[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Cleavage and Rearrangement of Ethers with Bases. I. The Reaction of Dibenzyl and Related Ethers with Potassium *t*-Butoxide[1]

BY DAVID Y. CURTIN AND SIDNEY LESKOWITZ

A re-examination of the reported cleavage of dibenzyl ether with potassium hydroxide at 200° has shown that the reaction actually observed was probably the uncatalyzed thermal cleavage. Dibenzyl ether has been shown to react with potassium *t*-butoxide to give desoxybenzoin, benzoic acid, benzyl alcohol and toluene. It is suggested that a possible intermediate in this reaction is benzylphenylcarbinol which is shown to give the same products. Dibenzhydryl ether has been shown to react with potassium *t*-butoxide at lower temperatures to give benzophenone and diphenylmethane. Diphenylbenzhydrylcarbinol, a possible intermediate in this reaction, reacts with potassium hydroxide in ethanol to give the same products. Two new ethers, 4,4'-dinitrobenzhydryl ether and bis-4,4'-dinitrobenzhydryl ether, have been prepared and their reactions with potassium *t*-butoxide studied. The former has been shown to give *p*-nitrobenzoic acid and tetraphenylethane while the latter gave 4,4'-dintrobenzophenone as the only product isolated.

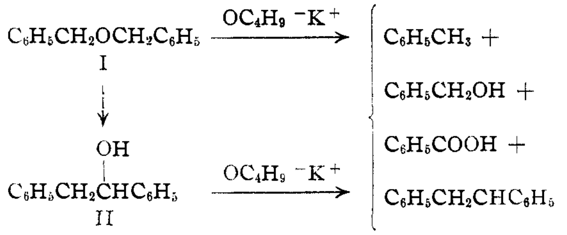
Dibenzyl ether (I) has been reported[2] to react with potassium hydroxide at 200° to give benzoic acid and toluene in unspecified yield. Since this reaction bears a formal resemblance to the cleavage of S-desylthioglycolic acid to desoxybenzoin with bases[3] in which we were interested it was decided to investigate the reaction of I in more detail.

When equimolar quantities of I and potassium hydroxide were heated at 250° for 27 hours, 78% of the starting ether was recovered. In addition benzoic acid (19 mole %), benzyl alcohol (1.1 mole %) and toluene (3 mole %) were obtained.[4] Since I is known to undergo an uncatalyzed thermal cleavage to toluene and benzaldehyde[5] it was heated under conditions similar to those above in the absence of sodium hydroxide. Within the limits of experimental error the same amount of I was recovered as in the preceding reaction. However, toluene (9 mole %) and benzaldehyde (11 mole %) were the only products isolated. It is evident that there is little or no catalysis of the cleavage of I by solid potassium hydroxide under these conditions. The effect of the potassium hydroxide seems to be to convert the benzaldehyde formed in the thermal cleavage to benzyl alcohol and benzoic acid in a Cannizzaro reaction. The large amount of benzoic acid relative to the amounts of toluene and benzyl alcohol is not surprising since both benzyl alcohol[6a] and toluene[6b] have been reported to react with potassium hydroxide under these conditions to give benzoic acid.

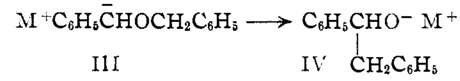
The effect of a stronger base, potassium *t*-butoxide, on I was next investigated. At 200° for one hour (conditions under which it undergoes no appreciable thermal cleavage) I reacted with an equimolar amount of potassium *t*-butoxide to give toluene (22 mole %), benzoic acid (11 mole %), benzyl alcohol (15 mole %), desoxybenzoin (13 mole %) and unreacted I (53%).

The critical step in the cleavage of I with potassium *t*-butoxide can be postulated as a β-elimination giving benzaldehyde and potassium benzylate as the initial products. However, I has been shown to undergo a different reaction with stronger bases such as phenyllithium in ether or potassium amide.

Wittig and Lohmann[7] showed that I reacts with phenyllithium in ether to give phenylbenzylcarbinol (II). They postulated that the reaction is



an intramolecular rearrangement



$$\underset{\text{III}}{M^+C_6H_5\bar{C}HOCH_2C_6H_5} \longrightarrow \underset{\text{IV}}{C_6H_5\underset{CH_2C_6H_5}{\underset{|}{C}}HO^-\ M^+}$$

This postulation has been confirmed by Hauser and Kantor[8] who also found that I reacted with potassium amide in diethyl ether to give II (51%), toluene (22%) and benzaldehyde (28%). Hauser and Kantor[8] considered the toluene and benzaldehyde to be formed by a β-elimination reaction which competed with the rearrangement.

