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REACTIONS OF 5-SUBSTITUTED DIBENZOTHIOPHENIUM SALTS WITH ORGANOLITHIUMS[1)]

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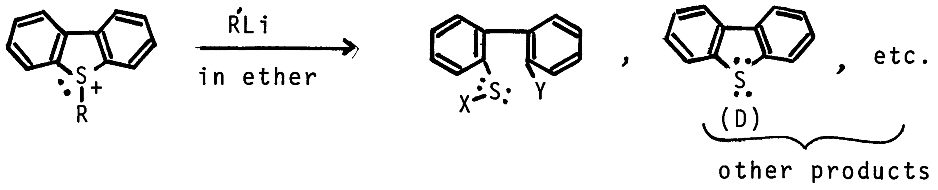
The reactions of 5-substituted dibenzothiophenium salts and 10-arylthioxanthenium salts with organolithiums have been found to yield ring opening products (A), ligand exchange ring opening products (B) and other products, as shown in Tables 1, 2, and 3, respectively. The formation of these compounds supports the assumption of the pseudorotation of pentacoordinated sulfur intermediates in these reactions.

On the reactions of triarylsulfonium salts or diaryl sulfoxides with organolithiums, many researches have been made until now, but with regard to the reaction mechanism, there still remain various problems. Recently Anderson[2)] and Trost[3)] have assigned very interesting pentacoordinate sulfur to the intermediates of this reaction, and have given some considerations to the reaction mechanism. We are interested, especially as to the mechanistic interpretation, in the nucleophilic reactions on the trivalent sulfur atom in cyclic sulfonium salts instead of open chain compounds, which are considerably complex in reaction analysis. In this communication, we would like to report on the mechanism of reaction between 5-substituted dibenzothiophenium salts[4)] and organolithiums.

A typical run of the reactions is the following. 5-p-Methoxyphenyldibenzothiophenium bromide (0.0025 mol) was added to 20 ml (0.02 mol) of 1.00N phenyllithium at room temperature under a nitrogen stream. After the reaction mixture was stirred for 5 hr, it was poured into 50 ml of 5% hydrochloric acid, and the ether layer was separated. The ether extract of the aqueous phase was combined with it, dried and evaporated. The reaction products were isolated by recrystallization from a suitable solvent after TLC on silica gel. Anisole etc. in other products were analysed by glc on 10% SE-30 column with phenethole as a standard in order to obtain the result summarized in Run 1 of Table 1. And also they were identified by means of glc retention time, nmr, ir, mass spectroscopic analysis, and elemental analysis. Furthermore, their desulfurization products obtained by the use of W-7 Raney cobalt such as o-terphenyl and p-methoxy-o-terphenyl were identified by comparing their spectroscopic data or glc retention time with those of the authentic samples. Other runs were treated similarly.

As to the mechanistic route to explain the products of the reactions of 5-substituted dibenzothiophenium salts with organolithiums, the following five mechanisms can be assumed: (A) nucleophilic substitution on the aromatic carbon atom, (B) benzyne mechanism, (C) intramolecular decomposition mechanism, (D) radi-

