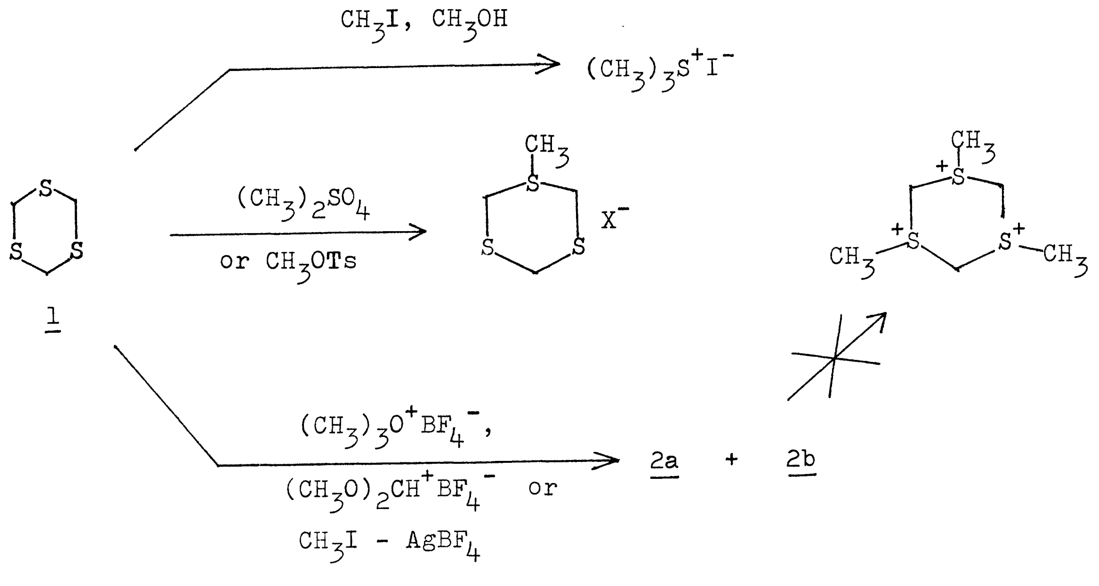
Methylation of 1 with excess trimethyloxonium fluoroborate (Meerwein's reagent)4) or dimethoxycarbonium fluoroborate (Borch reagent)5) in dichloromethane at room temperature with exclusion of moisture gave 1,3-dimethyl-1,3,5-trithianium bisfluoroborate (2) in 100 % yield.[6] The bissulfonium salt was recrystallized by dissolving in a minimum amount of deionized water followed by slow addition of ethanol to give the less soluble isomer 2a whose spectral properties indicated it to be the cis isomer: mp 147∼148°C decomp; nmr (CD_3CN) : a singlet at 3.26 (6H, CH_3-S^+), a double doublet at 4.90 (4H, S-CH_2-S^+, $\Delta\nu_{AB}$= 15.3 Hz, J_{AB}= 14.8 Hz), and a broad singlet at 5.21 (2H, S^+-CH_2-S^+). Note that chemical shift difference between the axial and equatorial ring protons flanked by the two sulfonium sulfur atoms vanishes in 2a.[7] The trans isomer 2b, mp 142∼144 °C decomp., was obtained from the mother liquor. Nmr (CD_3CN):a singlet at δ 3.29 (6H, CH_3-S^+), a broad singlet at 4.94 (4H, S-CH_2-S^+), and a broad singlet at 5.21 (2H, S^+-CH_2-S^+). The axial and equatorial groups are considered to be interconverting by the ring inversion. Nmr assay of the crude methylation products 2 revealed that 2a and 2b are formed in a ratio of 1.8 to 1.[8]



2a

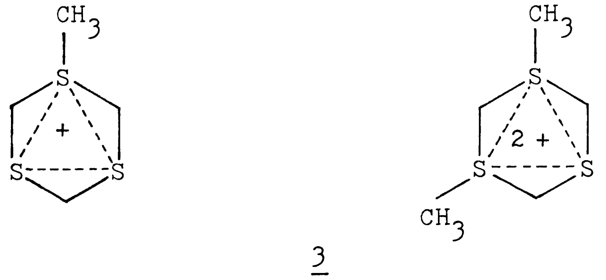


2b



The same product is obtained by the reaction of methyl iodide on a suspension of the preformed silver fluoroborate complex of 1 in 1,2-dichloroethane. Several attempts to effect trimethylation of 1 including, for example, the action of the Borch reagent without a solvent or in nitromethane at elevated temperature, were unsuccessful.

The distinctively stepwise methylation and resistance to the third methylation of 1 obtained above show that the nucleophilic reactivity of the second and third sulfur atoms is reduced by the first and second sulfonium centers introduced in the molecule in advance. Partial methylation of bissulfides is not without a precedent. Thus 1,4-dithiins are only monomethylated with a methyl iodide - silver fluoroborate combination.9) Conjugation between two sulfur atoms via two ethylene groups is apparent in these examples to reduce the nucleophilic reactivity of the second sulfur atom. No interaction between sulfur atoms of classical sense is present in 1,3,5-trithianes. The polar substituent effects of two $>S^{+}\text{-}CH_2\text{-}$ groups on the intact sulfur atom in 2 can explain only a part of the reduced reactivity. Previously we have proposed on the ESCA data10) the electron delocalization between the sulfur atoms in 1,3,5-trithiane. The present findings appear to provide chemical support for the importance of the conjugative interaction as shown in 3 which is formally a heterocyclic counterpart of the Winstein's trishomocyclopropenyl species.11,12)



3

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2) All new compounds gave satisfactory elemental analyses for C, H and S.

3) Mono-S-methylation of 1 with dimethyl sulfate was briefly reported by S. W. Lee and G. Dougherty, J. Org. Chem., 4 48 (1939). Methylation in methyl p-toluenesulfonate gave the same results as in dimethyl sulfate.

4) H. Meerwein, Org. Syn., 46, 120 (1966).

5) R. F. Borch, J. Amer. Chem. Soc., 90, 5303 (1968); J. Org. Chem., 34, 627 (1969).

6) The picrate of 2 has already been reported (I. Stahl, M. Hetschko, and J. Gosselck, Tetrahedron Lett., 4077 (1971)). Our comments on their description that the CH$_2$ appeared in nmr DMSO-d$_6$ as a singlet at δ 5.58 are reserved until their experimental detailes are at hand. See also C. P. Lillya, E. F. Miller, and P. Miller, Int. J. Sulfur Chem., Part A, 89 (1971).

7) In sharp contrast with the cyclohexane derivatives, the equatorial ring protons resonate at higher field than the axial ones in 1,3,5-trithianes.

8) The experiments are in progress to show whether the ratio is controlled kinetically or thermodynamically.

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12) Strictly speaking the analogy holds only to a limited extent. The pπ-dπ overlap is certainly responsible for the interaction in 3, while the tris-homocyclopropenyl species has better been described by the two-electron three-centered bond.$^{13)}$

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