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The Mechanism of the Alkaline Decomposition of Triarylsulfonium Bromide with Phenyllithium[1)]

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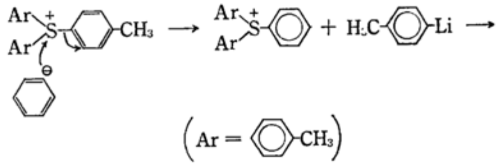
Tritolylsulfonium bromide was subjected to alkaline decomposition in order to clarify the mechanism of the reaction of triarylsulfonium bromide with phenyllithium in ether. Diaryl sulfides, diaryls, and other aryl derivatives were obtained and the combined yield was nearly quantitative. On the basis of the ratio of the products formed in the reaction, the alkaline decomposition is considered to proceed through two mechanistic routes, *i. e.*, one involving the nucleophilic attack of phenyl anion on the sulfur atom (about 70%) and the other the "benzyne" route (about 20%).

The reaction of triarylsulfonium halide with phenyllithium has been studied by Franzen[2)] and later by Andersen.[3)] However, their experimental procedures are not identical and the results they obtained are also somewhat different. The mechanisms suggested are also entirely different.

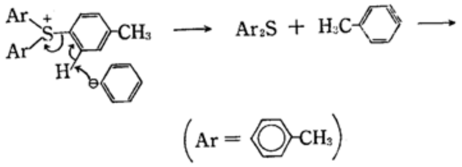
Franzen reported that triphenylsulfonium bromide exchanges phenyl groups with phenyllithium very rapidly and involves the initial formation of an unstable tetravalent sulfur intermediate and the succeeding extrusion of the phenyl group. On the other hand, Andersen proposed a mechanism involving "benzyne" intermediate on the basis of their observation that the addition of phenyllithium to diphenyl sulfoxide in ethyl ether gives diphenyl sulfide and diphenyl.

Franzen and Joschek[4)] later also presented evidence that tri-(2-methoxyphenyl)sulfonium chloride reacted with phenyllithium to give the corresponding aryne though in poor yield. Meanwhile, Sheppard[5)] suggested that the reaction between phenylsulfur trifluoride with phenyllithium to give both phenyl sulfide and diphenyl proceeds *via* the initial formation of tetraphenylsulfur intermediate by the replacement of the fluorines by phenyl groups, similar to the reaction between triarylsulfonium halide and aryllithium. However, the mechanisms of all these reactions have remained totally unclarified. In addition to the two mechanistic pathways hitherto mentioned, *i. e.*, the one involving the tetravalent sulfur intermediate and the other which includes "benzyne" intermediate, there are two other possibilities; namely, the reaction may proceed *via* the initial nucleophilic attack of phenyllithium on the carbon atom (mechanism 3) or may proceed *via* an intramolecular decomposition (mechanism 4). All these possible mechanisms are schematically illustrated with tolyldiphenylsulfonium compound as shown below.

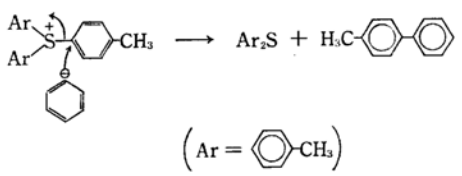
1) Nucleophilic attack on sulfur atom.



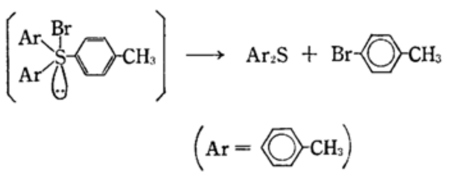
2) Benzyne mechanism.



3) Aromatic S_N reaction.



4) Intramolecular decomposition.



[1)] Paper II on Sulfonium Salt. Paper I, this Bulletin, **42**, 1622 (1969).

[2)] V. Franzen and C. Mertz, *Ann.*, **643**, 24 (1961).

[3)] K. K. Andersen and S. A. Yeager, *J. Org. Chem.*, **28**, 865 (1963).

