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ALPHA,BETA-DIPHENYLETHYL ETHER AND ALPHA-(PARA-METHOXYPHENYL-BETA-PHENYL)-ETHYL ETHER

BY CORLISS R. KINNEY AND W. GLEN BYWATER

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In an attempt to oxidize the secondary alcohol, *p*-methoxyphenylbenzylcarbinol, with nitrogen trioxide, an unknown substance containing neither carbonyl groups nor nitrogen was obtained. Analyses and molecular weight determinations, as well as chemical properties, showed that the carbinol had been dehydrated to the corresponding ether, α-(*p*-methoxyphenyl)-β-phenylethyl ether. A similar reaction has been observed by a number of investigators,[1] who have shown that various acid reagents dehydrate diphenylcarbinol to its ether.

The new substance was also obtained in the preparation of *p*-methoxyphenylbenzylcarbinol, using the reaction of benzylmagnesium chloride with anisaldehyde.[2] The largest yields of the compound were obtained when the magnesium derivative was decomposed with a mixture of ice and concentrated hydrochloric acid. Following this procedure, no carbinol was isolated at all, and the major product was the dimolecular ether. Suspecting that dehydration of the carbinol was effected by the hydrochloric acid, several experiments were conducted using the pure carbinol, and varying ether–hydrochloric acid solutions. When the solution contained considerable acid, the carbinol was dehydrated to form *p*-methoxystilbene exclusively. Smaller concentrations of acid, however, in contact with anhydrous calcium chloride did give small amounts of the ether. The remainder of the carbinol was unchanged. The effect of the nitrogen trioxide gas, then, appeared to be that of an acid dehydrating agent similar to, but more effective than, hydrochloric acid. The larger yield of the ether from the Grignard reaction indicated that the dehydration occurred during the reaction or the process of decomposition of the magnesium derivative with the acid rather than a subsequent dehydration of the carbinol in an acidic ether extract.

Phenylbenzylcarbinol was transformed into its ether with somewhat greater difficulty than the methoxyl derivative. The method using nitrogen trioxide was not nearly as effective, nor was any ether isolated from the product of the reaction of benzylmagnesium chloride with benzalde-

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[1] (a) Linnemann, *Ann.*, **133**, 6 (1864); (b) Zagumenny, *ibid.*, **184**, 174 (1876); (c) Hofmann, Roth, Höbold and Metzler, *Ber.*, **43**, 2629 (1910); (d) Adams and Weeks, THIS JOURNAL, **38**, 2516 (1916); (e) Szperl and Wierusz-Kowalski, *Chem. Polski*, **15**, 23 (1917), *Chem. Abst.*, **13**, 2865 (1919).

[2] The ether of diphenylcarbinol was also obtained, among other products, by Oddo, *Gazz. chim. ital.*, [II] **37**, 356–66 (1907), from bromobenzene, magnesium. pyridine and benzaldehyde.

hyde. Small quantities of the ether were obtained, however, by the action of hydrochloric acid in an ether solution of the carbinol in contact with anhydrous calcium chloride.

Experimental Part

Preparation of α-(*p*-Methoxyphenyl)-β-phenylethyl Ether. (a) By the Action of Nitrogen Trioxide on *p*-Methoxyphenylbenzylcarbinol.—Thirty grams of pure *p*-methoxyphenylbenzylcarbinol was dissolved in 100 cc. of absolute ether and a slow stream of nitrogen trioxide from arsenic trioxide and nitric acid (sp. gr. 1.3) passed through the solution for twenty hours. The solid that crystallized out weighed nearly 8 g. and melted at 140–145°.

(b) **Preparation of the Ether in the Reaction of Benzylmagnesium Chloride with Anisaldehyde.**—The reaction of benzylmagnesium chloride with anisaldehyde normally gave yields of 64% of *p*-methoxyphenylbenzylcarbinol melting at 53–56° when the reaction mixture was carefully poured on ice and the precipitated basic magnesium salts dissolved with dilute sulfuric acid. None of the ether was isolated in such experiments. However, when the reaction mixture was poured into cracked ice and concentrated hydrochloric acid, the dimolecular ether separated from the solution, in which it was only slightly soluble, in large amounts. The oily residue failed to yield any of the carbinol, which is low melting.

(c) **Preparation by the Action of Hydrochloric Acid.**—Dry hydrogen chloride was passed into an absolute ether solution of 4 g. of *p*-methoxyphenylbenzylcarbinol for one hour. The carbinol was largely dehydrated to *p*-methoxystilbene, as proved by a mixed melting point determination. The yield was 2.54 g. or 69%.

Two grams of the carbinol and 2 cc. of concentrated hydrochloric acid were dissolved in about 40 cc. of ether and allowed to stand over calcium chloride (anhydrous) for several hours. As before, the carbinol was changed into *p*-methoxystilbene. The yield was 1.1 g. or 60%.