It seemed possible to us that the reaction of I with potassium *t*-butoxide might proceed not by a simple β-elimination but by a rearrangement to II analogous to the phenyllithium reaction followed by a base-catalyzed cleavage of II to benzaldehyde and toluene.

As a test of this hypothesis the potassium salt of II was prepared by the reaction of potassium and II in *t*-butylbenzene and subjected to conditions comparable to those used in a reaction of I with potassium *t*-butoxide. II underwent cleavage more rapidly than I to give products which were identical with those obtained in the ether cleavage.[9] It is of interest that although the potassium salt of II underwent 70% reaction in one hour at 200° the

---

(1) Abstracted from the Ph.D. thesis submitted to Columbia University by Sidney Leskowitz.

(2) R. F. Bacon, *Am. Chem. J.*, **33**, 97 (1905).

(3) S. Teich and D. Y. Curtin, THIS JOURNAL, **72**, 2481 (1950).

(4) When a similar reaction was allowed to proceed for seventy-two hours at 200°, 90% of unreacted ether was recovered.

(5) C. W. Lowe, *Ann.*, **241**, 374 (1887).

(6) (a) G. Lock, *Ber.*, **63**, 551 (1930); (b) H. Schrader, *Ges. Abhandl. Kenntnis Kohle*, **4**, 323 (1921) [*Chem. Zentr.*, **92**, I, 537 (1921)].

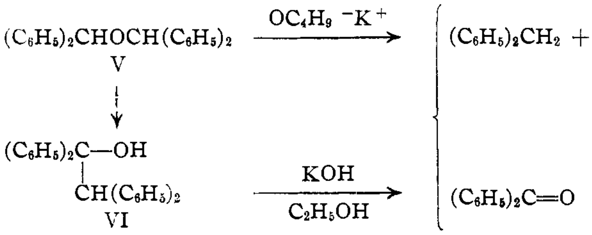
(7) G. Wittig and L. Lohmann, *Ann.*, **550**, 260 (1942).

(8) C. R. Hauser and S. W. Kantor, Abstracts of Papers presented at the 116th Meeting of the American Chemical Society, September, 1949, p. 46M. We did not learn of these results until our own experimental work was completed. Since then Professor Hauser has very kindly sent us a copy of their paper on this subject.

(9) Similar results were obtained by heating II with potassium *t*-butoxide. A small amount of stilbene was obtained from II but not from I. Since it is impossible to reproduce exactly the environment II would have as an intermediate in the reaction of I this observation is of uncertain significance.

lithium salt was recovered unchanged after such treatment.[10]

The behavior of dibenzhydryl ether (V) toward potassium *t*-butoxide was next investigated. V, which undergoes no appreciable thermal cleavage at 150° in one day, was cleaved to benzophenone and diphenylmethane (each in 80% yield) by treatment for one-half hour at 150° with an equimolar amount of potassium *t*-butoxide. Cleavage could also be effected by boiling the ether with 1 *N* potassium *t*-butoxide in dioxane. If the reaction of this compound involved rearrangement followed by cleavage the intermediate alcohol would be benzhydryldiphenylcarbinol (VI). This compound had been reported by Koelsch[11] to react with ethanolic potassium hydroxide to give benzophenone and



diphenylmethane. Roger and McGregor[12] had been unable to repeat this work, however, and had reported the formation of benzhydrol as the only product obtained from the reaction. We, therefore, prepared VI and treated it with potassium hydroxide in ethanol. Under conditions in which the reaction of V was too slow to be observed, VI was completely converted to benzophenone (100% yield) and diphenylmethane (75% yield).