[4)] V. Franzen, H. I. Joschek and C. Mertz, *Ann.*, **654**, 82 (1962).

[5)] W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).

In order to make a choice among these possible mechanistic pathways for the reaction between triarylsulfonium compound and aryllithium, we have undertaken detailed analyses of the products formed in the reaction between tritolylsulfonium compound and phenyllithium. This paper will describe a detailed account of the investigation. In the previous studies by both Franzen and Andersen there was a technical difficulty in choosing a plausible mechanism, since the yields of reaction products in both cases were entirely different. However, by the use of tritolylsulfonium compound with phenyllithium, one can readily test the "benzyne" mechanism (Mechanism 2) and the intramoleclular decomposition (Mechanism 4), since the "benzyne" mechanism will require the formation of both *m*- and *p*-substituted ditolyls, while the intramolecular decomposition mechanism (4) will give tolyl bromide and diaryl sulfide.

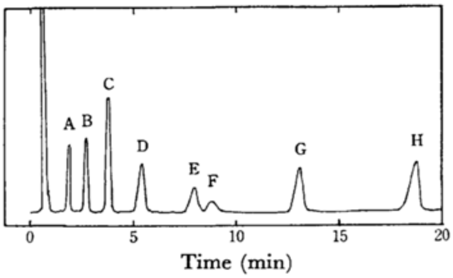
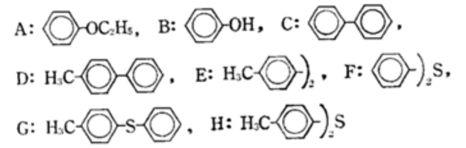


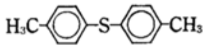
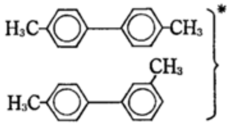
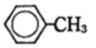
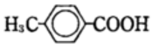
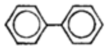
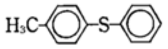
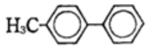
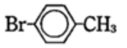
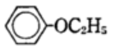
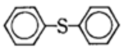
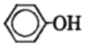
Fig. 1. Vapor phase chromatography (packing: 30%-PEGA, 70%-fiber brick) at 178°C.



Results and Discussion

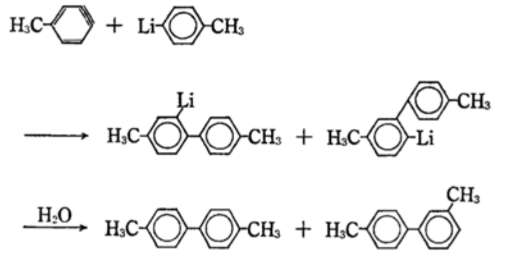
The products obtained are shown in Table 1. The reaction of tritolylsulfonium bromide with phenyllithium was carried out in boiling ether and after the reaction was completed the reaction mixture was carbonated. The products contained in ether layer were carefully fractionated by gas chromatography and identified by comparing their mp, infrared and NMR spectra with those of the authentic samples. A typical gas chromatogram of the products formed is shown in Fig. 1. One finds peaks of *p*-ditolyl sulfide, phenyl *p*-tolyl sulfide, ditolyl, *p*-methyldiphenyl, diphenyl, phenetole, phenol, and *p*-tolyl bromide in the vapor phase chromatogram. However, ditolyl and diphenyl sulfide were obtained as a mixture without being well-separated and their products ratio was determined by NMR spectra. Further, through the careful inspection of the infrared absorption spectra it was found that ditolyl consists of a mixture of two isomers, *i. e.*, *p,p'*-dimethyldiphenyl and *m,p'*-isomer in the ratio of about 1:3. Since *m,p'*-dimethyldiphenyl is formed only through the "benzyne" route (mechanism 2) through which nearly the same amount of *p,p'*-isomer would be also formed. Therefore, the "benzyne" route shown below would account for approximately 20% of the products formed in the reaction. Tolyllithium being a stronger nucleophile than phenyllithium, apparently reacts preferentially with "benzyne" formed. When the reaction was performed in the presence of a 2.0 molar equivalent of lithium thiophenoxide, a nucleophile which reacts more rapidly than phenyl-

