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FORMATION OF 1,3-DITHIOLYLIUM SALTS BY REACTION OF 2-ALKOXY- AND 2-ALKYLTHIO-1,3-DITHIOLES WITH TRITYL SALT

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The reaction of 2-alkoxy-1,3-dithioles with trityl tetrafluoroborate gave 1,3-dithiolylium tetrafluoroborates and alkoxytriphenylmethanes in excellent yields. Similarly, 2-alkylthio-1,3-dithioles reacted with trityl tetrafluoroborate to give 1,3-dithiolylium tetrafluoroborates and alkylthiotriphenylmethanes.

1,3-Dithiolylium ion possesses a potential aromatic sextet, its aromaticity having been the subject of considerable interest.[1)] Furthermore, in connection with the recent discovery of the highly conducting charge transfer salts of tetrathiafulvalenes with tetracyanoquinodimethane, the synthesis of 1,3-dithiolylium salts has been intensively studied since they serve as precursors of tetrathiafulvalenes.[2)] We now found that 2-alkoxy- and 2-alkylthio-1,3-dithioles react with trityl salt to give 1,3-dithiolylium salts in excellent yields.

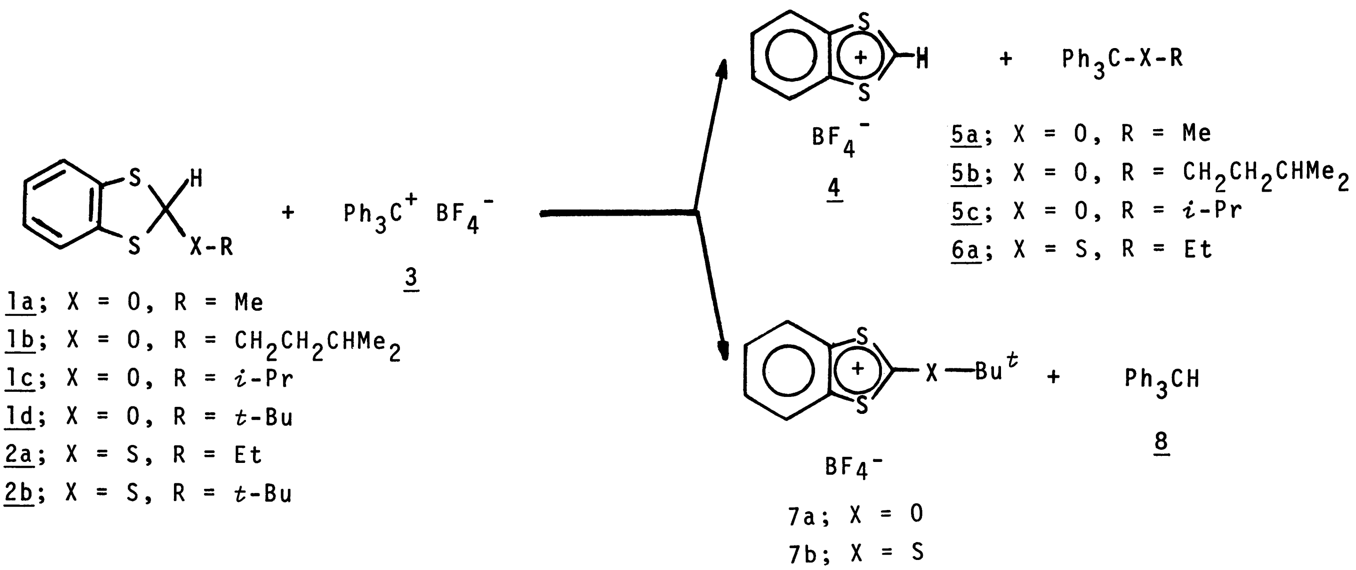
The reaction of trityl salt with 1,3,5-cycloheptatriene[3)] and 1,3-benzodithiole[4)] gives tropylium and 1,3-benzodithiolylium salts, respectively. Moreover, the reaction of trityl salt with 7-methoxy-1,3,5-cycloheptatriene also gives methoxytropylium salt.[3,5)] Thus, the reaction of 2-alkoxy-1,3-benzodithioles with trityl salt would be expected to give 2-alkoxy-1,3-benzodithiolylium salts by hydride exchange reaction. However, treating 2-methoxy-1,3-benzodithiole (1a)[6)] with trityl tetrafluoroborate (3) in acetonitrile at 0°C afforded 1,3-benzodithiolylium tetrafluoroborate (4) (93%), mp 149-150°C (decompn.) [lit.,[4)] 149-150°C (decompn.)], along with methoxytriphenylmethane (5a) (88%) by methoxide exchange reaction. Similarly, 2-isopentyloxy-1,3-benzodithiole (1b)[7)] and 3 gave the tetrafluoroborate 4 (80%) and the ether 5b (56%). The same reaction also occurs with 2-ethylthio-

