[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

The Migration of Alkyl Radicals. I. Transfer of Some Tertiary Alkyl Radicals from Phenols to Hydrocarbons

BY RICHARD A. SMITH

In a study of alkyl phenyl ether rearrangement it was found that the migrating alkyl group can be introduced into a different molecule instead of merely rearranging to another part of the same molecule.[1] In this report the migration has been extended to apply to the change of position from the phenol nucleus to the benzene nucleus. As with the migration quoted, the reaction offers a means of preparation of alkylated benzenes. In some studies of rearrangements performed in this Laboratory by Niederl and the author, which have not been reported, it has been observed that alkyl groups in the phenolic ring can be made to change ring position under the influence of rearranging agents such as are used to effect phenyl ether isomerizations. It was thought that this migration might be intermolecular, in which case it should be possible to effect the migration to a foreign nucleus. Para substituted tertiary alkyl phenols were chosen as being very likely to undergo migration with the least possible side reactions. The action of aluminum chloride in the presence of benzene at room temperature and at reflux temperature upon *p*-*t*-butylphenol, *p*-*t*-amylphenol and 4-(1,1,3,3-tetramethobutyl)-phenol has been studied. The products are phenol and corresponding alkylbenzenes. With the butylphenol a good yield of *t*-butylbenzene was obtained; the reaction was carried out at the reflux temperature. The migration of the amylphenol was performed at room temperature. The migration of the octylphenol was performed at both room temperature and at the reflux temperature. There was no fundamental change in the reaction. The products identified were free phenol and *t*-butylbenzene. It will be noticed that the octyl group underwent scission. This is not unexpected as a Friedel-Crafts reaction between diisobutylene and benzene yields *t*-butyl substituted benzenes.[2] If this migration is bimolecular, the results may be interpreted as additional evidence for the para position of the octyl group in 4-(1,1,3,3-tetramethobutyl)-phenol.[3]

Procedure

I. The Action of Aluminum Chloride upon *p*-*t*-Butylphenol.—A half mole of the phenol, two-thirds of a mole of technical anhydrous aluminum chloride, and 150 cc. of benzene were refluxed for eight hours. The whole was then poured upon ice, the organic layer separated and water washed. The aqueous layers were extracted with ether, the ether layer dried with anhydrous sodium sulfate, the ether evaporated on a steam-bath, and the residual liquid purified by distillation and identified as phenol. The organic layer was washed with Claisen solution, water and then dried with anhydrous sodium sulfate. The product was purified by fractional distillation. A small Hempel column was found useful.

t-Butylbenzene, b. p. 167–168°; n^{24}_{D} 1.4958; d^{24} 0.868; yield 70%. *Anal.* Calcd. for $C_{10}H_{14}$: C, 89.6; H, 10.4. Found: C, 89.3; H, 10.1.

II. The Action of Aluminum Chloride upon *p*-*t*-Amylphenol.—A half molar quantity of the phenol and corresponding quantities of aluminum chloride and benzene as in (I) were allowed to stand at room temperature for twelve days. The whole was then worked up as in (I). Phenol was again obtained. The other product was purified by fractional distillation using appropriate sized columns.

t-Amylbenzene, b. p. 188–190°, n^{24}_{D} 1.5032; d^{24} 0.864; yield 25%.

III. The Action of Aluminum Chloride upon 4-(1,1,3,3-Tetramethobutyl)-phenol.—A six molar quantity of the phenol was treated with equivalent amounts of aluminum chloride and benzene at room temperature as in (II). A half molar quantity was treated at the reflux temperature as in (I). The products soluble in Claisen solution, in addition to phenol, are still under investigation.

t-Butylbenzene.—Yield in the cold (a) 50%; in the hot (b) 70%. Calcd. for $C_{10}H_{14}$: C, 89.6; H, 10.4. Found: (a) C, 89.9, 89.2; H, 10.4, 10.1.

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Summary

1. The migration of alkyl groups from a phenol nucleus to a benzene nucleus has been demonstrated.

2. The above migration has been performed

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[1] Smith, THIS JOURNAL, 56, 714 (1934); also see Sowa, Hinton and Nieuwland, *ibid.*, 55, 3402 (1933); Behaghel and Freiensehner, *Ber.*, 67, 1368 (1934).

