[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS'

THE METALATION OF DIBENZHYDRYL ETHER AND CARBONATION WITH ALLYLIC REARRANGEMENT

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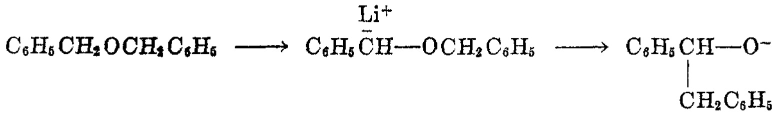
Received July 24, 1953

Dibenzyl ether was shown by Wittig and Lohman (1) to rearrange to benzylphenylcarbinol when treated with phenyllithium and evidence has been advanced (1, 2) that the reaction involves a hydrogen exchange to give the lithium derivative (A) followed by an internal displacement leading to (B). On the other hand,



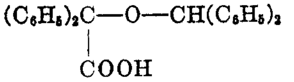
$$C_6H_5CH_2OCH_2C_6H_5 \longrightarrow C_6H_5\overset{Li^+}{\bar{C}}H{-}OCH_2C_6H_5 \longrightarrow C_6H_5\underset{CH_2C_6H_5}{\underset{|}{C}}H{-}O^-$$

A B

it has been found (3) that dibenzhydryl ether (I) is recovered unchanged after treatment with phenyllithium under the same conditions or even after considerably longer times. It seemed likely that the additional phenyl groups in I should not hinder, but, if anything, should aid, the hydrogen exchange reaction. This suggested that the lithium derivative of I was formed but was unable to rearrange. Were this the case it should be possible to demonstrate its presence with a suitable reagent.

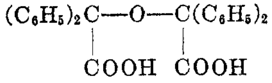
For this reason, I was allowed to react for 48 hours at room temperature with an equivalent amount of butyllithium and the solution was then treated with carbon dioxide. A complex mixture of acids was formed from which it was possible to isolate a single acid (II), m.p. 206°, in low yield. The use of excess butyllithium gave a 40–45% yield of solid acids (based on unrecovered starting material) from which II could be isolated in a yield of 7%.

The analysis and neutralization equivalent of II indicated that it was not the



$$(C_6H_5)_2\underset{COOH}{\underset{|}{C}}{-}O{-}CH(C_6H_5)_2$$

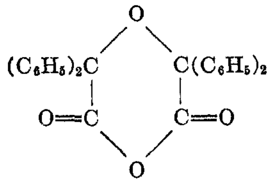
C



$$(C_6H_5)_2\underset{COOH}{\underset{|}{C}}{-}O{-}\underset{COOH}{\underset{|}{C}}(C_6H_5)_2$$

D

expected monobasic acid (C) but was a dibasic acid. It was therefore assigned the tentative structure D.



E

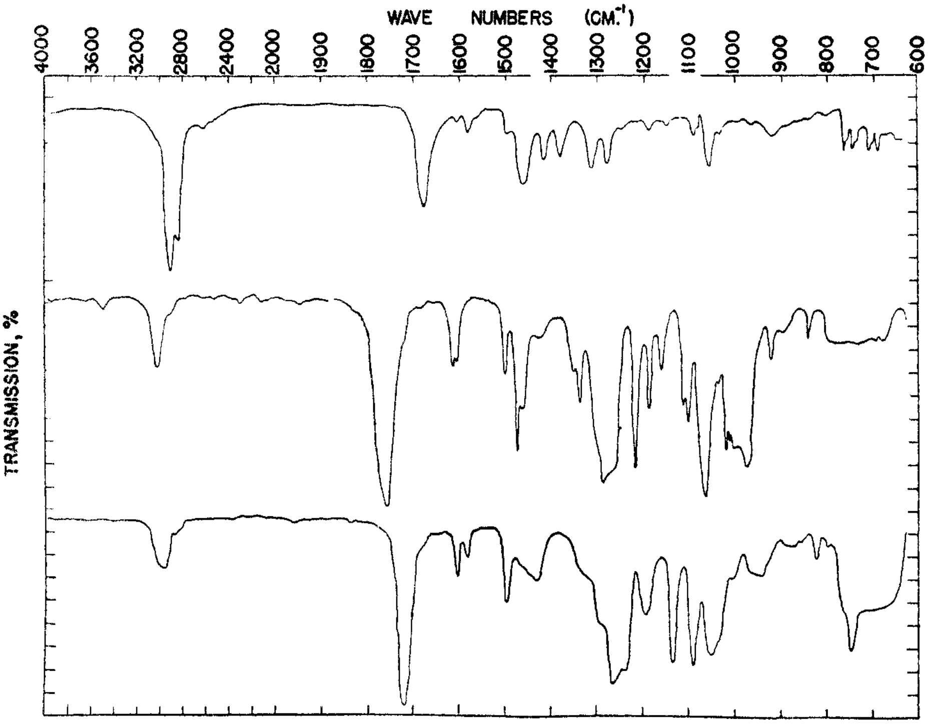
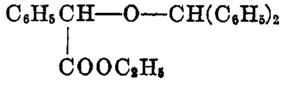


