# Mechanism of Rearrangement of Alkyl Phenyl Ethers catalysed by Aluminium Bromide

By **M. J. S. Dewar** * and **P. A. Spanninger**, Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Rearrangement of [2-$^2$H]isobutyl phenyl ether with aluminium bromide in chlorobenzene leads to a mixture of s-butylphenols and chloro-s-butylbenzenes in which deuterium has been scrambled between the 2- and 3-positions. This result supports a recent conclusion that such rearrangements do not involve $\pi$-complex intermediates but are of carbonium ion type.

SOME years ago Dewar and Puttnam[1] concluded from studies of the products formed by acid-catalysed rearrangement of isobutyl phenyl ether (I) that the reactions involve two distinct mechanisms, one an intramolecular process proceeding *via* a $\pi$-complex and leading almost exclusively to *o*-isobutylphenol (II), the other taking place by a carbonium ion mechanism and leading predominantly to *p*-isobutylphenol (III). The retention of optical activity in analogous rearrangements of optically active alkyl aryl ethers was attributed to the $\pi$-complex mechanism which should lead to complete retention of configuration. The product formed by rearrangement of the ether (I) with aluminium bromide in chlorobenzene was almost exclusively the *ortho*-isomer, implying that the reaction proceeded almost entirely by the $\pi$-complex path.

Recently Spanninger and von Rosenberg[2] have tested this prediction by studying the rearrangement of optically active ether (I). When aluminium bromide was added to a solution of (I) in chlorobenzene (' normal addition '), the isomers (II) and (III) were formed with racemization accompanied by partial *inversion* of configuration while the *o*-(IV), *m*-(V), and *p*-(VI) chloroisobutylbenzenes simultaneously formed were completely racemic. The ratio (II) : (III) was *ca.* 3 : 1. They deduced from this result that the rearrangement of the ether (I) under these conditions is predominantly intermolecular, a molecule of the complex (I),$AlBr_3$ alkylating a second molecule of the ether (I). If the reaction is of $S_N1$ type, the isobutyl group would be transposed with racemization and partial inversion, as observed. Since the solvent was less nucleophilic than the ether (I), reaction with it would be slower so the intermediate isobutylium ions would have more time to racemize.

When the reaction was carried out by adding a solution of the ether (I) in chlorobenzene to one containing one equiv. of aluminium bromide in the same solvent (' inverse addition '), the ratio (II) : (III) in the product rose to 14 : 1 and (II) was now formed with partial *retention* of configuration (54%) while the isomer (III), and the three chloroisobutylbenzenes formed simultaneously, were racemic. They concluded that under these conditions rearrangement took place *via* an intermediate ion pair, s-$Bu^+PhOAlBr_3^-$, the predominance of the *ortho*-isomer in the product being due to the smaller separation of charge in the configuration of the ion pair leading to it. The retention of configuration was attributed to the reaction of the isobutylium ion at the *ortho*-position taking place so rapidly after heterolysis of the O–Bu bond that the butyl group does not have time to rotate. A similar explanation seems to account for the predominant *cis*-addition of hydrogen halides to olefins.[3]

While this work rules out the $\pi$-complex mechanism for these reactions, one point remains to be cleared up. It is not easy to see why the retention of configuration during rearrangement of the ether (I) should be so much less than that in the rearrangement of optically active phenyl 1-phenylethyl ether where 76% retention of configuration has been reported.[4] Since the 1-phenylethylium must be much more stable than isobutylium cation, its lifetime should be greater and the tendency to racemization likewise greater.

Spanninger and von Rosenberg[2] suggested that this discrepancy might be due to an alternative mode of racemization in the isobutylium ion, not available to the 1-phenylethylium cation, *i.e.* migration of hydrogen between the 2- and 3-positions. This could clearly be tested by studying the rearrangement of compound (I) labelled at the 2-position by deuterium. This experiment could also provide further support for the carbonium ion mechanism for rearrangement of (I) to (II) and (III).

## EXPERIMENTAL

Reduction of methyl ethyl ketone with lithium aluminium deuteride gave [2-$^2$H]isobutyl alcohol which was converted to [2-$^2$H]isobutyl phenyl ether as described.[2] Rearrangement of the deuteriated ether (I) by ' inverse addition ' was also carried out under the conditions of ref. 2. A solution of the [2-$^2$H]ether (I) (18·3 g, 121 mmol) in chlorobenzene (21 ml) was added slowly with stirring to a chlorobenzene solution (125 ml) of aluminium bromide (31·3 g, 121 mmol) at just below 5 °C. Phenolic materials were removed with alkali and the neutral residue distilled, giving mixtures of chloroisobutylbenzenes, and of chlorodi-isobutylbenzenes. The former was separated by preparative g.l.c. into the *o*-, *m*-, and *p*-chloroisobutylbenzenes (0·10 : 1·00 : 0·25) all of which were 98% pure (g.l.c., i.r.,

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[1] (*a*) M. J. S. Dewar and N. A. Puttnam, *J. Chem. Soc.*, 1959, 4080, 4086, 4090; (*b*) M. J. S. Dewar in ' Molecular Rearrangements,' ed. P. de Mayo, Wiley, New York, 1963, pp. 306—344.

