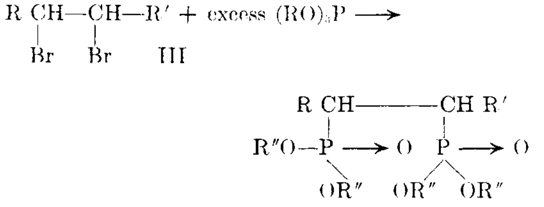

(2)

EXPERIMENTAL

Debromination of trans-dibenzoylethylene dibromide (Ia). A 20-g. sample of *trans*-dibenzoylethylene dibromide and 5.5 ml. of trimethyl phosphite were dissolved in 150 ml. of dry toluene and the solution was refluxed for 20 hr. The solvent was removed and the residue crystallized from ethanol. There was obtained 10.7 g. (92%) of product, m.p. 108–10°, which did not depress the melting point of an authentic sample of *trans*-dibenzoylethylene (IIa).

Debromination of chalcone dibromide (Ib). A 5.0-g. sample of chalcone dibromide and 1.9 ml. of trimethyl phosphite were dissolved in 75 ml. of dry toluene and the solution was refluxed for 2 hr. The solvent was removed and the residue was crystallized from ethanol. There was obtained 2.3 g. (80%) of product, m.p. 55–56°, which did not depress the melting point of an authentic sample of chalcone (IIb).

Debromination of cinnamic acid dibromide (Ic). A 10.0-g. sample of cinnamic acid dibromide and 4.5 ml. of trimethyl phosphite were dissolved in 150 ml. of dry toluene and the solution was refluxed for 20 hr. The reaction mixture was worked up identically to the previous reactions and yielded 4.4 g. (92%) of cinnamic acid IIc.

Reaction of trans-dibenzoylethylene dibromide with excess phosphate (IIIa). A 10.0-g. sample of *trans*-dibenzoylethylene dibromide and 7.0 ml. (2 mole equiv.) of trimethyl phosphite were dissolved in 75 ml. of dry toluene and the solution was refluxed for 20 hr. The solvent was removed and the residue was crystallized from benzene-hexane. There was obtained 7.5 g. (65%) of product, m.p. 131–134°. Three recrystallizations from benzene-hexane afforded the analytical sample, m.p. 134–135°.

Anal. Calcd. for $C_{20}H_{24}O_8P_2$: C, 52.9; H, 5.3; P, 13.6. Found: C, 53.2; H, 5.6; P, 13.9.

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Reaction of Benzyl Methyl Ether with Sodium Metal

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Shorigin[1] has demonstrated the rearrangement of benzyl ethers upon attempted sodium cleavage whereby reaction of benzyl ethyl ether with sodium at 170–210° for four and one-half hours led to 1-phenylpropanol in 30% yield. In the case of the corresponding benzyl methyl ether, no studies with sodium metal have been reported, although it has been shown that benzyl methyl ether (a) rearranges to 1-phenyl ethanol in 35% yield upon treatment with lithium phenyl,[2] (b) forms an uncharacterized product, b.p. 185–190° (12 mm.), in 30% yield when treated with potassium amide[3] in refluxing ether for nineteen hours, and (c) undergoes cleavage to lithium benzyl in 75–83%[4] yield (see however ref. 5 in which a yield of only 11% was obtained) with lithium wire in tetrahydrofuran at ±5°.

We have now found that, unlike the results with lithium which apparently cleaves the ether without rearrangement, the action of sodium on benzyl methyl ether leads consistently to 1-phenylethanol, the product of rearrangement.

