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FORMATION OF 1-ARYL-1-BENZOTHIOPHENIUM IONS IN BROMINATION OF *o*-ARYLTHIOPHENYL-SUBSTITUTED ETHYLENES

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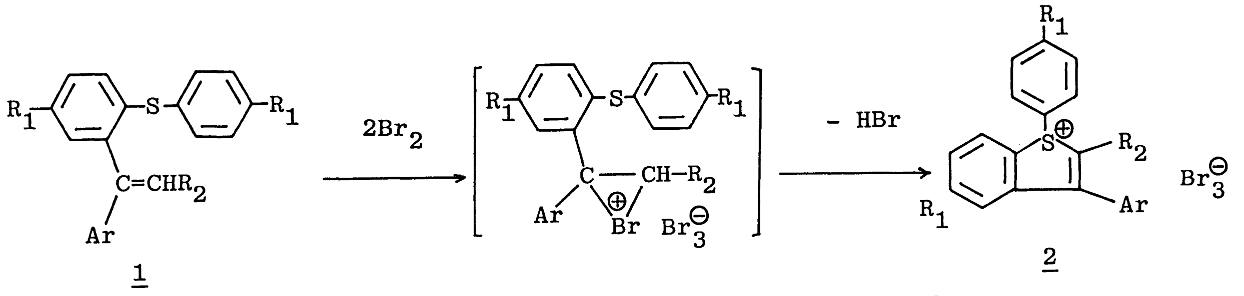
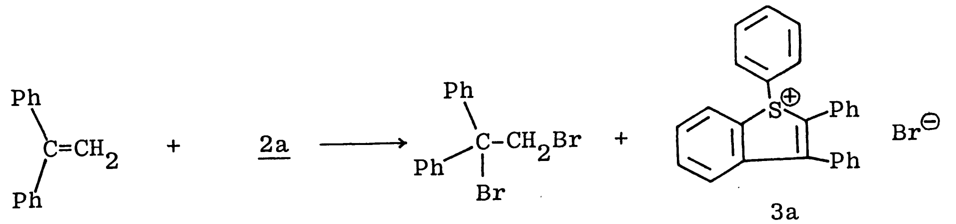
Bromination reaction of *o*-arylthiophenyl-substituted ethylenes gave 1-aryl-1-benzothiophenium ions by intramolecular cyclization in the bromonium intermediates. The substituent and solvent effects are also discussed.

In general, addition of bromine to olefins is a conventional method for preparing organic bromides.1) In our continuing study on photolysis of arylvinyl halides concerning intramolecular cyclization,2) we found a clear-cut heteroatom effect on bromination of *o*-arylheteroatom-substituted-phenylethylenes. That is, *o*-arylthiophenyl-substituted olefins afforded 1-aryl-1-benzothiophenium ions, while the corresponding *o*-aryloxyphenyl-substituted ones did not give the corresponding cyclized products at all. Here we report the result as a novel approach for the preparation of stable 1-aryl-1-**benzothiophenium ions.**3)

Bromination of 1-(*o*-phenylthiophenyl)-1,2-diphenylethylene (1a: R_1 = H, R_2 = Ar = Ph)(1 g) with an equimolar bromine in dichloromethane (50 ml) was carried out at 0 °C. After workup, it was found that the bromination reaction provided the starting olefin 1a and a mixture of products. Then, for completion of the bromination reaction, 2 equivalent moles of bromine was used. The bromination of 1a with 2 equivalent moles of bromine gave orange crystals, mp 154-155 °C, which were assigned as 1,2,3-triphenyl-1-benzothiophenium tribromide (2a)4) from the elemental analysis and the following chemical behaviors. (1) Addition of the orange crystals into 1,1-diphenylethylene in $CDCl_3$ yielded 1,2-dibromo-1,1-diphenylethane and 1,2,3-triphenyl-1-benzothiophenium bromide (3a),4) quantitatively. (2) Passing the crystals through a column of alumina with ethanol gave 3a. (3) Refluxing the crystals in ethanol also resulted in removal of a bromine molecule to give 3a. Similarly, *p*-tolylthiophenyl-substituted ethylene 1b (R_1 = Me, R_2 = Ar = Ph) yielded the corresponding 1-benzothiophenium tribromide 2b,4) but β-methyl-substituted ethylene 1c (R_1 = H, R_2 = Me, Ar = Ph) gave 2-bromo-1-phenyl-1-(*o*-phenylthiophenyl)propene (4c)5) together with the 1-benzothiophenium tribromide (2c).4) As has been discussed in detail on bromination of olefins,1b) the 1-benzothiophenium tribromides 2 may be formed from the A_d 3 mechanism.