FIG. 1. INFRARED SPECTRA OF DI-*o*-CARBOXYBENZHYDRYL ETHER (II) IN A NUJOL MULL (upper curve); *o*-carboxybenzhydrol lactone (IV) as a 5% solution in ethylene dichloride (middle curve); and the methyl ester (III) of II as a 10% solution in methylene dichloride (lower curve).

II gave the anticipated dimethyl ester (III) when treated with diazomethane. Since a substance with structure D might be expected readily to form a 6-membered anhydride with structure E, II was heated at 215° for one-half hour and found to give a neutral substance (IV) with the correct analysis for E. As might be anticipated, IV could be obtained more easily (in 85% yield) by the reaction of II with excess thionyl chloride.

In spite of this evidence for the structures of II, III, and IV, there were two reasons for regarding them with suspicion. First the infrared spectrum (Fig. 1) of the dimethyl ester (III) showed its carbonyl absorption to be at 1720 cm.$^{-1}$, a frequency characteristic of conjugated esters, although the closely related model compound (V) shows the normal unconjugated ester carbonyl band at 1745 cm.$^{-1}$ (5). Second, the infrared spectrum of IV (Fig. 1) showed a single



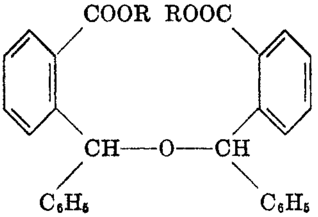
$$\underset{\displaystyle COOC_2H_5}{C_6H_5CH}—O—CH(C_6H_5)_2$$

V

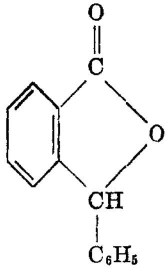
absorption band (at 1760 cm.$^{-1}$) in the carbonyl region while anhydrides have two characteristic bands (one at 1750–1800 and the second at 1800–1860 cm.$^{-1}$)

(4). An attempt to hydrolyze IV back to II was therefore made. IV dissolved slowly in boiling 10% potassium carbonate solution but the compound precipitated by the addition of hydrochloric acid to the solution was not II but, instead, was recovered IV!

The behavior of IV on hydrolysis together with its infrared absorption spectrum suggested that it was not an anhydride but rather a γ-lactone [expected absorption 1760–1800 cm.$^{-1}$ (4)]. Consideration of these additional inferences lead to the following formulae for II, III, and IV.[1]



II, R = H
III, R = CH_3



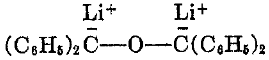
IV

IV had been prepared previously (6) by the reduction of *o*-benzoylbenzoic acid and repetition of this synthesis gave material identical with that obtained from the reaction of II with thionyl chloride.

It may be noted that the conversion of the dicarboxylic acid II to the lactone IV in yields of considerably more than 50% means that IV must have come from each half of II and, therefore, that each carboxyl group in II occupies an *ortho* position.

The formation of carboxylic acids from I in 40–45% yield indicates that I is extensively converted to its mono- or even di-lithium derivative and that the reason for the absence of the rearrangement previously observed is due either to the greater stability of the dibenzhydryl ether lithium derivative as compared with the dibenzyl ether derivative or to the greater steric strain in the transition state for rearrangement of the former.

It seems highly probable that II is formed from an α-lithium derivative such as (F) of I, with a rearrangement analogous to the formation of *o*-tolylcarbinol



$$(C_6H_5)_2\overset{Li^+}{\bar{C}}—O—\overset{Li^+}{\bar{C}}(C_6H_5)_2$$

F

from benzylmagnesium chloride (7). It is of interest, however, that arylphenylmethanes, where Ar is phenyl, *p*-tolyl, or naphthyl when treated with butyllithium and carbon dioxide give the unrearranged diarylacetic acids in yields of 20, 50, and 80% and in no case was any of the rearranged acid isolated (8).

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[1] It is of interest that the lactone (IV, $C_{14}H_{10}O_2$) has, coincidentally, the same elementary analysis as the anhydride (E), $C_{28}H_{20}O_4$, so that the analysis which was obtained was correct for either.