Table 1. Reactions of 5-Aryldibenzothiophenium Salts with Aryllithiums



Run	R-	R'-	*	X-	Y-	mp(°C)	Yields(%)	Other products(%)
1	p-MeOC6H4	C6H5	(A)	p-MeOC6H4	C6H5	132	74.4	MeOC6H5(trace)[b]
			(A)	C6H5	p-MeOC6H4	142	6.6	
			(B)	C6H5	C6H5	88	4.0	(D)(trace)[c]
1[a]	p-MeOC6H4	C6H5	(A)	p-MeOC6H4	C6H5	132	79.5	
			(A)	C6H5	p-MeOC6H4	142	6.5	MeOC6H5(trace)[b]
			(B)	p-MeOC6H4	p-MeOC6H4	oil	1.6	(D)(trace)
			(B)	C6H5	C6H5	88	2.6	
2	C6H5	p-MeOC6H4	(A)	p-MeOC6H4	C6H5	132	69.0	(D)(trace)
			(A)	C6H5	p-MeOC6H4	142	6.0	
			(B)	p-MeOC6H4	p-MeOC6H4	oil	15.5	
			(B)	C6H5	C6H5	88	4.0	
3	m-MeOC6H4	C6H5	(A)	m-MeOC6H4	C6H5	oil	26.0	
			(A)	C6H5	m-MeOC6H4	oil	36.4	MeOC6H5(trace)[b]
			(B)	m-MeOC6H4	m-MeOC6H4	oil	6.0	(D)(trace)
			(B)	C6H5	C6H5	88	26.4	
4	C6H5	C6H5	(A) (B)	C6H5	C6H5	88	72.0	(D)(trace)
5	C6H5	p-Me2NC6H4	(A)	p-Me2NC6H4	C6H5	113	60.0	(D)(trace)
			(B)	p-Me2NC6H4	p-Me2NC6H4	190	29.5	
			(B)	C6H5	C6H5	88	5.4	
6	p-FC6H4	C6H5	(A)	C6H5	p-FC6H4	93	8.0	oils
			(B)	C6H5	C6H5	88	27.0	(D)(trace)
7	p-ClC6H4	C6H5	(A)	C6H5	p-ClC6H4	101	30.0	oils
			(B)	C6H5	C6H5	88	24.4	(D)(trace)
8	o-MeOC6H4	C6H5	(A)	o-MeOC6H4	C6H5	152	5.7	
			(A)	C6H5	o-MeOC6H4	81	12.1	MeOC6H5[b]
			(B)	C6H5	C6H5	88	65.9	(D)(trace)
9	o,p(MeO)2C6H3	C6H5	(A)	o,p(MeO)2C6H3	C6H5	87	10.6	
			(A)	C6H5	o,p(MeO)2C6H3	oil	3.8	m-(MeO)2C6H4[b]
			(B)	C6H5	C6H5	88	78.9	(D)(trace)
10	C6H5	o-MeOC6H4	(A)	o-MeOC6H4	C6H5	152	23.5	(D)(trace)
			(A)	C6H5	o-MeOC6H4	81	67.3	
11	C6H5	o,p(MeO)2C6H3	(A)	o,p(MeO)2C6H3	C6H5	87	66.7	(D)(trace)
			(A)	C6H5	o,p(MeO)2C6H3	oil	24.0	
12	Me	C6H5	(A)	Me	C6H5	58	37.4	(D)(40) (CH2)n

* (A) : Ring opening products, (B) : Ligand exchange ring opening products.

a) 1 equivalent of 5-p-methoxyphenyldibenzothiophenium perchlorate was treated with 1 equivalent of phenyllithium. b) was afforded by a ligand exchange reaction.

c) Quantitative analysis of biphenyl derivatives (trace) is impossible because excess organolithium is used.

cal mechanism, and (E) nucleophilic attack on the trivalent sulfur atom. Comparison of respective products of Runs 1 and 2 of Table 1 denies the mechanisms of A - D and strongly suggests the mechanism of E. Thus, Mechanism A is unacceptable because no significant difference was found between the respective yields of ring opening products of Runs 1 and 2 shown in Table 1. Mechanisms B and C are denied because m-terphenyl and its derivatives were not formed by the reaction between W-7 Raney cobalt and any of the products shown in Table 1; bromobenzene derivatives such as p-bromoanisole were not formed by the reaction between 5-p-methoxyphenyldibenzothiophenium bromide and phenyllithium. Mechanism D is clearly denied by Run 4 because all the reaction products were simple compounds as shown in Table 1 and no ESR spectra of free radicals were observed during all the runs.

By the reactions of ligand exchange or ligand coupling, Mechanism E would generate pentacoordinated sulfur which possesses a trigonal bipyramidal geometry. If the pentacoordinated sulfur gives the reaction products through pseudorotation by analogy to phosphorane chemistry etc.[6,7,8], followings must be assumed: (1) Muetterties rule and bulky effect of ligands hold. (2) The five-membered ring in the equatorial-apical orientation requires that θ = 90°. (3) Attacking and eliminating groups involve apical positions. (4) The lone pair occupies the most electronegative equatorial orbital. Further, when a five-membered ring in a compound occupies equatorial-equatorial orientation (θ = 120°), the compound is also a pseudorotational conformer.

Thus, the formation mechanisms of ring opening products (A in Runs 1 and 2 of Table 1) and other products (R-R' and dibenzothiopene) in Table 2 are shown below.