1,3-benzodithiole (2a)8) which, on treatment with 3, gave the salt 4 (82%) and ethylthiotriphenylmethane (6a) (86%). These exchange reactions may proceed either via an oxonium (or sulfonium) intermediate 9a or directly through transition state 9b without formation of intermediate. In either case, the reactions involve the initial electrophilic attack of trityl cation on the hetero atom of 2-alkoxy- or 2-alkylthio-group, and therefore if the alkyl substituent of alkoxy- or alkylthio-group is very bulky and hence the approach of the cation to the hetero atom is impossible due to steric hindrance, it should react with a methine hydrogen to give triphenylmethane (8) and 2-alkoxy- or 2-alkylthio-1,3-benzodithiolylium ions. Thus, the reaction of 2-t-butylthio-1,3-benzodithiole (2b)8) with 3 gave 8 (96%) and 1,3-benzodithiole-2-thione (10) (34%), mp 164-165°C (lit.,9) mp 165°C), supporting the above description. Compound 10 is the result of decomposition of the primary product, 2-t-butylthio-1,3-benzodithiolylium salt 7b; support for this explanation is found in the fact taht 2-phenacylthio-1,3-dithiolylium bromide decomposes to 1,3-dithiole-2-thione and phenacyl bromide when it is dissolved in warm acetonitrile.10) 2-t-Butoxy-1,3-benzodithiole (1d)11) and 3 gave 8 (46%), a small amount of a few unidentified products, and intractable tars.12) The formation of 8 also suggests that the salt 7a is initially formed although it can not be isolated. 2-Isopropoxy-1,3-benzodithiole (1c)13) and 3 gave the salt 4 (83%) and the ether 5c (74%), indicating that isopropoxy group is not bulky enough to inhibit the attack of trityl cation on the oxygen atom.

The reaction is also applicable to 1,3-dithioles without a fused benzene ring; 2-methoxy-1,3-dithiole (11a)14) and 3 gave 1,3-dithiolylium tetrafluoroborate (12)15) (95%), mp > 200°C (decompn.), and the ether 5a (84%), and likewise 2-methylthio-1,3-dithiole (11b)15) and 3 gave 12 (91%) and the sulfide 6b (88%).

The reaction provides a new general synthetic method of 1,3-dithiolylium salts from 2-alkoxy- and 2-alkylthio-1,3-dithioles. The following procedure is typical;

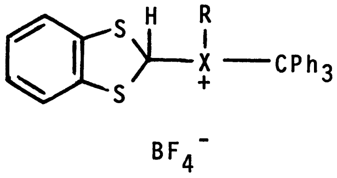
To a stirred and ice-cooled solution of 1a (5 mmol) in anhydrous acetonitrile (5 ml) was added dropwise a solution of 3 (5 mmol) in anhydrous acetonitrile (10 ml) over a period of 15 min. After being stirred for 30 min, anhydrous ether (80 ml) was added to the yellow mixture. The resulting precipitate was collected to give 1.11g (93%) of 4 as near-white crystals. The filtrate was washed with water, dried, and evaporated. The white crystalline residue was washed with a small amount of cold methanol to give the ether 5a, 1.21g (88%), mp 82-83°C (lit.,16) mp 82.6-82.9°C).



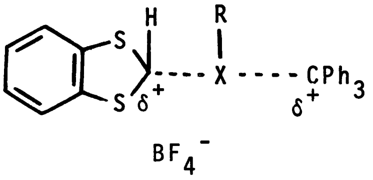
1a; X = O, R = Me
1b; X = O, R = $CH_2CH_2CHMe_2$
1c; X = O, R = *i*-Pr
1d; X = O, R = *t*-Bu
2a; X = S, R = Et
2b; X = S, R = *t*-Bu

5a; X = O, R = Me
5b; X = O, R = $CH_2CH_2CHMe_2$
5c; X = O, R = *i*-Pr
6a; X = S, R = Et

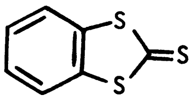
7a; X = O
7b; X = S



9a (X = O or S)



9b (X = O or S)



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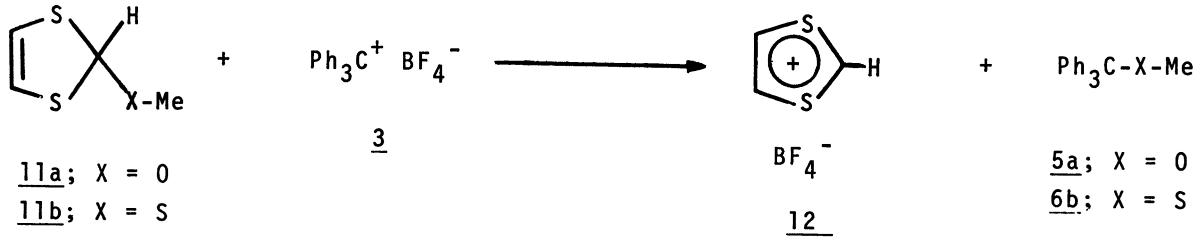

11a; X = O
11b; X = S

5a; X = O
6b; X = S

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References and Notes

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11) This compound was prepared in 84% yield by treating the tetrafluoroborate 4 with t-butyl alcohol in acetonitrile; mp 83-84°C, δ ($CDCl_3$) 1.30 (9H, s), 6.65 (1H, s), and 7.0-7.6 (4H, m).

12) Unreacted 3 was recovered in 43% yield as trityl alcohol.

13) This compound was prepared in 80% yield by treating 4 with 2-propanol; bp 105-108°C/0.5 mmHg, δ (CCl_4) 1.15 (6H, d), 3.82 (1H, heptet), 6.60 (1H, s), and 6.9-7.5 (4H, m).

14) This compound was prepared in 72% yield by treating the salt 12 with methanol in the presence of sodium hydrogencarbonate; bp 70-72°C/13 mmHg, δ (CCl_4), 3.05 (3H, s), 6.20 (2H, s), and 6.99 (1H, s).

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