[2] P. A. Spanninger and J. L. von Rosenberg, *J. Amer. Chem. Soc.*, 1972, **94**, 1970, 1973; *Chem. Comm.*, 1970, 795.

[3] M. J. S. Dewar and R. C. Fahey, *Angew. Chem. Internat. Edn.*, 1964, **3**, 245.

[4] H. Hart and R. J. Elia, *J. Amer. Chem. Soc.*, 1954, **76**, 3031.

and n.m.r.). The chlorodi-isobutylbenzenes fraction consisted mainly (>90%) of one isomer, chloro-3,5-di-isobutylbenzene (*vide infra*). The phenolic fraction was resolved by preparative g.l.c. into a main fraction, composed (>98%; g.l.c.) of *o*-isobutylphenol, and a minor fraction shown by i.r. and g.l.c. to consist of a mixture of the three isobutylphenols in the ratio *p* : *m* : *o* : : 7 : 2 : 1. The amount of the second fraction was insufficient for further purification.

The amount of hydrogen at each position in the isobutyl group was determined by n.m.r. spectroscopy, using a Varian HA 60 spectrometer and the signal for the four aromatic protons as reference.

*Chloro*-3,5-*di-isobutylbenzene*.—Separated by preparative g.l.c., the compound was a liquid, $n_D^{22}$ 1·5025, $\nu_{max.}$ 880 and 703 cm$^{-1}$ indicative of a 1,3,5-substituted benzene [5] (Found: C, 75·0; H, 9·3. Calc. for $C_{14}H_{21}Cl$: C, 74·85; H, 9·35%), δ ($CDCl_3$) 0·83 (m, 6H), 1·22 (s on d, 6H), 1·58 (m, 2·9H), 2·50 (sex, 1·3H), and 6·88 p.p.m. (aromatic, $A_2B$, 3H, $J_{AB} = J_{BA} = 1·6$ Hz). The $A_2B$ aromatic signals clearly indicate that the two alkyl groups are both *meta* to chlorine.

## RESULTS AND DISCUSSION

The Table shows the results of the n.m.r. analyses for the various products. In all cases the two methyl groups in the isobutyl groups each contained three protons, within the limits of experimental error, indicating that the deuterium is scrambled only between the secondary and tertiary positions.

Results of n.m.r. analysis

| Compound | Number of protons in CH and $CH_2$ groups of isobutyl | |
|---|---|---|
| | CH | $CH_2$ |
| [2-$^2$H]Isobutyl phenyl ether [2-$^2$H]-(I) | 0·0 | 2·0 |
| *o*-Isobutylphenol (II) | 0·5 | 1·6 |
| *m*-Isobutylphenol<br>*p*-Isobutylphenol (III) } (mixture [a]) | 0·6 | 1·3 [a] |
| *o*-Chloroisobutylbenzane (IV) | 0·5 | 1·5 |
| *m*-Chloroisobutylbenzene (V) | 0·7 | 1·4 |
| *p*-Chloroisobutylbenzene (VI) | 0·7 | 1·4 |
| Chloro-3,5-di-isobutylbenzene | 1·3 | 2·9 |

[a] Corrected for contamination by *ca.* 10% *ortho*-product.

Statistical distribution of the deuterium, due to complete scrambling, would lead to **1/3** of the deuterium at each of the three positions, *i.e.*, **0·67** protons at the methine carbon and **1·33** protons at the methylene one. It will be seen on this basis that scrambling was complete, within the limits of error for the *m*- and *p*-chloroisobutylbenzenes and for the mixture of *m*- and *p*-isobutylphenols.

These reactions must take place by a carbonium ion mechanism rather than *via* an intermediate π-complex because no scrambling could occur during the formation or rearrangement of such an intermediate. The bond linking the apical group (here isobutyl) to the donor in a π-complex is a normal covalent bond [6] and does not permit rearrangement of the apical group.

The distribution in *o*-isobutylphenol on the other hand is not statistical though it indicates extensive scrambling. This moreover was the *only* product that retained optical activity in the rearrangement of optically active ether (I).[2] Rearrangement of the ether (I) *via* an ion pair, involving the isobutylium cation, could of course take place with partial or complete retention of configuration, the degree of retention depending on the intimacy and lifetime of the ion pair. One would, however, expect hydrogen migration to lead to complete loss of activity [process (1)].

$$\left[\underset{X^-}{CH_3-\overset{+}{C}D-CH_2-CH_3}\right] \text{active} \longrightarrow \left[\underset{X^-}{CH_3-CHD-\overset{+}{C}H-CH_3}\right] \text{inactive} \qquad (1)$$