Formation Mechanisms of Ring Opening Products
and Other Products

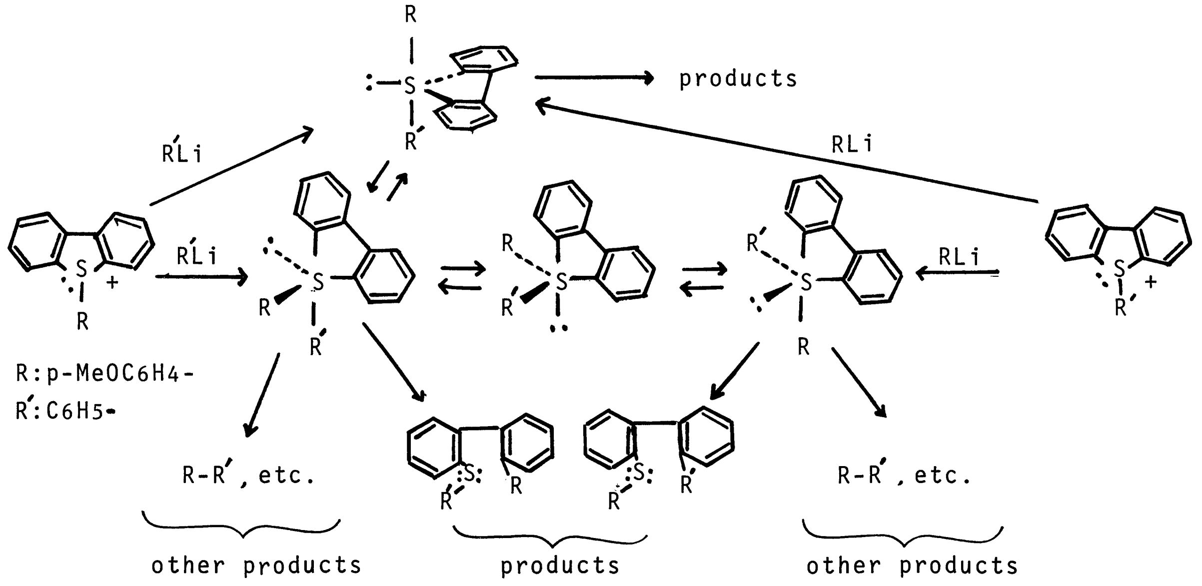
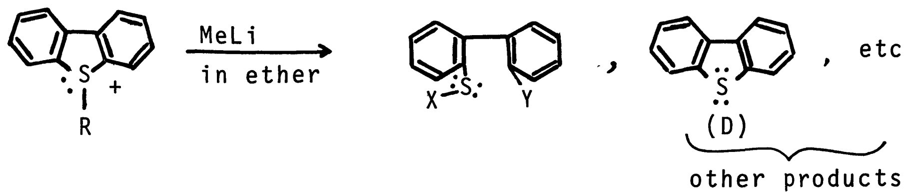


Table 2. Reactions of 5-Aryldibenzothiophenium Salts with Alkyllithium

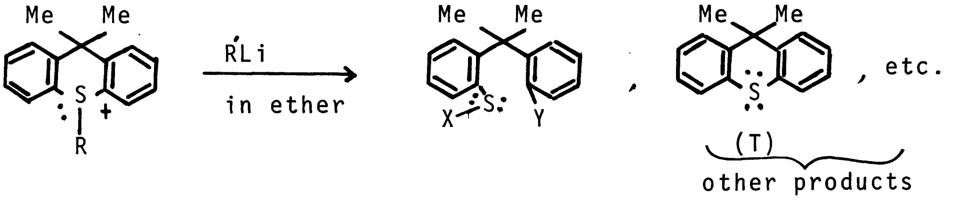


Run	R-	*	X-	Y-	mp(°C)	Yields(%)	Other products(%)
1	p-MeOC6H4	(A)	Me	p-MeOC6H4	77	25.5	(D)(42.4)
		(B)	p-MeOC6H4	p-MeOC6H4	oil	13.0	MeOC6H5(26.0)a)
		(B)	Me	Me	52	3.6	p-MeC6H4OMe(trace)
2	o-MeOC6H4	(A)	Me	o-MeOC6H4	105	7.7	(D)(84.0)
		(B)	o-MeOC6H4	o-MeOC6H4	oil	0.6	MeOC6H5(81.7)a)
		(B)	Me	Me	52	7.0	o-MeC6H4OMe(3.2)
3	m-MeOC6H4	(A)	Me	m-MeOC6H4	64	24.3	(D)(44.0)
		(B)	m-MeOC6H4	m-MeOC6H4	oil	21.0	MeOC6H5(14.0)a)
		(B)	Me	Me	52	3.0	m-MeC6H4OMe(3.4)

* (A) : Ring opening products, (B) : Ligand exchange ring opening products.

a) was afforded by a ligand exchange reaction.

Table 3. Reactions of 9,9-Dimethyl-10-arylthioxanthenium Salts with Aryllithiums



Run	R-	R'-	*	X-	Y-	mp(°C)	Yields(%)	Other products(%)
1	p-MeOC6H4	C6H5	(A)	p-MeOC6H4	C6H5	103	21.3	(T)(trace)
			(A)	C6H5	p-MeOC6H4	——	3.0	
			(B)	p-MeOC6H4	p-MeOC6H4	110	5.0	MeOC6H5a)
			(B)	C6H5	C6H5	109	64.0	
2	C6H5	p-MeOC6H4	(A)	p-MeOC6H4	C6H5	103	13.4	(T)(trace)
			(A)	C6H5	p-MeOC6H4	——	2.0	
			(B)	p-MeOC6H4	p-MeOC6H4	110	59.0	
			(B)	C6H5	C6H5	109	1.0	
3	o,p-(MeO)2C6H3	C6H5	(B)	C6H5	C6H5	109	84.0	(T)(17.9) m-(MeO)2C6H4a) (67.1)

* (A) : Ring opening products, (B) : Ligand exchange ring opening products.

