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Cationic Arylation. VIII. Reactions of Benzenediazonium Tetrafluoroborate with Some Sulfur Compounds

Michio KOBAYASHI, Hiroshi MINATO, Junko FUKUI, and Nobumasa KAMIGATA
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya, Tokyo 158

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Synopsis. Reactions of benzenediazonium tetrafluoroborate (I) with thioanisole in acetonitrile yielded dimethylphenylsulfonium tetrafluoroborate, diphenyl sulfide, methylthiobiphenyls and acetanilide. Reaction of I with cyclohexene yielded 1-cyclohexylcyclohexene and cyclohexyl phenyl ether. Reactions of I with dimethyl sulfide yielded trimethylsulfonium tetrafluoroborate and thioanisole. Mechanisms of these reactions were discussed in terms of the attack of phenyl cation toward the lone electron pair of sulfur atoms and the benzene electrons.

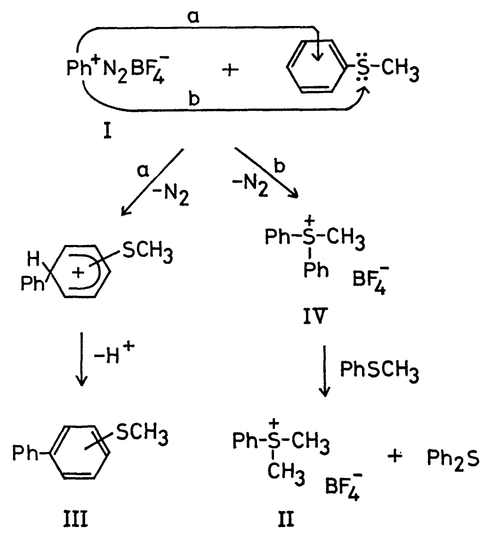
Many papers have described the arylation of aromatic compounds with aryldiazonium tetrafluoroborate (I)[1–3] or some other aryl cation sources.[4–7] However, very few papers have been published on the reaction of aryl cation with compounds other than arenes. Nesmeyanov and his coworkers found that the reaction of I with diaryl sulfides gave triarylsulfonium salts in low yield, but no other products were described.[8]

In order to determine the reactivity of phenyl cation toward compounds other than arenes, the reactions of I with some sulfides, disulfides and cyclohexene have been investigated. The results are described in this paper.

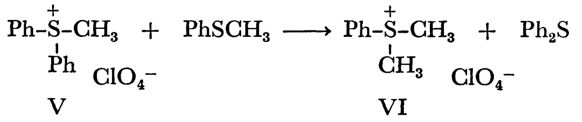
Results and Discussion

I is insoluble in aromatic solvents, but soluble in such aprotic polar solvents as acetonitrile and nitromethane. Therefore, the reaction of I with thioanisole was carried out in acetonitrile. The reaction products were dimethylphenylsulfonium tetrafluoroborate (II), diphenyl sulfide, isomeric methylthiobiphenyls (III), and acetanilide. Methyldiphenylsulfonium tetrafluoroborate (IV) which is the most-likely product from the reaction of phenyl cation with thioanisole was not isolated. The formation of acetanilide in the reaction of phenyl cation with acetonitrile is known.[3,8] Isomer distributions of methylthiobiphenyls formed by the phenylation of the thioanisole nucleus with I were *o*-57%, *m*-14%, *p*-29%; they are similar to those in cationic phenylation of anisole (*o*-64%, *m*-8%, *p*-28%) reported previously.[3]

The formation of products described above can be explained by assuming the following mechanism.



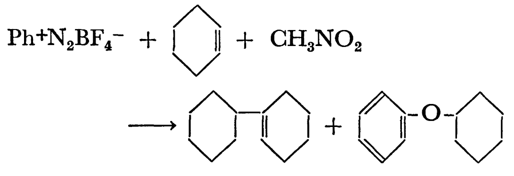
Phenyl cation attacks the aromatic nucleus and the sulfur lone pair of the thioanisole competitively, yielding III and IV; the latter further reacted with another molecule of the unchanged thioanisole to give II and diphenyl sulfide. Since IV was not isolated in the reaction mixture, the reaction of IV with thioanisole must be very rapid. In a separate experiment, methyldiphenylsulfonium perchlorate (V) was prepared and treated with thioanisole in acetonitrile. About equal amounts of dimethylphenylsulfonium perchlorate (VI) (33%) and diphenyl sulfide (38%) were found as expected.[9]



$$\underset{\text{V}}{\mathrm{Ph\text{-}\overset{+}{S}(Ph)\text{-}CH_3\ ClO_4^-}} + \mathrm{PhSCH_3} \longrightarrow \underset{\text{VI}}{\mathrm{Ph\text{-}\overset{+}{S}(CH_3)\text{-}CH_3\ ClO_4^-}} + \mathrm{Ph_2S}$$

These results show that the reactivities of the aromatic nucleus and sulfur atom of thioanisole toward phenyl cation are comparable.

Then the reaction of I with cyclohexene was investigated in nitromethane. The products found were 1-cyclohexylcyclohexene and cyclohexyl phenyl ether.