A possible interpretation of the reactions of the bases mentioned above with I would appear to be that in which the initial reaction leads to the anion (or ion pair) III which then rearranges to IV. In the reaction with phenyllithium, IV is stable to the reaction medium and the product isolated is II. In our reaction (with potassium *t*-butoxide) IV could be in part cleaved to benzaldehyde and toluene and in part oxidized by the benzaldehyde to desoxybenzoin. The reactions of V can be explained on a similar basis. The alternative postulated by Hauser and Kantor[8] that III can undergo rearrangement to IV or β-elimination to benzaldehyde as competing reactions has not been excluded.[13] It is reasonable that rearrangement might predominate in the phenyllithium reaction and that the proportion of β-elimination may increase with a change in medium and at higher temperatures. We have found that V is not rearranged by treatment with phenyllithium at room temperature in ether for 96 hours. This does not exclude rearrangement as the first step in the cleavage of V with potassium *t*-butoxide, however, since the latter reaction occurs at a considerably higher temperature and the differences in behavior of salts of different cations has already been noted.

The reaction of benzhydryl 4,4′-dinitrobenzhydryl ether (VII) with potassium *t*-butoxide was also examined. VII was prepared by the reaction of diphenyldiazomethane with 4,4′-dinitrobenzhydrol in the presence of *p*-toluenesulfonic acid. When it was treated for three hours with a refluxing 0.1 *N* solution of potassium *t*-butoxide in *t*-butyl alcohol (conditions toward which V was stable), *p*-nitrobenzoic acid (45 mole %) and tetraphenylethane (18 mole %) were obtained.[14] We are unable at present to suggest a satisfactory explanation for this reaction.

$$\underset{\text{VII}}{(p\text{-}NO_2C_6H_4)_2CHOCH(C_6H_4)_2} \xrightarrow{K^+OC_4H_9^-} p\text{-}NO_2C_6H_4COOH + (C_6H_5)_2CHCH(C_6H_5)_2$$

4,4′-Dinitrobenzhydrol was prepared by the reduction of 4,4′-dinitrobenzophenone with aluminum isopropoxide and converted to bis-4,4′-dinitrobenzhydryl ether (VIII). A preliminary experiment showed that a suspension of this compound in dioxane reacted readily with potassium *t*-butoxide to give a mixture from which a 23% yield of 4,4′-dinitrobenzophenone could be isolated.

$$\underset{\text{VIII}}{(p\text{-}NO_2C_6H_4)_2CHOCH(C_6H_4NO_2\text{-}p)_2} \xrightarrow{OC_4H_9^-K^+} (NO_2C_6H_4)C=O$$

Experimental[15]

Reaction of Dibenzyl Ether (I) with Potassium Hydroxide.—The suspension obtained by mixing I (99 g., 0.50 mole) with potassium hydroxide (28 g., 0.50 mole) was heated in a copper distillation apparatus for 27 hours at 250° (Woods metal-bath). In a typical run toluene (3.0 g., 0.033 mole) distilled out during the reaction. Benzoic acid (11.7 g., 0.096 mole, m.p. 121–122°) was separated by extraction with sodium bicarbonate solution and recrystallized from water. Benzyl alcohol (0.6 g.) and unreacted dibenzyl ether (77 g.) were recovered by distillation of the residue under reduced pressure.

When I (50 g., 0.25 mole) was heated for 24 hours at 250° in a copper flask which had been washed with acid, rinsed thoroughly with water and dried, toluene (3.0 g.) and benzaldehyde (3.0 g.) distilled out during the reaction. Distillation of the residue gave 42 g. of recovered diphenyl ether.

Reaction of I with Potassium *t*-Butoxide.—A slurry of potassium *t*-butoxide (56 g., 0.50 mole) and 99 g. (0.50 mole) of I was heated in a glass distillation apparatus for one hour at 200°. An outlet from the receiving flask was inserted into a solution of bromine in carbon tetrachloride to test for the evolution of isobutylene. No decolorization of the bromine was noted during the course of the reaction.

The distillate which collected was redistilled (b.p. 82°) and was found to be an azeotrope of toluene and *t*-butyl alcohol. The *t*-butyl alcohol was removed by treatment with phosphorus pentoxide and the toluene remaining (10 g., 0.11 mole) on redistillation boiled at 108–110° (760 mm.).

The red cake remaining in the reaction flask was added to 250 cc. of water and extracted with ether. The water layer on acidification gave benzoic acid which after crystallization from water amounted to 6.3 g. (0.052 mole) (m.p. and mixed m.p. with an authentic sample, 120–121°). The ether layer obtained above was fractionally distilled to give benzyl

---

[10] Compare W. E. Doering, G. Cortes and L. H. Knox, THIS JOURNAL, **69**, 1700 (1947), and Hauser and Kantor, ref. 9.