TABLE 1. THE REACTION OF TRITOLYLSULFONIUM BROMIDE WITH PHENYLLITHIUM IN ETHER

Sulfide group (yield %)	Diaryl group (yield %)	Aryl group (yield %)	Carboxylic acid (yield %)	Other product** (yield %)
 (57)	 (20)	 (small)	 (26)	 (5–8)
 (33)	 (29)	 (1–2)		 (∼3)
 (7)				 (3–5)

* The molar ratio of *m*- and *p*-isomers is about 1:1.

** All the products result in the formation of phenyllithium.

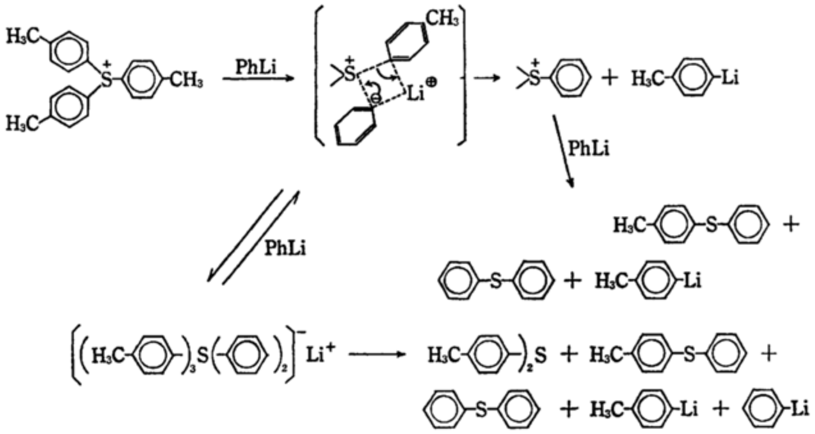


lithium with benzyne,[6] diphenyl sulfide (8%) and ditolyl (21%) were obtained. These yields of the two products do not differ much, regardless of the absence or presence of thiophenoxide in the reaction system. If the lithium thiophenoxide can compete with tolyllithium in the addition reaction to "benzyne," the yield of diphenyl sulfide would increase and the yield of ditolyl would decrease. If phenyllithium could compete with tolyllithium in addition to "benzyne," both *p*-methyldiphenyl and its *m*-isomer would be obtained; however, no such *m*-isomer could be detected. *p*-Tolyl phenyl sulfide and diphenyl sulfide are undoubtedly the products formed by the collapse of the tetravalent sulfur intermediate as shown below, while di-*p*-tolyl sulfide is formed not only *via* this route but also by other routes. The mechanistic route involving the aromatic nucleophilic substitution on the carbon atom with the phenyllithium with ditolyl sulfide as the leaving group (mechanism 3) could explain the formation of ditolyl sulfide and *p*-methyldiphenyl, but not that of *p*-tolyl phenyl sulfide. Therefore, this route, (mechanism 3) is rather unlikely.

Judging from the distribution of the whole product and the yields of tolyl compounds formed from the sulfonium bromide, the mechanism involving the nucleophilic attack on the sulfur atom (mechanism 1) seems to account for about 75% of the products formation. Previously Franzen calculated the portion of the reaction through the mechanistic route 1 only from the amount of benzoic acid formed by the carbonation in the reaction of triphenylsulfonium bromide with phenyllithium. By the use of tritolylsulfonium bromide with phenyllithium for the reaction, one can now include other tolyl compounds such as methyldiphenyl, ditolyl and toluene as the products formed by the mechanistic route 1.

In view of the substantial formation of ditolyl the exchange of aryl group *via* route 1 undoubtedly takes place very fast. Meanwhile, the formation of tolyl bromide could be explained in terms of the intramolecular decomposition[7] though the yield (2%) is very poor (mechanism 4). Another possible route for the formation of tolyl bromide would be the addition of bromide to aryne formed by the route 2.

