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PYROLYSIS OF TRIARYLSULFONIUM HALIDES

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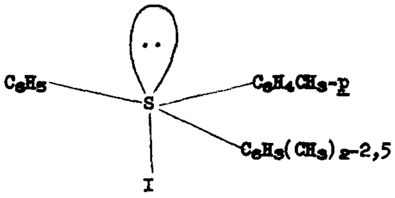
It is of practical value and theoretical interest that triarylsulfonium halides undergo pyrolysis at moderate temperatures to produce theoretical yields of diaryl sulfides and the corresponding aryl halides. ($R_3S^+, X^- \longrightarrow RX + R_2S$). The practical value lies in the fact that the products of pyrolysis are easily analyzed by vapor phase chromatography, and this constitutes the most convenient method for determining the structures and purity of a given sample of a triarylsulfonium halide. The theoretical interest arises from the ratios of pyrolysis products obtained from triarylsulfonium halides in which at least two different aryl groups are present and the implications oi these results with respect to the mechanism of reaction.

The results of a number of pyrolysis reactions conducted for 5-10 minutes at 250° are given in Table 1. It is clear that the product ratios cannot be explained on the basis of either an aromatic S_N1 mechanism or a bimolecular aromatic nucleophilic substitution process. For example, pyrolysis of phenyl-p-tolyl-2,5-dimethylphenylsulfonium iodide would be expected to give aryl iodides in the order of preference of iodobenzene > p-iodotoluene > 2,5-dimethyliodobenzene if a simple bimolecular nucleophilic aromatic substitution mechanism were operative. An aromatic S_N1 mechanism would be expected to product aryl iodides in the order of preference of 2,5-dimethyliodobenzene > p-iodotoluene > iodobenzene. A free radical process would also be expected to afford aryl iodides in the same order of preference as proposed for the S_N1 process. Furthermore, biaryls would probably be produced in a free radical process, and none were found.

It is also instructive to observe the relative amounts of 2,5-dimethylhalobenzene formed by pyrolysis of the chloride, bromide and iodide, respectively. The fact that the relative amount of 2,5-dimethyliodobenzene is greater than that of 2,5-dimethylbromobenzene, which, in turn, is distinctly greater than that of 2,5-dimethylchlorobenzene is also inexplicable in terms of any of the mechanisms cited above.

In our opinion, all of the results can best be explained in terms of the formation and subsequent intramolecular decomposition of a tetravalent sulfur compound, I. This decomposes preferentially in such a manner as to give maximum relief of steric strain; i.e., the 2,5-dimethylhalobenzene and phenyl p-tolyl sulfide are formed in the greatest amount of the three possible pairs of products, and the effect is larger the greater the size of the halogen. In each case the amount of the halobenzene produced exceeds that of the p-halotoluene. Since there are no major steric effects to consider in either of these alternative pathways of decomposition, the charge distribution in the transition state for the intramolecular decomposition of I is probably such that there is a greater electron density in the aryl groups than found in I; i.e., the intramolecular decomposition has some degree of the character of a nucleophilic substitution reaction but should not be confused with an uncomplicated bimolecular aromatic nucleophilic substitution mechanism.



I

The various triarylsulfonium halides were prepared by a modification of the procedure of Courtot and Tung (1).

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REFERENCES

(1) C. Cortot and T. Y. Tung, *Compt. rend.*, **197**, 1227 (1933).

Table 1

Pyrolyses of Triarylsulfonium Halides at 250°

Sulfonium Halide	Molar Ratio of Aryl Halides		
Phenyl-p-tolyl-2,5-dimethylphenylsulfonium chloride	C_6H_5Cl:	p-$CH_3C_6H_4Cl$:	2,5-$(CH_3)_2C_6H_3Cl$
	1.63	1.00	5.00
	1.38	1.00	5.00
Phenyl-p-tolyl-2,5-dimethylphenylsulfonium bromide	C_6H_5Br:	p-$CH_3C_6H_4Br$:	2,5-$(CH_3)_2C_6H_3Br$
	1.91	1.00	11.6
	1.92	1.00	11.9
Phenyl-p-tolyl-2,5-dimethylphenylsulfonium iodide	C_6H_5I:	p-$CH_3C_6H_4I$:	2,5-$(CH_3)_2C_6H_3I$
	3.40	1.00	12.4
	4.00	1.00	17.2
	2.40	1.00	17.6
Phenyl-p-tolyl-2,4-dimethylphenylsulfonium bromide	C_6H_5Br:	p-$CH_3C_6H_4Br$:	2,4-$(CH_3)_2C_6H_3Br$
	1.94	1.00	3.96
	1.88	1.00	4.32
Diphenyl-p-tolylsulfonium bromide	C_6H_5Br:	p-$CH_3C_6H_4Br$	
	3.40	1.00	
	3.40	1.00	
Diphenyl-2,5-dimethylphenylsulfonium bromide	C_6H_5Br:	2,5-$(CH_3)_2C_6H_3Br$	
	1.00	1.38	
	1.00	1.27	