[11] C. F. Koelsch, *ibid.*, **53**, 1147 (1931).

[12] R. Roger and A. McGregor, *J. Chem. Soc.*, 7850 (1934).

[13] Professor Hauser, since this manuscript was submitted, has kindly informed us that "benzylphenylcarbinol may be recovered essentially unchanged after standing with potassium amide in liquid ammonia under conditions employed in the rearrangement of dibenzyl ether." This result indicates that, at least with potassium amide, dibenzyl ether undergoes an elimination reaction to give benzaldehyde and toluene directly.

[14] Another run in dioxane gave 12% *p*-nitrobenzoic acid and 40% tetraphenylethane.

[15] All melting points are corrected. Analyses were carried out by the Clark Microanalytical Laboratory, Urbana, Illinois; the Elek Microanalytical Laboratories, Los Angeles, California; and the Schwarzkopf Microanalytical Laboratory, Elmhurst, Long Island.

alcohol (8.1 g., 0.075 mole, b.p. 63° (1.5 mm.), α-naphthylurethan (m.p. 130–132°), recovered I (52.3 g., 53%, b.p. 118–125° (1.3 mm.)) and desoxybenzoin (13.8, 0.065 mole, b.p. 135–137° (1.2 mm.)). The desoxybenzoin solidified on standing and, after recrystallization from ligroin and then from ethanol, melted at 55–55.5°. A semicarbazone, oxime and 2,4-dinitrophenylhydrazone were prepared and melted at the temperatures reported in the literature.

Thermal Decomposition of the Potassium Salt of Phenylbenzylcarbinol (II).—To a suspension of potassium sand (0.65 g., 0.016 mole) in *t*-butylbenzene (50 ml.) at room temperature was added 3.3 g. (0.016 mole) of II. The mixture was stirred for one hour at the end of which the potassium had reacted. The cloudy yellow solution was then refluxed for four hours under a calcium chloride drying tube. Benzoic acid (0.8 g., 0.0065 mole, 40 mole %) was isolated as above and melted at 120–121° (no depression when mixed with an authentic sample). The organic layer remaining after removal of the benzoic acid was subjected to distillation at 10 mm. pressure to remove the *t*-butylbenzene and ether. The residual oily solid was recrystallized from isoöctane to give 1.3 g. of impure solid which was brominated in ether to yield *trans*-stilbene dibromide (0.45 g.) and mixed m.p. with an authentic sample 240–242°). This is equivalent to 0.24 g. (7%) of stilbene. When the above filtrates were collected and treated with 2,4-dinitrophenylhydrazine (1.0 g.) and 2 ml. of concentrated hydrochloric acid, desoxybenzoin 2,4-dinitrophenylhydrazone, m.p. 195–200° (0.15 g., equivalent to 0.07 g. or 2% of desoxybenzoin). A mixed melting point with an authentic sample showed no depression.

As a control, dibenzyl ether (I) (0.50 mole) was heated with an equivalent amount of potassium *t*-butoxide in 200 ml. of *t*-butylbenzene with stirring under reflux for five hours at 160–165°. The starting ether (I) (83%) was recovered and, in addition, benzoic acid (9.4 mole %), benzyl alcohol (5.6 mole %) and desoxybenzoin (9%) were isolated.

Synthesis of Dibenzhydryl Ether (V).—The method of Ward[16] was less satisfactory for the synthesis of this compound than the following simple procedure. Benzhydrol (II) (2.0 g.) and 20 ml. of 85% phosphoric acid were heated at 75° for ten minutes. The slurry was poured into 100 ml. of water. The resulting white precipitate was collected and, after recrystallization from ethanol, yielded 1.8 g. (90% yield) of V, m.p. 108–109°.

Reaction of Dibenzhydryl Ether (V) with Potassium *t*-Butoxide (a) without Solvent.—A mixture of 10 g. (0.030 mole) of V and 3.2 g. (0.030 mole) of potassium *t*-butoxide was heated in a flask at 150° for 30 minutes, during which time an intense purple color developed. Extraction of the acid fraction of the product yielded 0.5 g. of benzoic acid, m.p. 116–120° (no depression when mixed with an authentic sample). Benzophenone was separated by crystallization of the 2,4-dinitrophenylhydrazone (8.4 g., m.p. 232–234°, equivalent to 4.2 g., 81% yield, of benzophenone) from the product mixture dissolved in 350 ml. of ethanol. A mixed m.p. with an authentic sample showed no depression. Evaporation of the alcoholic filtrate and steam distillation yielded 3.5 g. (73% yield) of diphenylmethane, b.p. 255° (760 mm.), $n^{25}\text{D}$ 1.5730. Similar results were obtained when the above reaction was carried out in *t*-butylbenzene at 150° for one hour.