In a typical experiment, benzyl methyl ether was heated under nitrogen at 115° for two hours with sodium which under the reaction conditions was a finely dispersed liquid. The purple-black reaction mixture led to a product shown by gas chromatographic analysis to consist of three components: toluene (23%), benzyl methyl ether (61%), and 1-phenylethanol (15%), identified by comparison of their retention times with authentic samples and by gas chromatographic analysis of samples to which authentic material was added. Further confirmation of the presence of 1-phenylethanol was obtained in a similar experiment by fractionation of the crude product and comparison of the infrared spectrum of the appropriate fraction with that of authentic 1-phenylethanol. The amount of 1-phenylethanol (5.5 g.) present in the crude product corresponds to 35% rearrangement.[6]

An experiment performed at 55° with the same reactants was interrupted after partial completion (two and one-half hours) by destroying unchanged sodium with water and isopropanol. Analysis by gas chromatography of the isolated organic layer indicated the presence of toluene (12%) and 1-phenylethanol (3%).

A single attempt to demonstrate the presence of sodium benzyl prior to the hydrolysis of a reaction conducted at 115° was unsuccessful. After completion of the two-hour heating period, a solution of benzophenone in benzyl methyl ether was added as a scavenger for sodium benzyl. However, analysis of the product showed a 63% recovery of benzophenone and no 1,1,2-triphenylethanol could be isolated from the reaction mixture.

In an effort to carry out the cleavage reaction under milder conditions, sodium dispersed in xylene was added to benzyl methyl ether chilled to

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[1] P. Shorigin, *Ber.*, **56**, 176 (1923); **57**, 1627, 1634 (1924).

[2] G. Wittig and L. Lohman, *Ann.*, **550**, 260 (1942).

[3] C. R. Hauser and S. K. Kantor, *J. Am. Chem. Soc.*, **73**, 1437 (1951).

[4] H. Gilman, H. A. NeNinch, and D. Wittenberg, *J. Org. Chem.*, **23**, 2044 (1958).

[5] J. F. Eastham and D. Y. Cannon, *J. Org. Chem.*, **25**, 1504 (1960).

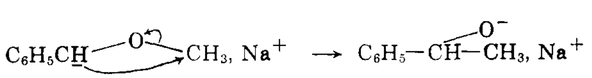
[6] This is a minimum figure. The actual amount of rearrangement is undoubtedly higher, as in the work-up 1-phenylethanol was not recovered from the washes—see Experimental.

0° by an ice-salt bath. The reaction mixture became dark purple immediately and a vigorous, short-lived, exothermic reaction raised the internal temperature to 190°. A 38% yield of 1-phenylethanol was observed among the products upon gas chromatography.

It is felt that the results of this work are accomodated by the presently accepted mechanism[1,2] of the ether → carbinol rearrangement. Cleavage of benzyl methyl ether by sodium benzyl (step 1) may be followed by proton exchange with benzyl methyl ether (step 2). Internal displacement (step 3) produces the anion of the observed product.

$$C_6H_5CH_2OCH_3 + 2Na \longrightarrow C_6H_5CH_2^-,Na^+ + CH_3O^-,Na^+ \quad \text{(Step 1)}$$

$$C_6H_5CH_2^-,Na^+ + C_6H_5CH_2OCH_3 \rightleftharpoons C_6H_5CH_3 + C_6H_5C^-HOCH_3,Na^+ \quad \text{(Step 2)}$$



$$C_6H_5C\underline{H}{-}O{-}CH_3,\ Na^+ \longrightarrow C_6H_5{-}\overset{O^-}{CH}{-}CH_3,\ Na^+$$

(Step 3)

While this mechanism does account qualitatively for the ultimate production of toluene although the solution is not an efficient source of benzyl anion for the scavenger benzophenone, the cause of the difference in the action of lithium (cleavage without rearrangement at −5°) and sodium (cleavage and rearrangement at 55° and higher) on benzyl methyl ether is not yet established.

EXPERIMENTAL

Columns for the gas chromatographic analyses were prepared as follows:

The silicone rubber packing was prepared by evaporative deposition of SE-30 Silicone Rubber[7] from chloroform solution onto four times its weight of Chromosorb W (60–80 mesh). The dry packing was introduced into a 6-ft. length of 0.25 in. O.D. copper tubing which was coiled and used in a Wilkens Aerograph Model A-90-C.