[2] Unpublished results of this Laboratory.

[3] Niederl, Smith and Whitman, THIS JOURNAL, 59, 715–718 (1937).

at room temperature and at the reflux temperature.

3. The scission of the octyl group of 4-(1,1,3,3-tetramethobutyl)-phenol has been demonstrated.

4. *t*-Butylbenzene has been prepared from 4-*t*-butylphenol and from 4-(1,1,3,3-tetramethobutyl)-phenol. *t*-Amylbenzene has been prepared from 4-*t*-amylphenol.

5. Further studies of this type of migration are being made. Systems now under investigation include migrations from phenol nuclei of different types of alkyl groups to simple and substituted (phenol, phenyl ether and naphthol) aromatic nuclei.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Equilibria of the Reactions between Acetylene and Heavy Water at 0 and 100° and the Heats of Reaction[1]

BY L. H. REYERSON AND BRUCE GILLESPIE

In a previous communication[2] the equilibrium constants for the reactions between acetylene and heavy water at 25° were given. At equilibrium six different molecular species were involved in seven possible reactions and the constants for five of them were calculated from the experimental results. The experimental technique involved the accurate determination of the deuterium content of the heavy water before and after exchange. This investigation has been extended and the equilibria of the reactions have been determined at 0 and 100°.

The experimental methods with some small refinements remained much the same as in the previously reported study, except that a heavily insulated constant temperature air thermostat was substituted for the water-bath used in the earlier investigations. At 100° the normal alkaline solutions attacked the Pyrex glass bulbs so strongly that several of them broke during the time required for equilibrium. As a result quarter normal solutions of sodium hydroxide were used in the experiments run at 100° and half normal solutions were used at 0°. Because of the high partial pressure of water vapor at 100° the partial pressure of the acetylene was kept at about half an atmosphere to reduce the hazard of explosions. In all cases the bulbs containing the acetylene and heavy water solutions were made up and run at room temperature for several days, after which they were run at either 100 or 0° for from forty-eight to sixty hours. At the conclusion of a given run the heavy water was recovered from the bulbs and its density determined in the same manner as previously reported.[2] From the changes in the density of the heavy water solutions and a knowledge of the equilibrium constants K_6 for the reaction $D_2O + H_2O \rightleftharpoons 2HDO$ and K_7 for the reaction $C_2D_2 + C_2H_2 \rightleftharpoons 2C_2HD$ it was possible to calculate the number of moles of each of the six reacting molecules at equilibrium. According to Topley and Eyring[3] K_6 has a value of 3.118 at 0° and 3.374 at 100°. Glockler and Morrell[4] gave the value of K_7 at 0° as 1.373 and at 100° as 1.584. Tables I and II give the results of these calculations at 0 and 100°.

Using the values given in Tables I and II the equilibrium constants for the following exchange reactions were calculated.

$$C_2H_2 + HDO \rightleftharpoons C_2HD + H_2O \quad (1)$$

$$C_2HD + HDO \rightleftharpoons C_2D_2 + H_2O \quad (2)$$

$$C_2H_2 + D_2O \rightleftharpoons C_2HD + HDO \quad (3)$$

$$C_2HD + D_2O \rightleftharpoons C_2D_2 + HDO \quad (4)$$

$$C_2H_2 + D_2O \rightleftharpoons C_2D_2 + H_2O \quad (5)$$

Table III gives the equilibrium constants for the exchanges at 0° and Table IV gives the values at 100°. The equilibrium constants at 100° are all higher than those previously reported at 25° and the values at 0° are all lower than at 25°.

It is of interest to note that Hiroto and Okamoto[5] calculated the equilibrium constant K_1 at 25° from spectroscopic data. They obtained a value of 0.59 where our experimentally determined value was 0.599. The agreement is excellent and

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[1] This investigation was made possible by a grant from the Graduate School of the University of Minnesota.

[2] L. H. Reyerson and Bruce Gillespie, THIS JOURNAL, **58**, 282 (1936).

[3] Topley and Eyring, *J. Chem. Phys.*, **2**, 217–230 (1934).

[4] Glockler and Morrell, *ibid.*, **4**, 15 (1936).

[5] Hiroto and Okamoto, *Bull. Chem. Soc. Japan*, **11**, 349-351 (1936).