(b) **In Dioxane.**—When a solution of 11.2 g. (0.010 mole) of potassium *t*-butoxide and 8.7 g. (0.025 mole) of V was heated in refluxing dioxane (100 ml.) for three hours, 0.9 g. of benzoic acid was obtained together with 5.0 g. (equivalent to 2.5 g. or 60% of benzophenone) of benzophenone 2,4-dinitrophenylhydrazone and 3.2 g. (82%) of diphenylmethane, b.p. 250° (760 mm.), $n^{25}\text{D}$ 1.5750. A portion of the diphenylmethane was converted to the tetranitro derivative, m.p. 165–169°, according to the procedure of Matsumura.[17] Unreacted V (0.5 g., 5.8%, m.p. 104–106°) was recovered.

Reaction of Diphenylbenzhydrylcarbinol (VI) with Potassium Hydroxide in Ethanol.—A suspension of VI (1.0 g., 0.0030 mole), prepared by the method of Roger and McGregor,[18] was heated for two hours in a refluxing solution of 1.0 g. (0.018 mole) of potassium hydroxide in 20 ml. of ethanol. Benzophenone was isolated by crystallization of the 2,4-dinitrophenylhydrazone (1.1 g., m.p. and mixed m.p. with an authentic sample 239–242°, equivalent to 0.52 g., 100% of benzophenone). Diphenylmethane was isolated as the tetranitro derivative[17] (0.75 g., m.p. 168–170°, equivalent to 0.36 g., 75% yield of diphenylmethane). A mixed m.p. with an authentic sample showed no depression.

4,4′-Dinitrobenzhydrol.—4,4′-Dinitrobenzophenone (72.7 g., 0.26 mole), prepared by the method of Staedel,[19] in toluene (1 l.) was heated under reflux with 120 g. (0.59 mole) of practical grade aluminum isopropoxide for four hours. Isopropyl alcohol was then added and slow distillation carried out with the aid of a Hahn condenser.[20] After ten hours 35 ml. of solution had distilled.

The reaction mixture was treated with 300 ml. of 20% sulfuric acid and the tan precipitate which formed was recrystallized from ethanol (1 l.) yielding 46.3 g. (63% yield) of 4,4′-dinitrobenzhydrol, m.p. 167–169°. Concentration of the ethanolic solution yielded an additional 14.5 g. (20%), m.p. 166–168°. The compound was recrystallized twice from benzene and melted at 168–169°.

Anal. Calcd. for $C_{13}H_{10}O_5N_2$: C, 57.1; H, 3.6; N, 10.2. Found: C, 57.2; H, 3.4; N, 10.3.

Benzhydryl 4,4′-Dinitrobenzhydryl Ether (VII).—4,4′-Dinitrobenzhydrol (30 g., 0.11 mole) and *p*-toluenesulfonic acid monohydrate (21 g., 0.11 mole) were added to boiling benzene (2.1) and 100 ml. of the solution was distilled to remove the water. To the hot solution was added dropwise a solution of 21 g. (0.11 mole) of diphenyldiazomethane.[21] The red color of the diazo compound was discharged immediately. The solution was refluxed for ten minutes and allowed to stand for ten hours. The solid obtained after distillation of the benzene was recrystallized from ethanol to give 28 g. (61%) of VII, m.p. 161–163° (thick platelets). Further recrystallization from dioxane gave a sample m.p. 164–164.5°.

Anal. Calcd. for $C_{26}H_{20}O_5N_2$: C, 70.9; H, 4.6; N, 6.4. Found: C, 70.9; H, 4.5; N, 6.7.