If it is assumed that migration of hydrogen is the only process leading to racemisation, and that the migration of hydrogen between the 2- and 3-positions of the isobutylium cation is not subject to significant secondary deuterium isotope effects, it can be shown that equation (2) obtains where $N_D$ is the fraction of isobutyl groups retaining deuterium at the 2-position and $N_A$ the fraction that retains optical activity. From the data in the Table, $N_D$ for isobutylphenol lies between 0·5 and 0·6, corresponding to values of $N_A$ in the range of 0·4—0·54. It can also be shown that the value of $N_A$ would be reduced if racemisation took place in any way other than that indicated in equation (2) or if any part of the reaction took place *via* a π-complex (with complete

$$N_D - 1/3 = 2/3 . N_A^{3/2} \qquad (2)$$

retention of deuterium and configuration). Since the observed [2] value for $N_A$ was 0·54 (*i.e.* 54% retention), and since this is the upper limit of the range predicted on the basis that the rearrangement takes place only *via* an ion pair, and racemisation only by hydrogen migration, it seems unlikely that the other possible processes can have been important.

According to the n.m.r. results the scrambling of deuterium in the *o*-chloroisobutylbenzene was also incomplete. This measurement was repeated several times so there seems no question concerning the difference between the *ortho*-isomers and the *meta*- and *para*-ones. The most obvious explanation would be that the isobutylium cation can be trapped by coordination to chlorine from where it migrates preferentially to the *ortho*-position.[7] One must then explain why the *ortho*-isomer is not [2] the main product, as is the case for the isobutylphenols. It is in fact quite possible that *o*-chloroisobutylbenzene is the main product initially but that it undergoes subsequent

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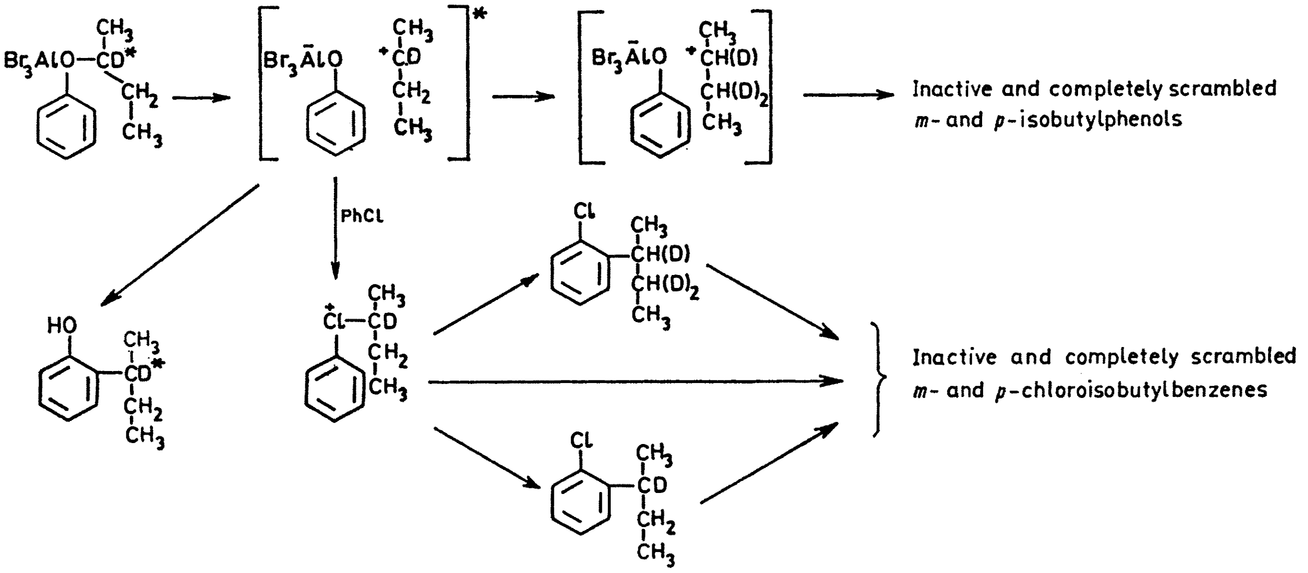
[5] R. M. Silverstein and G. C. Bassler, 'Spectrometric Identification of Organic Compounds,' Wiley, New York, 1967, 2nd edn., p. 73.

[6] M. J. S. Dewar, 'The Electronic Theory of Organic Chemistry,' Clarendon Press, Oxford, 1949; 'The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969.

[7] (*v*) P. Koviac and J. J. Hiller, jun., *J. Org. Chem.*, 1965, **30**, 1581; (*b*) D. A. Simpson, S. G. Smith, and P. Beale, *J. Amer. Chem. Soc.*, 1970, **92**, 1071.

rearrangement, catalysed by aluminium bromide. Independent experiments[8] showed that the chloroisobutylbenzenes are in fact rapidly isomerized to an equilibrium mixture under the conditions used to rearrange the ether (I).

The mechanisms suggested here are summarized by the Scheme, an asterisk indicating an optically active species.



SCHEME

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[8] P. A. Spanninger, Ph.D. Thesis, Clemson University, Clemson, South Carolina, 1970.