Finally 0.77 g. and 0.73 g. were allowed to stand over calcium chloride (anhydrous) in ether solutions containing one and two drops of concentrated hydrochloric acid, respectively. The first yielded 0.05 g. of the ether and the second 0.03 g. The remainder of the carbinol was recovered practically quantitatively.

Properties and Analyses of α(*p*-Methoxyphenyl)-β-phenylethyl Ether.—The ether was best purified by solution in a small amount of chloroform followed by dilution with several volumes of hot methyl alcohol. It crystallized in needles of m. p. 148–149° (uncorr.), was readily soluble in chloroform, moderately in acetone, slightly soluble in ether or alcohol and insoluble in petroleum ether.

Anal.[3] Subs., 0.2409, 0.2886: CO_2, 0.7274, 0.8643; H_2O, 0.1531, 0.1770. Calcd. for $C_{30}H_{30}O_3$: C, 82.19; H, 6.82. Found: C, 82.35, 81.96; H, 7.11, 6.86.

Mol. wt.: Calcd. for $C_{30}H_{30}O_3$: 438. Found: in chloroform, subs., 1.3866, 1.567; wt. of chloroform, 77.61; b. p. elevation, 0.200, 0.205°; mol. wt. 326.5, 368. Mol. wt. in camphor: subs., 0.0198, 0.0277, 0.3092; m. p. depression, 6.5, 6.9°; mol. wt., 393, 425.

The ether did not react with phenylhydrazine, hydroxylamine, sodium bisulfite, Schiff's reagent, sodium metal, nor benzoyl chloride. When boiled with hydrogen iodide in a Zeisel apparatus methyl iodide was produced, showing that the methoxyl group had not entered into a reaction. Oxidation with chromic anhydride in glacial acetic acid yielded benzoic and anisic acids. Distillation yielded a new substance melting at 107–108°, which was not *p*-methoxystilbene, m. p. 136°. Bromination with

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[3] Analysis made by Mr. D. P. Langlois of this Laboratory.

evolution of hydrogen bromide yielded a bromide melting at 174–175°. The bromide was not the dibromide of *p*-methoxystilbene, m. p. 177°.

Preparation of α,β-Diphenylethyl Ether. (a) By the Action of Nitrogen Trioxide.—Seven grams of phenylbenzylcarbinol was dissolved in dry ether and nitrogen trioxide, obtained as before, passed into the solution overnight. The ether was evaporated and the residue extracted with methyl alcohol, which dissolved the unchanged carbinol, leaving 0.5 g. of a substance melting at 129–130°.

Several other experiments, in which dry nitrogen trioxide was used, failed to produce the compound.

(b) By the Action of Hydrochloric Acid.—Three grams of phenylbenzylcarbinol was dissolved in ether and 4 cc of concentrated hydrochloric acid and anhydrous calcium chloride were added. The mixture was allowed to stand for one hour and then refluxed for an hour. More anhydrous calcium chloride was added and the flask set aside for three and one-half days. The ether solution was filtered and evaporated. The residue was dissolved in hot methyl alcohol, and on cooling 1.95 g. of slightly impure carbinol crystallized out. This material was extracted with a small amount of methyl alcohol, which left 0.135 g. of ether melting at 123–127°.

Properties and Analyses of α,β-Diphenyl Ethyl Ether.—The ether was purified by recrystallization from boiling methyl alcohol. It crystallized in needles, m. p. 129.5–130.5° (uncorr.), was readily soluble in chloroform, slightly soluble in ether or alcohol and insoluble in petroleum ether.

Anal.[4] Subs., 0.0512: CO_2, 0.1675; H_2O, 0.0322. Calcd. for $C_{28}H_{26}O$: C, 88.88; H, 6.87. Found: C, 89.21; H, 7.04.

Mol. wt.: Calcd. for $C_{28}H_{26}O$: mol. wt., 378. Mol. wt. in camphor: subs., 0.0031; wt. of camphor, 0.0478; depression of melting point, 6.4°. Mol. wt. found: 383.8.

Summary

p-Methoxyphenylbenzylcarbinol and phenylbenzylcarbinol have been found to be dehydrated to their ethers under certain acidic conditions.

Salt Lake City, Utah

[Contribution from the Rockefeller Physical Laboratory and the Baker Laboratory of Chemistry at Cornell University]

THE ABSORPTION SPECTRA OF THE GAMMA-PYRONES AND PYROXONIUM SALTS[1]

By R. C. Gibbs, John R. Johnson and E. C. Hughes[2]

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The unusual properties of the pyrone ring have resulted in considerable speculation concerning its structure. Investigations of the physical and chemical properties of the compounds in this group have led to the formulation of several different structures for the nucleus, none of which has been firmly established or generally accepted.

[4] Analysis made by Mr. Berne Woolley of this Laboratory.

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[2] Heckscher Research Assistant in Chemistry and Physics at Cornell University, 1928–1930.