Reaction of VII with Potassium *t*-Butoxide (a) Dioxane.—To a hot solution of 11 g. (0.10 mole) of potassium *t*-butoxide in 100 ml. of dry dioxane was added 6.9 g. (0.015 mole) of VII in small portions. Each addition was accompanied by vigorous boiling and the appearance of a deep blue-green color. After the addition was complete the solution was refluxed for 30 minutes. The solution was then poured into 500 ml. of water and the aqueous solution on separation and acidification yielded 0.3 g. of *p*-nitrobenzoic acid (0.3 g., 12 mole %, m.p. and mixed m.p. with an authentic sample 235–240°). The gummy neutral organic residue was continuously extracted in a Soxhlet extractor with ether for four hours. The ether was distilled and the residue heated at 160° at 1 mm. pressure in a sublimation apparatus to give 2.0 g. (40 mole %) of tetraphenylethane which after recrystallization from acetic acid melted at 211–213°. Mixed melting points with an authentic sample in approximate ratios of 1:3, 1:1 and 3:1 showed no depression.

(b) **In *t*-Butyl Alcohol.**—A solution of 4.4 g. (0.01 mole) of VII and 2.2 g. (0.02 mole) of potassium *t*-butoxide in 200 ml. of *t*-butyl alcohol was refluxed (calcium chloride drying tube) for three hours. The solution was concentrated to 50-ml. volume and extraction with sodium bicarbonate solution gave *p*-nitrobenzoic acid (0.75 g., 45 mole %), m.p. 234–240°. The neutral fraction in ether was treated with charcoal, filtered and evaporated to yield 0.6 g., 18 mole % of the tetraphenylethane, m.p. 205–210°.

Bis-4,4′-dinitrobenzhydryl Ether (VIII).—A mixture of 4,4′-dinitrobenzhydrol (40 g., 0.15 mole) and 10 g. (0.05 mole) of *p*-toluenesulfonic acid monohydrate was heated under reflux in 300 ml. of chlorobenzene for one hour. The white precipitate which had formed was collected by filtration after dilution of the reaction mixture with pentane. The precipitate was washed several times with ethanol and pentane and after recrystallization from nitromethane yielded 29 g. (77%) of VIII, m.p. 286–287°.

Anal. Calcd. for $C_{26}H_{18}O_9N_4$: C, 58.9; H, 3.4; N, 10.6. Found: C, 59.2; H, 3.6; N, 10.6.

---

[16] A. M. Ward, *J. Chem. Soc.*, 2285 (1927).

[17] K. Matsumura, THIS JOURNAL, **51**, 817 (1929).

[18] R. Roger and A. McGregor, *J. Chem. Soc.*, 1850 (1934).

[19] W. Staedel, *Ann.*, **194**, 370 (1878).

[20] A. L. Wilds, "Organic Syntheses," Vol. II, 3rd ed., John Wiley and Sons, Inc., New York, N. Y., p. 197.

[21] L. I. Smith, *Organic Syntheses*, **24**, 53 (1944).

Reaction of VIII with Potassium *t*-Butoxide.—A suspension of 5.0 g. (0.0095 mole) of VIII was heated under reflux with 1.1 g. (0.010 mole) of potassium *t*-butoxide in dioxane for 2.5 hours. The mixture (green-black) was poured into 300 cc. of water. Extraction with Girard T reagent yielded 0.60 g. (23% yield) of 4,4'-dinitrobenzophenone, m.p. and mixed m.p. with authentic sample 188–190°. No other crystalline product could be obtained.

NEW YORK 27, N. Y. RECEIVED NOVEMBER 25, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

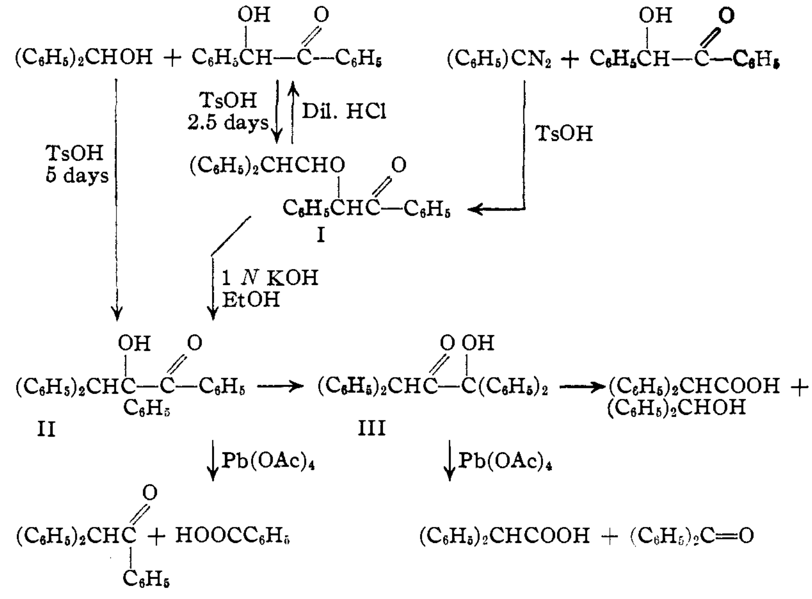
Cleavage and Rearrangement of Ethers with Base. II. Reaction of the Benzhydryl and Trityl Ethers of Benzoin with Potassium Hydroxide[1]