The Reoplex column was prepared by evaporative deposition of Reoplex 400[8] from chloroform solution onto four times its weight of Chromosorb W (60–80 mesh). The dry packing was suspended in water and the *p*H of the solution was adjusted to 7.4 by additions of 1% aqueous sodium carbonate and 1% aqueous acetic acid. The packing was dried at 110° for 2.5 hr. A test portion of the dry packing when resuspended in water gave a *p*H of 7.2. An 18-ft. copper column was employed in the determinations.

The benzyl methyl ether was distilled before use and had the constants: b.p. 93–94° (61 mm.); n_D^{20} 1.5013; water by Karl Fischer, 0.0167%. Infrared spectra were obtained with a Perkin-Elmer instrument, model 21.

Reaction of sodium with benzyl methyl ether. Freshly cut sodium cubes (6.0 g., 0.26 mole) were added to benzyl methyl ether (6.1 g., 0.5 mole). The mixture was stirred rapidly and blanketed with nitrogen throughout the reaction. Heat was applied to bring the internal temperature to 115° as rapidly as possible. A brief transition period occurred between 90 and 100° as the sodium melted and was thereafter present as finely dispersed globules. During this transition the pale yellow color of the reactants deepened and soon became purple-black. The internal temperature was maintained at 110–115° for 2 hr. at which time the sodium had disappeared. After cooling to room temperature, water (100 ml.) was added cautiously, the first several drops sufficing to discharge the purple color. The pale yellow organic layer was washed twice with saturated salt solution and dried over sodium sulfate. Filtration gave a pale yellow oil (37 g.) which was examined by gas chromatography on the Reoplex column at 150° and a flow of 50 cc./min., and on the silicon column at 238° and a flow of 30 cc./min. Three components were present: toluene (23%, 8.5 g.), unchanged benzyl methyl ether (61%, 22.5 g.), and 1-phenylethanol (15%, 5.5 g.). The identity of each component was established by its retention time on both columns and by observing the effect on the trace of adding a suspect component to the reaction mixture. By this method benzyl alcohol and 2-phenylethanol were shown to be absent from the products.

From a companion experiment the crude product was fractionated, and the infrared spectrum (neat) of the appropriate fraction was found to be that of 1-phenylethanol contaminated with benzyl methyl ether.

The reactions at lower temperatures were conducted in the same fashion except that the internal temperature was maintained at 50–60°.

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[7] Obtained from the General Electric Co., Silicone Products Dept., Waterford, N. Y.

[8] Obtained from Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

Derivatives of 1,3-Diazaspiro[4.5]decane

EDGAR SCHIPPER AND EDWIN CHINERY

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Because of the interesting pharmacological properties of a number of 1-substituted 1,3-diazaspiro-[4.5]dec-2-en-4-ones,[1] it became necessary to extend our work to the synthesis of other derivatives of the 1,3-diazaspiro[4.5]decane ring system.

As starting materials for this investigation we selected appropriately substituted 1-aminocyclohexanecarboxamides which are readily accessible from their corresponding aminonitriles.[1] Reaction between 1-(methylamino)cyclohexanecarboxamide and benzoyl chloride resulted directly in the formation of 1-methyl-2-phenyl-1,3-diazaspiro[4.5]dec-2-en-4-one (I); the corresponding reaction with 1-aminocyclohexanecarboxamide[1] led to 2-phenyl-1,3-diazaspiro[4.5]dec-1-en-4-one (II) whose structural assignment to the class of 5(4*H*)imidazolones is based on its ultraviolet spectrum which exhibits peak absorption at 230 mμ (log ε 4.24) but no absorption in the 260 mμ –270 mμ region.

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[1] E. Schipper and E. Chinery, *J. Org. Chem.*, **26**, in press.