

### 579. *The Rearrangement of Benzyl p-Tolyl Ether.*

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The rearrangement of benzyl *p*-tolyl ether in a homogeneous medium catalysed by antimony trichloride is described and its mechanism discussed. The conversion of the ether into 2-benzyl-4-methylphenol takes place predominantly by an intramolecular process; scission into *p*-cresol occurs also. The titanium tetrachloride-catalysed rearrangement in benzene solution is also described.

PREVIOUS work indicates that the rearrangement of alkyl aryl ethers may be inter- or intra-molecular or a combination of both,<sup>1,2</sup> depending on the catalyst and the experimental conditions. It can proceed with great facility in the presence of suitable catalysts; for example, Tarbell and Petropoulos<sup>3</sup> and Dewar and Puttnam<sup>1</sup> noted that such reactions

<sup>1</sup> Dewar and Puttnam, *J.*, 1959, 4080 *et seq.*, and references given therein.

<sup>2</sup> Cullinane and Bailey-Wood, *Chem. and Ind.*, 1959, 543.

<sup>3</sup> Tarbell and Petropoulos, *J. Amer. Chem. Soc.*, 1952, **74**, 244.

are very rapid in homogeneous solution when catalysed by aluminium bromide; these authors favour an intramolecular mechanism.

Benzyl *p*-tolyl ether was chosen in the present work since here only *ortho*-migration occurs. Braun and Reich<sup>4</sup> previously used hydrochloric acid to promote the transformation of this ether to 2-benzyl-4-methylphenol. Hart and Elia<sup>5</sup> later effected the rearrangement of the analogously constituted  $\alpha$ -methylbenzyl *p*-tolyl ether in chlorobenzene solution, catalysed by aluminium bromide, and found that the product, 4-methyl-2- $\alpha$ -methylbenzylphenol, retained 76% of its configuration; from this they concluded that the reaction was mainly intramolecular.

We first studied the transformation for a benzene solution in the presence of titanium tetrachloride: as well as 2-benzyl-4-methylphenol and *p*-cresol, 2,6-dibenzyl-4-methylphenol, benzyl chloride, and a high-boiling product which had the properties of a benzyl polymer were obtained; not more than a trace of diphenylmethane, resulting from benzyl-ation of the solvent, was formed. Only a very small quantity of titanous chloride was used, since it had previously been observed<sup>5</sup> in a similar reaction that when 1 molar proportion of aluminium bromide was used in chlorobenzene solution the ether reacted completely in a few seconds even at  $-40^\circ$ . Our results (see Table 1) show the reaction with comparatively small amounts of titanous chloride in benzene at  $60^\circ$  to be complete in an hour

TABLE 1.

Rearrangement of benzyl *p*-tolyl ether (0.1 mole) catalysed by titanium tetrachloride in benzene (100 ml.) at  $60^\circ$

Time (hr.)	2-Benzyl-4-methylphenol (%)	2,6-Dibenzyl-4-methylphenol (%)	Benzyl chloride (%)	<i>p</i> -Cresol (%)	Ether recovered (%)
		(a) Catalyst, 0.009 mole.			
1	3.7	3.9	16.9	25.2	56.7
2	3.6	3.4	16.8	25.0	56.9
16.5	3.3	4.0	17.1	29.7	56.2
		(b) Catalyst, 0.018 mole.			
2	8.1	4.5	31.0	49.6	30.1

and to proceed to an extent proportional to the amount of chloride used. The catalyst is therefore used up in the reaction. This may be due to combination between the catalyst and the benzyl and *p*-tolyl-oxonium ions resulting from the scission of the ether, to give the product  $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{TiCl}_3$ , or, perhaps more probably, by a reaction such as the following, as this would account for the amount of benzyl chloride formed:  $\text{TiCl}_4 + 2\text{C}_6\text{H}_5\cdot\text{CH}_2^+ + 2\text{MeC}_6\text{H}_4\cdot\text{O}^- \longrightarrow (\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{O})_2 + 2\text{C}_6\text{H}_5\cdot\text{CH}_2\text{Cl}$ .

It was found that the kinetics of the reaction could be best studied in contact with antimony trichloride since its catalytic activity is known to be low. However, in experiments carried out in benzene solution, even for several days and with large amounts of catalyst, very little alkali-soluble material was obtained. More satisfactory results were achieved in the absence of solvent provided that temperatures were used at which the mixture became liquid and homogeneous. The plot of moles % of products against time is presented in Fig. 1. The shapes of the *p*-cresol and the 2-benzyl-4-methylphenol curve show that each of these products is formed at a finite rate at zero time, and hence both must have arisen directly from the ether. However, the curve for 2,6-dibenzyl-4-methylphenol exhibits the characteristic shape of a secondary product. Moreover, the first-order plot for decomposition of the ether is a straight line, whereas the second-order plot is markedly curved (Fig. 2).