BY DAVID Y. CURTIN AND SIDNEY LESKOWITZ

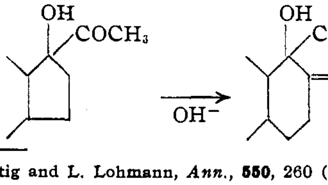
Benzhydryl desyl ether (I) has been prepared and found to rearrange on treatment with 1 *N* potassium hydroxide in ethanol to α-benzhydryl benzoin (II). II rearranges further to α-hydroxydibenzhydryl ketone (III). III can be cleaved to benzhydrol and diphenylacetic acid. Trityl desyl ether (VI) has also been prepared and found to react with 1 *N* potassium hydroxide in ethanol to give benzilic acid and triphenylmethane. The significance of these reactions is discussed.

In a continuation of the work on the reaction of ethers with bases discussed in the first paper of this series[2] it was considered desirable to investigate certain compounds which it was hoped would react under milder conditions than the ones previously studied. For this reason an investigation of benzhydryl desyl ether (I) was undertaken. This compound was readily prepared by the reaction of benzhydrol and benzoin in the presence of *p*-toluenesulfonic acid. The structure of I was confirmed by its ready hydrolysis to benzoin with dilute acid and by an alternative synthesis from the reaction of diphenyldiazomethane with benzhydrol in the presence of *p*-toluenesulfonic acid. An attempt to prepare I by the reaction of phenylbenzoyldiazomethane with benzhydrol in the presence of *p*-toluenesulfonic acid gave only desyl *p*-toluenesulfonate.

When I was treated for one hour under reflux with a 1 *N* solution of potassium hydroxide in ethanol it was converted to a mixture of products from which were isolated two new solid substances (II and III), benzhydrol, diphenylacetic acid and small amounts of tetraphenylethane and benzoic acid. II could also be obtained in 56% yield from benzoin and benzhydrol in the presence of acid when the reaction was allowed to proceed for a longer time than was used for the preparation of I. II was shown to be α-benzhydrylbenzoin by cleavage with lead tetraacetate to benzoic acid (81% yield) and phenyl benzhydryl ketone (50% yield). III was identified as α-hydroxydibenzhydryl ketone by cleavage with lead tetraacetate to benzophenone (68%) and diphenylacetic acid (80%). It was further found that II could be converted to III in 74% yield with ethanolic potassium hydroxide. When III was treated with a refluxing solution of 1 *N* potassium hydroxide for 90 minutes, benzhydrol (35%), diphenylacetic acid (45%) and unreacted starting material (40%) were obtained. We feel, therefore, that the initial reaction of I is a rearrangement to II followed by rearrangement of II to III and finally cleavage of III to benzhydrol and diphenylacetic acid. These reactions are summarized as shown.



The base-catalyzed rearrangement of I to II seems to be analogous to the rearrangement of dibenzyl ether with phenyllithium[3] or potassium amide[4] or to the Stevens rearrangement[5] and probably proceeds by a similar mechanism. The isolation of tetraphenylethane is of interest since benzhydryl 4,4'-dinitrobenzhydryl ether gives this substance as one of the principal products on treat-



---

[1] Abstracted from the Ph.D. thesis submitted to Columbia University by Sidney Leskowitz.

[2] D. Y. Curtin and S. Leskowitz, THIS JOURNAL, 73, 2630 (1951).

[3] G. Wittig and L. Lohmann, *Ann.*, **550**, 260 (1942).

[4] C. R. Hauser and S. W. Kantor, Abstracts of Papers presented at the 116th Meeting of the American Chemical Society, September, 1949, p. 46M.

[5] See J. L. Dunn and T. S. Stevens, *J. Chem. Soc.*, 279 (1934).