Acknowledgement. The authors are indebted to the E. I. Du Pont de Nemours and Company, Inc. for a Grant-in-Aid which supported this work.

EXPERIMENTAL

We are indebted to Mr. Joseph Nemeth, Mrs. E. Fett, and Mrs. Katherine Pih for the microanalyses and to Miss Helen Miklas for the infrared spectra which were determined with a Perkin-Elmer Double Beam Spectrophotometer, Model 21 with sodium chloride cells.

Reaction of dibenzhydryl ether (I) *with butyllithium and carbon dioxide.* To a solution of 70 g. (0.20 mole) of I in 250 ml. of dry benzene was added 800 ml. of a 1.2 *N* solution of butyllithium (0.96 mole) in ether. Heat was evolved spontaneously for about 10 minutes. The solution was allowed to stand for 50 hours and then poured onto a slurry of Dry Ice and ether. Addition of 200 ml. of concentrated hydrochloric acid in 200 ml. of distilled water, extraction of the acid solution with benzene, and extraction of the ether-benzene layer with 10% sodium bicarbonate solution, followed by decolorization of the basic solution with activated charcoal, and acidification gave 25 g. of crude acid. Of this material, 18.0 g. was heated with two 50-ml. and two 10-ml. portions of nitromethane to give 9.8 g., m.p. 180–185° This fraction was now suspended in 300 ml. of boiling nitromethane and filtered while still hot to give 3 g. of II, m.p. 203–206°.

Anal. Calc'd for $C_{28}H_{22}O_5$: C, 76.7; H, 5.0; Neut. equiv., 219.

Found: C, 77.0; H, 4.9; Neut. equiv., 219 ± 1.

The benzene-ether layer remaining after extraction of the acids above was dried and evaporated to give an oil from which it was possible to isolate 20.3 g. of starting I, m.p. 102–107°, by extraction of impurities with small amounts of cold acetone and crystallization from methanol.

The dimethyl ester (III) *of II* was prepared by treating 1.0 g. (0.0023 mole) of II in 100 ml. of ether with diazomethane (9) in ether until the yellow color of the diazomethane persisted. After 15 minutes, the excess diazomethane was decomposed with a few drops of acetic acid. Evaporation of the ether after washing with water and drying over magnesium sulfate gave 1 g. (93%) of an oil which soon solidified on standing and then had m.p. 96–102°. Two recrystallizations from heptane gave 0.6 g. of III, m.p. 103–105° and further recrystallization from the same solvent brought the m.p. to 104–104.5°.

Anal. Calc'd for $C_{30}H_{20}O_5$: C, 77.2; H, 5.6.

Found: C, 77.3; H, 5.6.

Reaction of II with thionyl chloride. To 2.0 g. (0.0045 mole) of II was added 2 ml. of freshly purified thionyl chloride. The mixture was allowed to stand for 12 hours (protected from external moisture with a calcium chloride drying tube). Addition of 10 ml. of heptane to the resultant oil gave white crystals which, after being washed with heptane, amounted to 1.6 g. (84%) and melted at 113–115°. Further recrystallization gave pure IV, m.p. 116.5–117°.

Anal. Calc'd for $C_{14}H_{10}O_2$: C, 80.0; H, 4.8.

Found: C, 80.2; H, 4.8.

Mixture melting points with the lactone prepared by the reduction of *o*-benzoylbenzoic acid by the method of Ullmann (6) showed no depression.

Thermal conversion of II to IV. II (0.40 g., 0.00091 mole) was heated at 215–225° under a pressure of 50–60 mm. for 30 minutes. On cooling, the light brown melt solidified and was treated with 30 ml. of boiling heptane. A small amount of brownish immiscible oil was disregarded. Evaporation of the solution to a volume of about 15 ml. and cooling gave 0.18 g. (47%) of IV, m.p. 112–114°. Further recrystallization gave a m.p. and mixture m.p. with IV, above, of 115–116°.

SUMMARY

Dibenzyl ether has been found to undergo hydrogen exchange with butyllithium to give a lithium derivative which, on treatment with carbon dioxide, is

converted to a mixture of solid acids from which only di-(*o*-carboxybenzhydryl) ether could be isolated.

This observation indicates that the previously reported failure of dibenzhydryl ether to undergo rearrangement with butyllithium under conditions which caused rearrangement of dibenzyl ether was not due to failure of the lithium derivative to form in the benzhydryl case but rather to its failure to rearrange.

In the course of the proof of structure of di-(*o*-carboxy)benzhydryl ether it was shown to be converted to the lactone of *o*-carboxybenzhydrol on treatment with thionyl chloride at room temperature or on heating at 215°.

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