

TABLE II
ANALYSIS OF SAPONIFIED POLYMERS FOR CARBOXYL

Ester:styr. ratio in polymer, moles	Sol. of polymer in C ₂ H ₅ , %	Softening point of original polymer, °C.	M. e. of -COOH/g. of sapon. polymer	Max. m. e. of -COOH possible ^a	-COOH in sapon. poly- mer, % ^b
Polystyrene	100	140-145	0.00813 ^c		
1:9.1	100	75-80	.141	0.781	17.0
1:8.8	PS ^d	74-77	.233, 0.225	.784	27.7
1:7.6	20.1	Infus.	.303, 0.250	.873	30.8
1:6.1	13.5	Infus.	.365, 0.294	1.01	28.2
1:6.1 ^e	13.5	Infus.	.257, 0.253	1.01	24.4
1:5.1	5.1	Infus.	.313, 0.320	1.13	27.6

^a Calculated from composition of unsaponified polymer on assumption that all the linoleic acid was bound to the chain through linoleic double bonds. ^b Found from 100 α column 4/column 5. ^c This was deducted from the values below in calculating column 6. ^d Partially soluble. ^e Heated with base 10 hours to saponify, others 5 hours.

ml. of concd. sulfuric acid to precipitate the hydrolyzed polymer. The product was filtered, washed on the filter with methanol and water, and then washed by successive agitations on a mechanical shaker for several hours with slightly acidulated 3:1 methanol-water, pure water and absolute methanol.

The dried product was analyzed for carboxyl by titration in benzyl alcohol solution, using phenolphthalein and 0.05 *N* potassium hydroxide dissolved in 10% methanol-90% benzyl alcohol.¹⁴ The results obtained are shown in Table II. That the time for the saponification of the original polymer was long enough was shown by the fact that the carboxyl content of the saponified polymer was not increased by doubling the heating period.

Acknowledgment.—The authors are indebted to the Armstrong Cork Company for a fellowship in support of this work, and to Dr. E. J. Pieper, Dr. L. H. Dunlap and Dr. F. W. Breuer for helpful advice.

(14) J. E. Waltz and G. B. Taylor, *Anal. Chem.*, **19**, 450 (1947).

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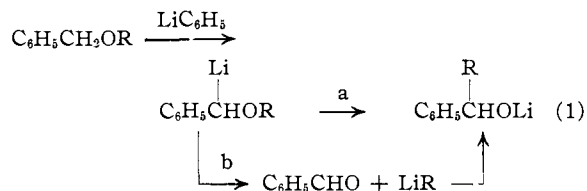
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Rearrangement of Benzyl Ethers to Carbinols by Potassium Amide. Mechanism of Isomerization of Carbanions Involving 1,2-Shifts^{1,2,3}

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The objective of this investigation was to establish the mechanism of intramolecular isomerizations of carbanions involving 1,2-shifts of alkyl groups without their bonding pair of electrons. These isomerizations, which include the Stevens rearrangement of quaternary ammonium and sulfonium ions by bases and the Wittig rearrangement of benzyl ethers by lithium phenyl, are to be distinguished from the common rearrangements of carbonium ions in which alkyl groups shift with their bonding pair of electrons. The work of Wittig was extended using lithium butyl and particularly potassium amide with which there can be no doubt that carbanions are actually the intermediates. The relative ease of isomerization of the carbanions of several ethers was established. The carbanion of dibenzyl ether not only isomerized to form the anion of benzylphenylcarbinol but also underwent partly β -elimination to form benzaldehyde and benzyl ion—a type of reaction that predominated with the carbanion of dibenzohydril ether. These isomerizations as well as those reported previously are in agreement with an internal displacement mechanism.

Wittig and co-workers⁴ showed that dibenzyl ether, benzyl methyl ether and certain related ethers are converted to carbinols by lithium phenyl. They considered that the ether is first metalated at an α -hydrogen and that the resulting lithium derivative undergoes intramolecular isomerization,⁵ course a in eq. (1). They rejected course b in (1), involving β -elimination followed by recombination, because lithium phenyl converted benzyl methyl ether to phenylmethylcarbinol without forming a detectable amount of benzohydril, some



(1) Paper I on Isomerizations of Carbanions.

(2) This work was carried out under Contract N7onr-455 with the Office of Naval Research.

(3) Presented at the Atlantic City Meeting of the American Chemical Society, September, 1949.

(4) (a) Wittig and Lohman, *Ann.*, **550**, 260 (1942); (b) Wittig and Happe, *ibid.*, **557**, 205 (1947).