<sup>4</sup> Braun and Reich, *Annalen*, 1925, **445**, 225.

<sup>5</sup> Hart and Elia, *J. Amer. Chem. Soc.*, 1954, **76**, 3031.

*Mechanism of the Reaction.*—The results of the antimony trichloride-catalysed reaction indicate that the formation of 2-benzyl-4-methylphenol (I) occurs mainly by an intramolecular process. The most satisfactory interpretation appears to be that the ether,

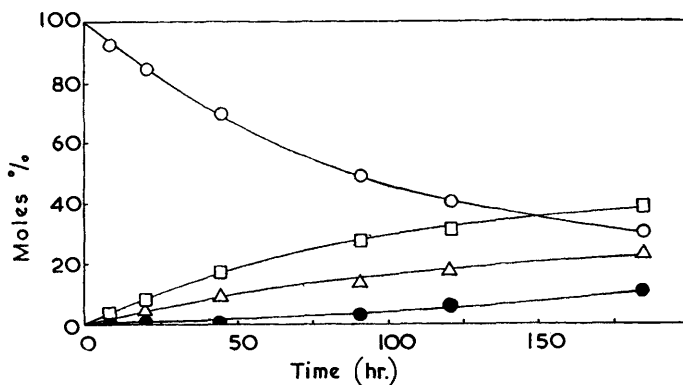


FIG. 1. Action of antimony trichloride on benzyl *p*-tolyl ether.  
 ○ Benzyl *p*-tolyl ether; □ 2-benzyl-4-methylphenol; △ *p*-cresol;  
 ● 2,6-dibenzyl-4-methylphenol.

which is assumed to form a complex with the catalyst immediately and completely, disappears by two reactions, (a) direct intramolecular isomerisation to the phenol (I) (reaction 1) and (b) scission into *p*-tolyl- and benzyl ions (reaction 2), the former ion

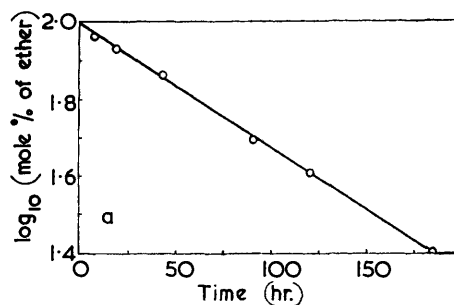


FIG. 2a.

FIG. 2. (a) First-order and (b) second-order plots for the disappearance of benzyl *p*-tolyl ether at 70°.

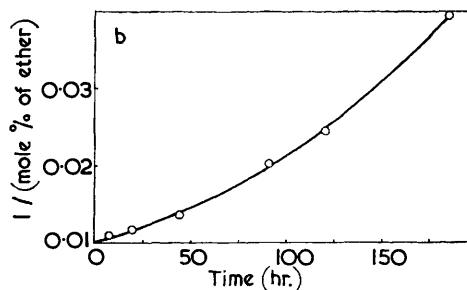
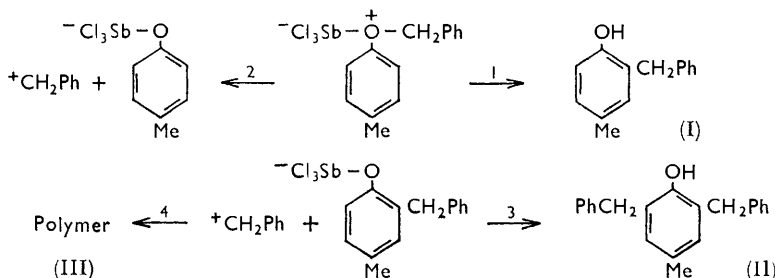


FIG. 2b.

yielding *p*-cresol and the latter subsequently reacting further to give partly 2,6-dibenzyl-4-methylphenol (II), as indicated in reaction 3, and to a greater extent a benzyl polymer (III) (reaction 4). The occurrence of reactions 3 and 4 is indicated by the fact that the proportion of (II) to (III) increases as the concentration of (I) increases (see Table 2).

It seems unlikely that the tolyloxy- and benzyl ions combine to give 2-benzyl-4-methylphenol since the *p*-cresol concentration increases continuously with time (Fig. 1). If the rearranged product were obtained in this way, as well as by the direct intramolecular process, one would expect the cresol curve to exhibit a maximum with a subsequent decline,



a result which is observed, for example, in the Fries rearrangement of *p*-tolyl acetate,<sup>6</sup> where the rearrangement product is postulated as arising in part from the two scission products,  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{O}^-$  and  $\text{CH}_3\cdot\text{CO}^+$ . This view is supported by Tarbell and Petropoulos's finding<sup>3</sup> that in the rearrangement of benzyl phenyl ether catalysed by aluminium bromide, *o*-benzylphenol, rather than being formed from the scission products of the ether, itself slowly

TABLE 2.