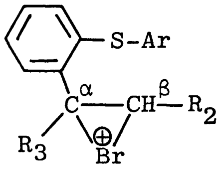




In order to clarify the scope and limitation of formation of the 1-benzothiophenium ions in the bromination of *o*-arylthiophenylethylenes 1, the substituent and solvent effects were examined. The bromination reaction produced the 1-benzothiophenium tribromide 2 which easily lost a bromine molecule. This is somewhat troublesome to analyze the products. Then, the products were analyzed by column chromatography on alumina because the 1-benzothiophenium tribromides 2 could be transformed into the corresponding stable 1-benzothiophenium bromides 3 by the column chromatography. All bromination reactions were carried out under the same conditions for comparison. The results are given in Table 1. Table 1 shows the following orders, α substituent: Ph > An, β substituent: Ph > Me > H, and solvent: CH_3CO_2H, CH_2Cl_2 > CCl_4, for the formation of 1-benzothiophenium bromides 3.

The reaction is determined by the competition of the intramolecular cyclization with the intermolecular substitution. Accordingly, the reaction is governed by the factors, i) the charge population on the α or β carbon in the bromonium ion and ii) the polarity of the solvent, as also observed in the bromination reactions of 2-butene derivatives.[6)]

Substituents (R_2 and R_3) affect strongly the charge population on the α and β carbons in the bromonium ion 5. Phenyl group on the β carbon, stabilizing the cation 6, yielded the cyclized product 3 predominantly, while methyl group and hydrogen atom led to the large contribution of the cation 7, giving the vinyl bromide 4 selectively. Similarly, *p*-methoxyphenyl group (An) on the α carbon, stabilizing the cation 7, produced the vinyl bromide 4.



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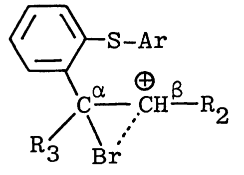

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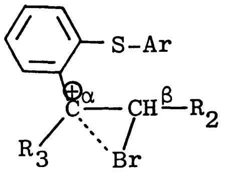

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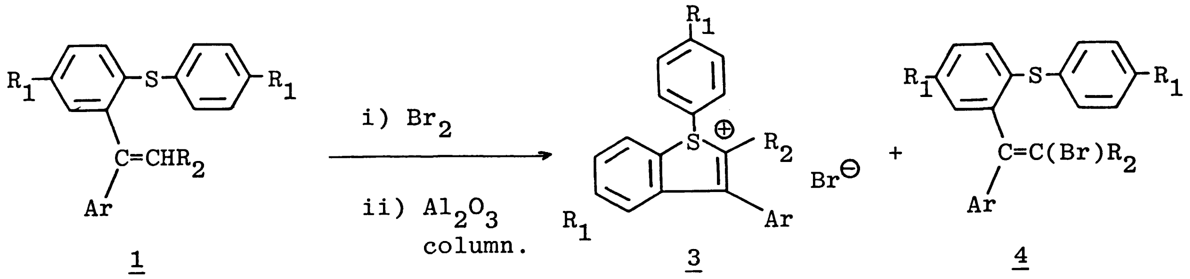