(5) For evidence for the intermediate formation of the lithium derivative of 9-fluorenylmethyl ether, see ref. 4b. Although the lithium-carbon bond may be largely covalent (see Rogers and Young, *This Journal*, **68**, 2748 (1946)), the isomerization may be considered to take place within the carbanion which is potentially present.

of which might have been expected had benzaldehyde been an intermediate.

As further evidence against course b, we have found that lithium butyl converts dibenzyl ether to benzylphenylcarbinol without forming an isolable amount of benzylbutylcarbinol. Judging from an experiment with benzaldehyde and a mixture of lithium butyl and lithium benzyl, both carbinols would have been produced in equal yield if benzaldehyde were an intermediate.

The present investigation was concerned mainly with the study of the reactions of benzyl ethers and related ethers with potassium amide which is a better ionizing agent than the lithium reagents. In general, the benzyl ethers in diethyl ether were added to two molecular equivalents of potassium amide in liquid ammonia, the ammonia replaced by diethyl ether and the mixture refluxed (Table I). The reaction mixtures were colored indicating the presence of the carbanions. With dibenzyl ether there were obtained benzylphenylcarbinol (61-67%),⁶ toluene (16%) and benzamide (14%, isolated as benzoic acid). The benzamide was

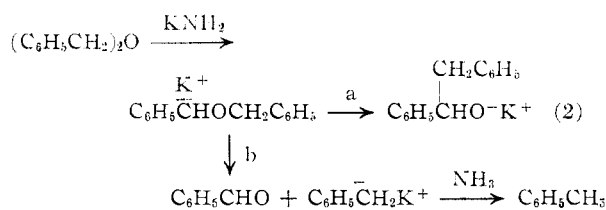
(6) Although sodium amide produced a similar red colored mixture, no benzylphenylcarbinol was obtained when the diethyl ether suspension was refluxed for several hours, 87% of the dibenzyl ether being recovered. Neither was the carbinol obtained when dibenzyl ether was refluxed with diethylaminomagnesium bromide in diethyl ether for several hours; in this case, 88% of the dibenzyl ether was recovered.

TABLE I
 CARBINOLS FROM ETHERS (0.1 MOLE) AND POTASSIUM AMIDE (0.2 MOLE)

Ether	Color of carbanion	Time, hr. ^a	Carbinol	°C. uncor.	B.p. Min.	Yield, %
Dibenzyl	Red	15	Benzylphenyl ^b	63-65	(M.p.)	61-67 ^b
Benzyl allyl	Purple	15.5	Mixture ^c	91-120	12	65 ^d
Diallyl	Light tan	12	1,5-Hexadien-ol-3 ^e	132-133 ^{e,f}	Atm.	40 ^g
Benzyl <i>s</i> -butyl	Light tan	140	Phenyl- <i>s</i> -butyl ^h	120-122 ⁱ	13	27 ^j
Benzyl methyl	Purple	13 ^k
Benzyl neopentyl	Red	44 ^l
Benzyl phenyl	Red	18 ^m
Benzyl ethyl	Brown	19	Benzyl alcohol ⁿ	96-99	12	40 ^o

^a Time of refluxing of the diethyl ether suspension on steam-bath. ^b See experimental for details. ^c Gave positive tests for the hydroxyl group and for unsaturation. ^d Residue, 16%; recovered ether, 7%. ^e Reported b.p. 133-134° (Levene and Haller, *J. Biol. Chem.*, **83**, 185 (1929)). ^f Found n_D^{20} 1.4458; reported n_D^{20} 1.4464 (ref. in note e), n_D^{20} 1.4445 (Hou, *Compt. rend.*, **208**, 41 (1939)). ^g Material, b.p. 134-252°, plus residue, 33%; recovered ether, 15%. ^h Oxidized with chromic acid to α -methyl *n*-butyrophenone; 2,4-dinitrophenylhydrazone, m.p. 127-127.5°. *Anal.* Calcd. for C₁₇H₁₈N₂O₄: C, 59.64; H, 5.30; N, 16.36. Found: C, 59.36; H, 5.11; N, 16.87. ⁱ Reported b.p. 120° at 13 mm. (Dumesnil, *Ann. chim.*, **8**, 79 (1917)). ^j Material, b.p. 124-220° at 13 mm., plus residue, 43%. When the reaction mixture was refluxed for 20 hours, there was obtained 15% of phenyl-*s*-butylcarbinol, 12% of residue and 50% of recovered ether. ^k Material, b.p. 185-190° at 12 mm., plus residue, 43%; recovered ether, 64%. When the reaction was carried out with 0.1 mole each of benzylmethyl ether and potassium amide, refluxing the diethyl ether suspension for 19 hours, there was obtained 30% of high boiling material, 61% of the ether being recovered. ^l Recovered ether, b.p. 90-91° at 10 mm., 92%. ^m Recovered ether, b.p. 162-164° at 20 mm., 80%; a qualitative test for benzohydroxol with sulfuric acid was negative. ⁿ Phenylurethan, m.p. 76.5-78°; α -naphthylurethan, m.p. 133-134°. ^o Material b.p. 103-133° at 12 mm., plus residue, 21%; recovered ether, 27%.

