# The Mechanism of the Rearrangement of Alkyl Aryl Ethers. Evidence Against a π-Complex Intermediate

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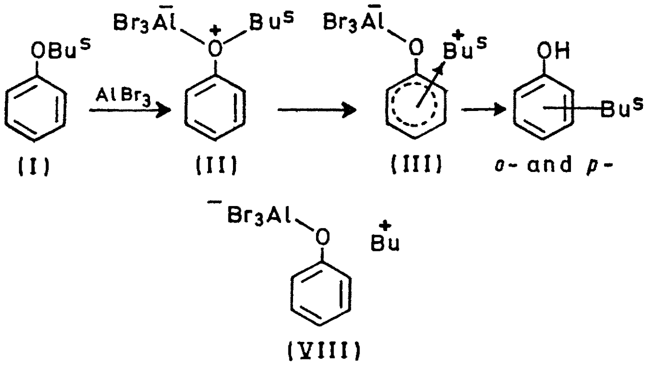
*Summary* Evidence is presented that a π-complex intermediate is not operative in the $AlBr_3$-catalysed rearrangement of s-butyl phenyl ether.

THE acid-catalysed rearrangement of alkyl aryl ethers to alkyl phenols was first reported in 1892.[1] Since that time there has been some evidence that the rearrangement proceeded *via* both an intermolecular and intramolecular pathway.[2] Dewar[3] concluded that the extent of intramolecular migration was dependent on the catalyst and homogeneity of the reaction media. However, $AlBr_3$ dissolved in chlorobenzene seemed to favour strongly the intramolecular route.[2d] Furthermore, the experimental evidence[3c] suggested that rearrangement of s-butyl phenyl ether (I) under these conditions took place almost exclusively by an intramolecular route. The suggested mechanism for the intramolecular process involved a π-complex intermediate (III) which demanded *complete* retention of configuration of the migrating s-butyl cation to both the *ortho* and *para* positions. The π-complex mechanism has also been applied to explain high *ortho* : *para* ratios in alkylations of anisole.[4a] Although recently questioned [4b] from data using (±)-1-methylheptyl phenyl ether, Dewar's intramolecular mechanism has heretofore never been studied using an optically-active ether with an examination made of *both* the *o*- and *p*-alkylated phenols. We report the results of such a test.



As previously described,[3c] a homogeneous solution of $AlBr_3$ in chlorobenzene was added slowly with stirring to (+)-(*S*)-(I), $[\alpha]_D + 27{\cdot}3°$ (neat, *l* 1) in chlorobenzene at 5°.† The phenolic products were found, by g.l.p.c., to

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† The configuration of the s-butyl phenyl ether is based upon the method of preparation from 2-bromobutane of known configuration. See: E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1937, 1196, 1199. The rotation given corresponds to an estimated 51·0% optical purity when based on the known purity of the active 2-bromobutane.

consist of 46·0% phenol; 36·0% (−)-(*R*)-*o*-s-butylphenol (IV), $[\alpha]_D$ − 1·33° (neat, *l*, 1), 7·2% optical purity;[5] 13·0% (−)-(*R*)-*p*-s-butylphenol (V) $[\alpha]_D$-6·98° (*c* 6·73, benzene), 26·5% optical purity;‡ 3·0% (−)-2,4-di-s-butylphenol (VI), $[\alpha]_D$ −8·59° (*c* 5·35, benzene); and <2% 2,6-di-s-butyl phenol. The rotations of (IV) and (V), corrected for optical purity of the starting ether, correspond to 14·1% and 52·0% respectively, net *inversion* of configuration. Significant quantities of both *o*- and *p*-s-butyl s-butylphenyl ethers (VII) were detected by g.l.p.c. during the course of the rearrangement. These disappeared entirely after complete addition of $AlBr_3$.

The rearrangement was also found to produce butylated chlorobenzenes in about 50% yield. These were shown to consist of 46% *racemic o*-, *m*-, and *p*-s-butyl chlorobenzenes and 4% *racemic* di-s-butylchlorobenzenes of undetermined orientations.

When the reaction was performed in benzene a yield of 73% (−)-(*R*)-s-butylbenzene, $[\alpha]_D$ − 0·88° (neat, *l* 1), 3·1% optical purity, was produced. Insufficient butylated phenols were available for analysis.

It is clear, therefore, that the major pathway of rearrangement under these conditions does not involve a $\pi$-complex intermediate. Our data are more consistent with two competing processes; one which involves a bimolecular displacement and the other, ion-pair formation. Thus, $S_N2$ type attack on (II) by (I) produced (VII) which upon further reaction produced (IV) and (V) with inversion of configuration of the butyl group. With benzene as solvent, similar reaction between (II) and benzene undoubtedly occurred leading to s-butylbenzene with inversion of configuration. Chlorobenzene, being less nucleophilic than benzene, was apparently unable to act in the same manner.

The large amount of racemic butylated chlorobenzene formed, in addition to the lack of complete inversion of configuration in (IV) and (V), indicated that (II) also dissociated to form ion-pair (VIII). Solvent separation of (VIII) and subsequent reaction of racemized s-butyl cation with solvent, and (I) would result in racemic butylated chlorobenzenes and racemic (IV) and (V), respectively. Collapse (internal return to the *ortho* position) would give (IV) with retention of configuration;[6] while any hydride shifts within the cation would be accompanied by racemization.

Striking evidence for the duality of mechanisms was given when the reaction was performed under the same conditions but with inverse addition; *i.e.* no excess of (I) present. Thus, (−)-(*R*)-(I), $[\alpha]_D$ − 15·1°, 30% optical purity, gave a phenolic extract which contained: 52% phenol; 43% (−)-(*R*)-(IV), $[\alpha]_D$ − 2·38°; and 3% *racemic* (V). The rotation of IV in this case corresponds to 54·2% net *retention*. Additionally 53·5% *racemic o*-, *m*-, and *p*-s-butylchlorobenzenes were found.

The possibility of hydride shifts in the ion pair being responsible for racemization is being investigated.

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‡ The configuration and optical purity of (V) was determined as follows: Reaction of (+)-(*S*)-s-butanol with toluene-*p*-sulphonyl chloride followed by reaction of the tosylate with *p*-anisylmagnesium bromide yielded (−)-(*R*)-*p*-s-butylanisole. Treatment of the (−)-(V) with dimethyl sulphate gave the identical product. See: J. Kenyon, H. Phillips, and V. Pittman, *J. Chem. Soc.*, 1935, 1080; D. J. Cram and F. A. Abd Elhafez, *J. Amer. Chem. Soc.*, 1952, **74**, 5860.

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