Rearrangement of benzyl *p*-tolyl ether (0.1 mole), catalysed by antimony trichloride (0.025 mole) at 70°.

Time (hr.)	2-Benzyl-4-methylphenol (%)	2,6-Dibenzyl-4-methylphenol (%)	Benzyl polymer (%)	<i>p</i> -Cresol (%)	Ether recovered (%)
8.0	2.3	0.5	3.1	3.7	82.2
20.0	4.7	1.4	5.7	8.2	84.8
44.5	9.6	1.5	15.0	17.2	70.0
91.0	13.7	3.7	25.8	27.4	49.2
121.0	17.5	6.1	27.5	31.2	40.6
185.0	22.2	11.3	31.0	38.8	25.4

decomposes, yielding phenol. A similar mechanism doubtless applies to the titanium tetrachloride-catalysed reaction.

The rate constant for the overall reaction obtained from the slope of the first-order plot gave a value of  $2.11 \times 10^{-6}$  sec.<sup>-1</sup>.

From the kinetics of the reaction the equation  $-dE/dt = (k_1 + k_2)E$  can be derived, where  $E$  is the concentration of unchanged ether. The ratio of the concentrations of cresol to ether reacted remains fairly constant throughout the reaction, which suggests that the former undergoes further reaction only to a negligible extent. Moreover, the sum of the concentrations of (I), (II), and cresol are seen (Table 2) to be roughly equal to the concentration of ether reacted. The values of  $k_1$  and  $k_2$ , calculated from the initial slopes of the 2-benzyl-4-methylphenol and the cresol curve, were found to be  $0.74 \times 10^{-6}$  sec.<sup>-1</sup> and  $1.40 \times 10^{-6}$  sec.<sup>-1</sup>, respectively. This agrees well with the value for the overall reaction obtained from the first-order plot.

#### EXPERIMENTAL

*Action of Benzyl Chloride on p-Cresol.*—Curtin and Wilhelm<sup>7</sup> prepared benzyl *p*-tolyl ether, together with other products, by refluxing benzyl bromide and the sodium derivative of *p*-cresol. In our experiments *p*-cresol (1.5 mole) and benzyl chloride (0.1 mole) were heated under reflux with 2*N*-sodium hydroxide (600 ml.). The yield was improved when the reaction was continued

<sup>6</sup> Cullinane and Edwards, *J.*, 1957, 3016.

<sup>7</sup> Curtin and Wilhelm, *J. Org. Chem.*, 1958, 23, 9.

for 3 hr., in place of the 1 hr. recommended by Gomberg and Buchler.<sup>8</sup> The product was dissolved in benzene and the organic layer washed successively with sodium hydroxide and water, to remove alkali-soluble material. After removal of the benzene, benzyl *p*-tolyl ether was distilled *in vacuo*; it had b. p. 136°/2.5 mm. Crystallisation from ethanol gave colourless plates, m. p. 41°, in 50% yield. Benzyl 2-benzyl-4-methylphenyl ether was obtained at 180—190°/0.3 mm. and crystallised from ethanol as plates, m. p. 45° (4%) (Found: C, 87.6; H, 6.9. Calc. for C<sub>21</sub>H<sub>20</sub>O: C, 87.5; H, 6.9%) (Curtin and Wilhelm<sup>7</sup> describe it as an oil). A still higher fraction (b. p. 200°/0.3 mm.) crystallised from light petroleum in needles, m. p. 39° (*ca.* 2%); this was 2,6-dibenzyl-4-methylphenol, previously described as an oil; <sup>7,9,10</sup> its  $\alpha$ -naphthylurethane formed needles, m. p. 162° (Found: C, 83.8; H, 5.9; N, 3.1. C<sub>32</sub>H<sub>27</sub>NO<sub>2</sub> requires C, 84.0; H, 5.9; N, 3.1%).

Acidification of the alkaline extract gave an oil, b. p. 135—136°/0.7 mm., which furnished needles (from light petroleum) of 2-benzyl-4-methylphenol<sup>10</sup> (20%), m. p. 36°. The  $\alpha$ -naphthylurethane<sup>4</sup> had m. p. 146° (Found: C, 81.6; H, 5.8; N, 3.8. Calc. for C<sub>25</sub>H<sub>21</sub>NO<sub>2</sub>: C, 81.7; H, 5.7; N, 3.8%), and the *aryloxyacetic acid* m. p. 119° (Found: C, 75.0; H, 6.2. C<sub>16</sub>H<sub>16</sub>O<sub>3</sub> requires C, 75.0; H, 6.25%). The *p*-cresol remained in solution.