formed presumably by the action of the excess potassium amide on benzaldehyde.⁷ This aldehyde was isolated in 28% yield in another experiment in which equivalent amounts of dibenzyl ether and potassium amide were allowed to react for a few hours in liquid ammonia and the reaction stopped by the addition of ammonium chloride. Under these conditions, the yield of benzylphenylcarbinol was 51% and of toluene, 22%. The carbinol is considered to be formed by intramolecular isomerization of the intermediate carbanion, course a in (2), and the benzaldehyde and toluene, by β -elimination, course b in (2). Since the potassium salt of the carbinol was found to be stable under the same conditions, benzaldehyde and toluene appear not to arise by rearrangement followed by β -elimination.



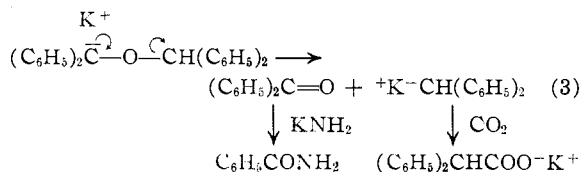
It is unlikely that the benzaldehyde and potassium benzyl are intermediates in the formation of the carbinol, since the potassium benzyl should react with ammonia to form toluene much faster than with benzaldehyde to form the carbinol. Moreover, the equilibrium of the acid-base reaction with potassium benzyl and ammonia is so far on the side of toluene that the addition of the latter to potassium amide in liquid ammonia failed to produce enough benzyl ion to color the solution, and subsequent addition of benzaldehyde failed to yield any of the carbinol.⁸

Although the β -elimination was only a side reaction with the carbanion of dibenzyl ether, this

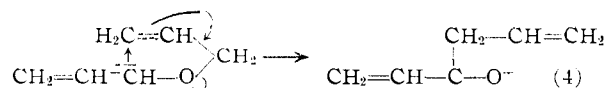
(7) Bergstrom and Fernelius, *Chem. Revs.*, **12**, 103 (1933).

(8) Instead, the usual products from benzaldehyde and alkali amides in liquid ammonia, including lophine, were obtained; see ref. 7.

type of reaction was found to predominate with the carbanion of dibenzohydril ether which formed benzophenone and potassium diphenylmethide, most of the benzophenone being cleaved by the potassium amide to benzamide and presumably benzene.⁹ The potassium diphenylmethide was converted to diphenylacetic acid by carbonation of an ether suspension of the reaction mixture. None of the rearranged carbinol was found.



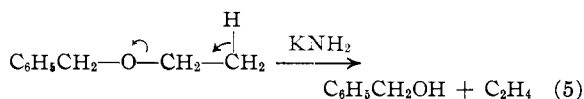
It can be seen from Table I that, like the carbanion of dibenzyl ether, the carbanions of benzyl allyl ether, diallyl ether and benzyl *s*-butyl ether isomerized to the anions of carbinols. As might be expected, a mixture of carbinols was obtained from benzyl allyl ether. The carbinol from diallyl ether might have been formed by a 1,2-shift, like that with dibenzyl ether (2, course a), or by the cyclic mechanism (4).



Benzyl *s*-butyl ether gave a 27% yield of rearranged carbinol even after a relatively long reaction time. Benzyl methyl ether gave material boiling higher than the rearranged carbinol, phenylmethylcarbinol; this material might have arisen from further reaction of the potassium derivative of the rearranged carbinol. Benzyl neopentyl ether and benzyl phenyl ether failed to rearrange and they recovered. Benzyl ethyl ether appeared to give no rearranged carbinol; instead, benzyl alcohol was obtained. This product was formed presumably by β -elimination of type (5)

(9) Bergstrom and Fernelius, *Chem. Revs.*, **12**, 122 (1933).

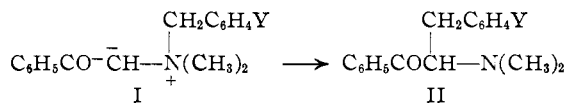
which took place preferentially to isomerization of the colored carbanion, $C_6H_5\bar{C}HOC_2H_5$. This type of β -elimination is to be distinguished from that represented by course b in (2).