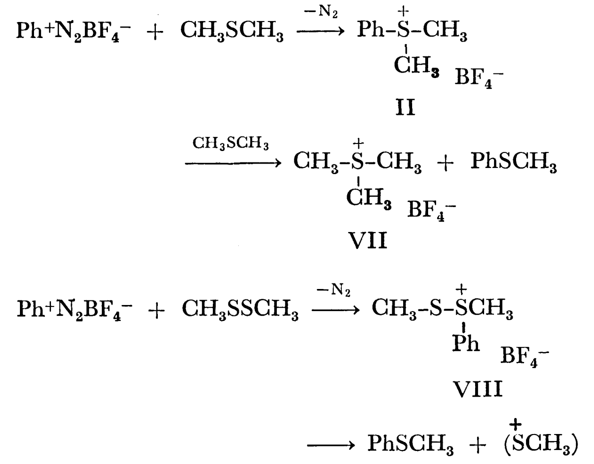


Cyclohexyl phenyl ether was probably formed *via* *O*-phenylation of nitromethane followed by the reaction with cyclohexene. 1-Cyclohexylcyclohexene was probably formed by protonation of cyclohexene, the addition of cyclohexyl cation to cyclohexene, and subsequent deprotonation.

When I was let to react with dimethyl sulfide in acetonitrile, the products found were II, trimethylsulfonium tetrafluoroborate (VII) and thioanisole.

Since II was found in the reaction mixture, the reaction of II with dimethyl sulfide is not so rapid as that of IV with thioanisole.

When I was let to react with dimethyl disulfide in acetonitrile, the only product which was identified was



$$\mathrm{Ph^+N_2BF_4^-} + \mathrm{CH_3SCH_3} \xrightarrow{-\mathrm{N_2}} \mathrm{Ph\text{-}\overset{+}{S}(CH_3)\text{-}CH_3\ BF_4^-}\ \text{(II)} \xrightarrow{\mathrm{CH_3SCH_3}} \mathrm{CH_3\text{-}\overset{+}{S}(CH_3)\text{-}CH_3\ BF_4^-}\ \text{(VII)} + \mathrm{PhSCH_3}$$

$$\mathrm{Ph^+N_2BF_4^-} + \mathrm{CH_3SSCH_3} \xrightarrow{-\mathrm{N_2}} \mathrm{CH_3\text{-}S\text{-}\overset{+}{S}(Ph)CH_3\ BF_4^-}\ \text{(VIII)} \longrightarrow \mathrm{PhSCH_3} + \mathrm{(\overset{+}{S}CH_3)}$$

thioanisole. The reaction probably involved the formation of methylmethylthiophenylsulfonium ion (VIII), which was attacked by some nucleophiles, yielding thioanisole. However, no products other than thioanisole were characterizable.

Experimental

Materials. I,[9] V,[10] and cyclohexene[11] were prepared according to the procedures described in the literature. Thioanisole was prepared by methylation of thiophenol with dimethyl sulfate; bp 75 °/15 mmHg. Dimethyl sulfide and dimethyl disulfide of Tokyo Kasei Co., Ltd. were used without further purification. Acetonitrile was refluxed over phosphorus pentoxide, and then distilled at 81 °C. Nitromethane was dried with calcium chloride and then distilled at 101 °C.

Reaction of I with Thioanisole. A solution of I (4.82 g, 25 mmol) and thioanisole (6.20 g, 50 mmol) in acetonitrile (12.2 g) was stirred at 40°C for 5 hr. After removal of acetonitrile, the ether-insoluble part of the residue was dissolved in aqueous acetone, and eluted through an ion exchange resin column (Amberlite I.R.A.–400) containing perchlorate anions; crystals of dimethylphenylsulfonium perchlorate were obtained (0.56 g, 2.34 mmol). The ether-soluble part was analyzed by glc (Apiezon L, 1 m, 200 °C): diphenyl sulfide (0.33 mmol) and III (isomeric mixture, 0.99 mmol) were found. A very small amount of acetanilide was isolated by the elution chromatography (Florisil) of the ether-soluble part (23 mg, 0.13 mmol).

Reaction of V with Thioanisole. A solution of V (0.60 g, 2.0 mmol) and thioanisole (1.20 g, 11 mmol) in acetonitrile (0.7 g) was stirred at 40 °C for 5 hr. After acetonitrile was evaporated, ether was added to the residue, and the ether-soluble part was analyzed by glc (Apiezon L, 1 m, 190 °C) and the amount of diphenyl sulfide formed was determined (0.76 mmol, 38%). The ether-insoluble part was submitted to NMR analyses, and the amounts of VI formed (0.66 mmol, 38%) and unchanged V (1.34 mmol, 67%) were determined.

Reaction of I with Cyclohexene in Nitromethane. A solution of I (1.01 g, 5.2 mmol) and cyclohexene (5.2 g, 63 mmol) in nitromethane (10 ml) was stirred at 40 °C for 5 hr. After nitromethane was evaporated, the residue was submitted to elution chromatography (Florisil) and the following products were identified by NMR and mass spectroscopy; 1-cyclohexylcyclohexene (82 mg, 0.52 mmol), cyclohexyl phenyl ether (44 mg, 0.25 mmol). Neither phenylcyclohexene nor phenylcyclohexanol was detected.

Reaction of I with Methyl Sulfide. A solution of I (0.96 g, 5 mmol) and methyl sulfide (1.55 g, 25 mmol) in acetonitrile (3.5 g) was stirred at 40 °C for 5 hr. Acetonitrile and methyl sulfide were evaporated, then the reaction products were determined quantitatively by NMR (internal standard: $\mathrm{CHCl_2CHCl_2}$). The following products were identified; thioanisole (1.9 mmol, 38%), II (0.48 mmol, 9.6%), and VII (1.63 mmol, 33%).

Reaction of I with Dimethyl Disulfide. A solution of I (1.92 g, 10 mmol) and dimethyl disulfide (1.50 g, 16 mmol) in acetonitrile (8.9 g) was stirred at 40 °C for 5 hr. After acetonitrile was evaporated, the reaction mixture was submitted to elution chromatography (Florisil); thioanisole (196 mg, 1.58 mmol) and acetanilide (177 mg, 1 mmol) were isolated.

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