*Benzyl 2-Benzyl-4-methylphenyl Ether.*—This was prepared by heating 2-benzyl-4-methylphenol (9.9 g.) under reflux for 3 hr. with benzyl chloride (6.5 g.) and a solution from sodium (2 g.) in ethanol (400 ml.). In addition to the expected ether (5.3 g.), 2,6-dibenzyl-4-methylphenol (1.5 g.) was obtained.

*Action of Titanium Tetrachloride on Benzyl p-Tolyl Ether.*—The general method adopted was as follows. To one neck of a 3-necked flask was attached a reflux water-condenser fitted with a calcium chloride guard-tube. Through the centre neck passed a glass stirring rod fitted with a mercury seal. To the third neck was attached a graduated tube fitted with a tap, the catalyst being introduced into the tube by driving it over with dry air from a storage bottle. The ether and benzene were introduced into the reaction vessel, which was cooled in ice-water, and the catalyst added gradually with vigorous agitation. The flask was then transferred to a thermostat-bath at the required temperature and the reaction allowed to proceed with continuous stirring for the requisite time. After being cooled in ice-water, the mixture was acidified with 4*N*-hydrochloric acid, giving a benzene and an aqueous layer; the former was extracted thoroughly with 2*N*-sodium hydroxide. Distillation with steam removed traces of benzene from the aqueous portion. After acidification and storage for 12 hr. the precipitated 2-benzyl-4-methylphenol was weighed; the *p*-cresol remained in solution and an aliquot part thereof was analysed for *p*-cresol by the potassium bromide-bromate method.<sup>6</sup> Tests showed that the amount of 2-benzyl-4-methylphenol present in the solution was negligible.

The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated on a water-bath; benzyl chloride was distilled over, followed by benzyl *p*-tolyl ether. A further fraction, b. p. 195—200°/0.3 mm., was composed of 2,6-dibenzyl-4-methylphenol, which had not dissolved in the alkali. A viscous oil remained; this was subjected to infrared and elementary analysis, which showed that it was a benzyl polymer. Such products are usually regarded<sup>11</sup> as having the formula (C<sub>7</sub>H<sub>6</sub>)<sub>x</sub> (Found: C, 92.5; H, 7.1. C<sub>7</sub>H<sub>6</sub> requires C, 93.3; H, 6.7%).

Reactions carried out for different times and with different proportions of catalyst are summarised in Table I.

*Action of Antimony Trichloride on Benzyl p-Tolyl Ether.*—(a) *In benzene.* The ether (0.15 mole), catalyst (0.15 mole), and benzene (300 ml.) were boiled under reflux for 144 hr. Almost all the ether was recovered; not more than 2% of 2-benzyl-4-methylphenol was formed. In a further experiment 0.4 mole of catalyst was used but very little more phenol resulted.

(b) *In the absence of solvent.* The reaction mixture was stirred continuously at 80° in a thermostat-bath, moisture being excluded. The procedure for the extraction and separation of the products was similar to that described, except that the acidified alkaline extract was shaken with ether and the solvent then evaporated. The amounts of *p*-cresol and 2-benzyl-4-methylphenol present were determined by infrared analysis with a Perkin-Elmer model 137 instrument, the former by reference to its absorption band at 740 cm.<sup>-1</sup> and the latter to the band at 728 cm.<sup>-1</sup>.

<sup>8</sup> Gomberg and Buchler, *J. Amer. Chem. Soc.*, 1920, **42**, 2066.

<sup>9</sup> Huston and Lewis, *J. Amer. Chem. Soc.*, 1931, **53**, 2379.

<sup>10</sup> Hickinbottom, *Nature*, 1938, **142**, 830; **143**, 520; Elkobaisi and Hickinbottom, *J.*, 1959, 1873.

<sup>11</sup> Jacobson, *J. Amer. Chem. Soc.*, 1932, **54**, 1513.

The total weight of alkali-insoluble products was determined and a known quantity, dissolved in cyclohexane, subjected to infrared analysis, the absorption peak at  $1176\text{ cm}^{-1}$  being used to ascertain the quantity of benzyl *p*-tolyl ether present. A further aliquot part in carbon tetrachloride gave the concentration of the 2,6-dibenzyl-4-methylphenol, the absorption at  $3550\text{ cm}^{-1}$  being measured on a Unicam S.P. 700 instrument. The results are presented in Table 2.

We thank Peter Spence & Sons Ltd. for a gift of titanium tetrachloride and Mr. G. Phillips for the infrared measurements; two of us (R. A. W. and G. B. C.) acknowledge maintenance grants from the Department of Scientific and Industrial Research.

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[Received, November 22nd, 1961.]

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