Table 1. Bromination of *o*-Arylthiophenylethylenes a)

	Ethylene 1			Solvent	Products (yield/% b))		
	R_1	R_2	Ar		1	3	4 d)
1b	Me	Ph	Ph	CCl_4	60	26	0
				CH_2Cl_2	42	51	0
				CH_3CO_2H e)	29	57	0
1c	H	Me	Ph	CCl_4	25	22	43
				CH_2Cl_2	0	49	47
				CH_3CO_2H e)	0	39	53
1d	H	H	Ph	CCl_4	0	0	94
				CH_2Cl_2	0	31	60
				CH_3CO_2H e)	0	47	47
1e	H	Ph	An c)	CCl_4	10	36	47
				CH_2Cl_2	9	50	32

a) To a solution of olefin 1 (1.0 g) in a solvent (130 ml), 1.1 mol equiv. of bromine was added. b) Isolated yields by column chromatography on alumina. c) *p*-$MeOC_6H_4$. d) A mixture of E- and Z-isomers. e) Carried out at a room temperature.

Acetic acid and dichloromethane also afforded the cyclized product 3 more selectively than carbon tetrachloride. Solvent effect on the product distribution may be attributed to the polarity of the solvent employed. Polar solvents produce a loose ion pair, i.e., a loose bromonium cation and bromide anion pair, compared with non-polar solvents which yield a tight ion pair.7) The intramolecular attack of the sulfur atom precedes the intermolecular attack of bromide anion in the loose ion pair, whereas the reverse is hold in the tight ion pair because of the proximity of bromide anion.

References

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3) For preparation of 1-benzothiophenium salts, alkylation of sulfur atom and reaction of sulphoxides with organometallics are appeared; P. A. Lowe, "The Chemistry of the Sulphonium Group," ed by C. J. M. Stirling and S. Patai, John Wiley & Sons, New York (1981), Chap. 11.

4) 2a: mp 154-155 °C; NMR ($CDCl_3$) δ = 7.21-7.92 (m, ArH) and 8.35-8.53 (m, ArH). 2b: mp 81-83 °C; NMR ($CDCl_3$) δ = 2.33 (s, Me), 2.49 (s, Me), 7.15-7.80 (m, ArH), and 8.30-8.50 (m, ArH). 2c: mp 134-136 °C; NMR ($CDCl_3$) δ = 2.39 (s, Me), 7.51-7.92 (m, ArH), and 8.08-8.35 (m, ArH). 3a: mp 238-240 °C; NMR ($CDCl_3$) δ = 7.20-8.12 (m, ArH) and 9.05-9.39 (m, ArH). 3b: mp 174-175.5 °C; NMR ($CDCl_3$) δ = 2.31 (s, Me), 2.46 (s, Me), 7.05-7.97 (m, ArH), and 8.79-8.95 (m, ArH). 3c: mp 187-188 °C; NMR ($CDCl_3$) δ = 2.35 (s, Me), 7.20-8.15 (m, ArH), and 8.73-8.83 (m, ArH). 3d: mp 213.5-215.5 °C; NMR ($CDCl_3$) δ = 7.30-8.15 (m, ArH) and 8.48-8.53 (m, ArH). 3e: hygroscopic crystals; NMR ($CDCl_3$) δ = 3.86 (s, OMe), 6.92-8.18 (m, ArH), and 8.79-8.92 (m, ArH).

5) A mixture of E- and Z-isomers. 4c: mp 90-91 °C; NMR ($CDCl_3$) δ = 2.23 (s, Me), 2.46 (s, Me), and 6.61-7.75 (m, ArH). 4d: mp 109-110 °C; NMR ($CDCl_3$) δ = 6.44 (s, =CH), 6.82 (s, =CH), and 6.95-7.58 (m, ArH). 4e: oil; NMR ($CDCl_3$) δ = 3.56 (s, OMe) and 6.37-7.47 (m, ArH).

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