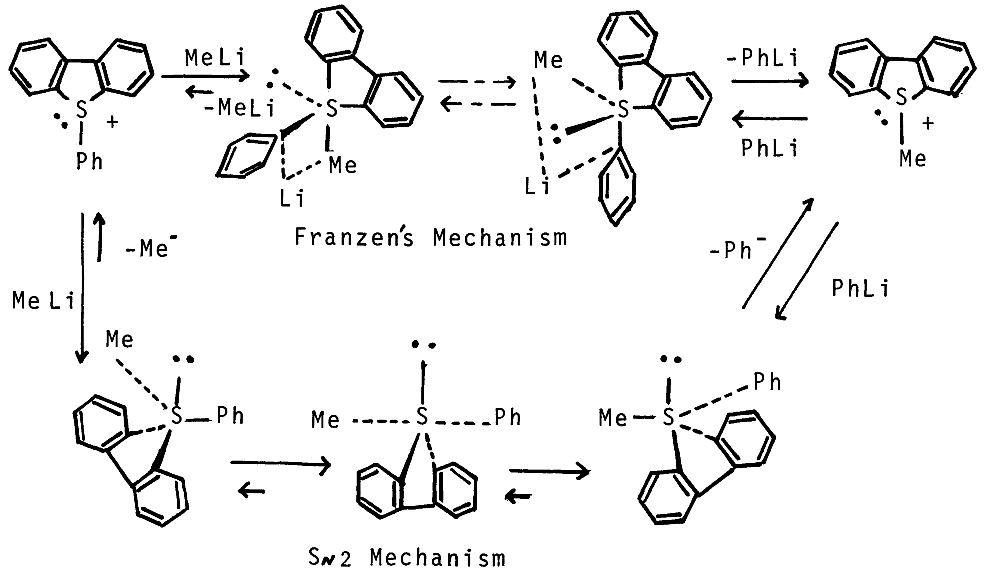
a) was afforded by a ligand exchange reaction.

Next, the formation of ligand exchange ring opening products (B in Runs 1 and 2 of Table 1) can be assumed as follows. Ligand exchange would proceed by the S_N2 mechanism9), because the transition state in S_N2 (θ of five-membered ring = 120°) does not need a perfect pentacoordinate trigonal bipyramidal geometry, and the ligand equilibration would result in the generation of a 5-substituted dibenzothiophenium salt, which is stereochemically relaxed, and an organolithium, which is more stable than the starting organolithium. And they would generate pentacoordinated sulfur by ligand coupling.

Thus, carrying out the reaction of methyllithium with 5-aryldibenzothiophenium salts (compare Table 2 with Run 12 in Table 1) and the reactions of aryllithiums with dibenzothiophenium salts having a bulky group at 5-position (compare Runs 8 and 9 with Runs 10 and 11 in Table 1) or with a compound of six-membered ring system such as 9,9-dimethyl-10-arylthioxanthenium salts[4)], expected results have been obtained. The sulfur-containing ring in 9,9-dimethyl-10-arylthioxanthenium salt is easily made planar owing to steric hindrance in the ligand exchange stage.

Franzen[10)] has claimed that the four-membered ring transition state is valid for ligand exchange in the reaction of triarylsulfonium salt and methyllithium. However, the ligand exchange seems to be better explained by the S_N2 mechanism. The ligand exchange mechanisms described above will be applied to the reaction of 5-phenyldibenzothiophenium salt and methyllithium as shown below.

Ligand Exchange Mechanisms



References

1) This work was presented at the 91st Annual Meeting of the Pharmaceutical Society of Japan, Fukuoka, April 9, 1971, Abstracts p.690 and also at the 6th Symposium on Organic Sulfur Chemistry, Hamamatsu, Feb. 7, 1972, Abstracts p.5.

Very recently, Trost and his co-worker have systematically reported reactions of organolithiums with triarylsulfonium salts. In the report they have also described about the reactions of 5-phenyldibenzothiophenium salt with phenyllithium and vinyllithium, but their reaction conditions were different from ours, because ligand exchange ring opening products (B in Tables) have not been reported. Cf., R. W. LaRochelle and B. M. Trost, J. Amer. Chem. Soc., 93, 6077 (1971).

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