Besides, diphenyl,[8,9] phenetole[10] and phenol[9] were obtained. These undoubtedly result from the reaction of phenyllithium formed in the reaction of bromobenzene with lithium in diethyl ether, since all these compounds can be found among the reaction mixture before the addition of the sulfonium salt and the amounts remain the same even after the addition of the salt.



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6) a) R. Huisgen in "Organometallic Chemistry," H. Zeiss, ed., Reinhold Publishing Corp., New York, N. Y. (1960), pp. 11, 36—87.

7) G. H. Wiegand and W. E. McEwen, *Tetrahedron Letters*, **1965**, 2639.

8) E. Muller and T. Topel, *Ber.*, **72B**, 273 (1939).

9) H. A. Pacevitz and H. Gilmann, *J. Am. Chem. Soc.*, **61**, 1603 (1939).

10) G. Wittig and U. Pockels, *ibid.*, **72B**, 884 (1939).

Experimental

Starting and Authentic Materials. Tritolylsulfonium bromide was prepared[11] from ditolylethoxysulfonium tetrafluoroborate[12] and tolyl Grignard reagent. mp 244—245°C (decomp.). *m*- And *p*-methyldiphenyls were prepared from the reaction of the corresponding diazonium salt with benzene and (*m*,*p*'- and *p*,*p*'-) dimethyldiphenyls were also obtained similarly. Diphenyl sulfide, phenyl tolyl sulfide and di-*p*-tolyl sulfide were prepared by the reaction of the corresponding aryldiazonium salts with thiophenolate.

The Reaction of Tritolylsulfonium Bromide with Phenyllithium. Tritolylsulfonium bromide (2.14 g, 0.0056 mol), in 10 m*l* of anhydrous ethyl ether was added to the ethereal solution of phenyllithium (0.024 mol) prepared from bromobenzene and lithium under a nitrogen stream. After the reaction mixture was refluxed for 45 min, it was poured onto dry ice, and hydrolyzed with 5% of hydrobromic acid. The ethereal layer was extracted with 10% sodium carbonate solution, and aqueous extract was acidified to isolate the mixture of benzoic and toluic acids. *p*-Toluic acid (0.2 g) was seperated by careful recrystallization from an alcohol-water mixture. The ethereal layer was washed, dried and fractionated by vapor phase chromatography. The identification and the determination of the yields of the products were performed using quantitative vapor phase chromatography and by comparison of their infrared spectra with those of authentic samples. The isolated compounds from the organic layer and their yields are shown in Table 1.

Meanwhile, the direct hydrolysis of the reaction mixture, after it was refluxed for 50 min, gave the products in almost same yields. However, in this case toluene (22%) was obtained instead of toluic acid.

The Reaction of Tritolylsulfonium Bromide with Phenyllithium-Thiophenoxide Mixture. Thiophenol (1.76 g, 0.008 mol) in 5 m*l* of anhydrous ethyl ether was added to the ethereal solution of phenyllithium (0.024 mol) and the mixture was kept stirring for 10 min at 40°C. Tritolylsulfonium bromide (1.4 g, 0.004 mol) in 10 m*l* of anhydrous ethyl ether was added to this mixture. After the reaction mixture was refluxed for 80 min, poured into ice water, acidified with 5% hydrobromic acid, and the ethereal layer was separated. The ether extract of the water layer was combined with it. Distillation of the organic layer gave almost the same products, and their yields in the case where only phenyllithium was used are shown in Table 1. The purities and yields of the products were checked by the usual quantitative vapor phase chromatography. (Diphenyl sulfide 8%, ditolyl 21%, toluene 20%.)

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[11] a) K. K. Andersen and N. E. Papanikolaov, *ibid.*, **1966**, 5445.

[12] C. R. Johnson and D. Macants, Jr., *ilid.*, **87**, 5408 (1965).