These results with potassium amide differ in certain respects from those obtained with lithium reagents. Thus, potassium amide rearranged dibenzyl ether in good yield (51–67%) accompanied by some β -elimination (2, course b), whereas lithium phenyl^{4a} and lithium butyl have effected the rearrangement in lower yields (30 and 51%, respectively) accompanied apparently by no β -elimination. No study appears to have been made of the reaction of the lithium reagents with dibenzohydril ether which underwent mainly β -elimination with potassium amide (3). The rearranged carbinol from benzyl methyl ether was not isolated with potassium amide whereas the carbinol has been obtained in 35% yield with lithium phenyl.^{4a} Like potassium amide, lithium phenyl effected β -elimination (5) with benzyl ethyl ether and has failed to rearrange benzyl phenyl ether, although lithium phenyl produced a different type of reaction with the latter ether.^{4a} The other ethers listed in Table I have apparently not been studied with the lithium reagents.

Mechanism of Isomerization of Carbanions.—

The intramolecular isomerization of carbanions involving the 1,2-shift of an alkyl group presumably without its bonding pair of electrons¹⁰ includes not only the rearrangement of ethers discussed above but also the Stevens rearrangement of quaternary ammonium ions¹¹ and sulfonium ions¹² by hydroxide or ethoxide ion to form tertiary amines and sulfides, respectively. In the Stevens rearrangement the intermediate carbanion is a dipolar one¹³ such as I which isomerizes to II.



Although Stevens¹⁴ and Wittig^{4a} established the intramolecular nature of this type of isomerization, they apparently did not recognize the mechanism of migration of the alkyl group. Stevens apparently believed that I undergoes β -elimination, similar to course b in (1) and (2), followed by re-

(10) This type of 1,2-shift is to be distinguished from that brought about by the elimination of halide ion from a carbanion as occurs, for example, in the rearrangement of the carbanion, $(C_6H_5)_2C=\bar{C}Cl$ to form $C_6H_5C\equiv CC_6H_5$, in which the phenyl group migrates presumably with its bonding pair of electrons. See Hauser, *THIS JOURNAL*, **62**, 933 (1940).

(11) Stevens and co-workers, *J. Chem. Soc.*, 279 (1934), and earlier papers; see also Wittig, Mangold and Felletschin, *Ann.*, **560**, 116 (1948).

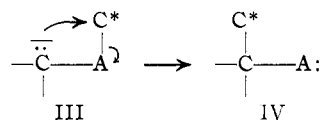
(12) Thomson and Stevens, *ibid.*, 69 (1932).

(13) Evidence for the formation of a colored intermediate dipolar ion with 9-fluorenyltrimethylammonium salts has been reported. See Hughes and Ingold, *ibid.*, 69 (1933); also Wittig and Felletschin, *Ann.*, **555**, 133 (1944).

(14) Stevens, *J. Chem. Soc.*, 2107 (1930), showed that a mixture of two isomeric quaternary ammonium ions such as I isomerized without "crossed" reaction.

combination of the benzyl ion with the unsaturated system; however, the benzyl ion should be expected to react more readily with the medium (alcohol or water). Wittig regarded such rearrangements as "cationic isomerizations in which the migrating constituent in the molecule is positively charged" and "migrates as a positive fragment." This mechanism would presumably involve an internal S_N1 reaction. However, Wittig could hardly have meant that the substituted benzyl group in I migrated actually as a carbonium ion since Stevens had previously shown that the relative unimolecular rates of isomerization of a series of I decrease as the substituent Y is made more electron releasing; thus, when Y is para, the rates decrease in the order: $NO_2 \gg \text{halogen} > CH_3, H > OCH_3$. If the benzyl group were to migrate as a carbonium ion, the reverse order should be expected since the relative unimolecular rates for the hydrolysis of the corresponding benzyl chlorides (involving the carbonium intermediate, S_N1) are in the reverse order, in so far as determined.¹⁵ Moreover, if the migration involved the carbonium ion intermediate, racemization should be expected but a rearrangement has been realized in which racemization does not occur (see below).

For several years, we have employed as a working hypothesis the internal displacement mechanism, III to IV; in III, A is positively charged nitrogen with quaternary ammonium ions, positively charged sulfur with sulfonium ions, and neutral oxygen with ethers, and in IV, A becomes neutral nitrogen, neutral sulfur and negatively charged oxygen, respectively.^{15a} This displacement mechanism is



in agreement with the following experimental results: The relative rates of isomerization of the series of I observed by Stevens are, in general, related directly (although qualitatively) to the bimolecular rates of displacement of the corresponding benzyl chlorides by iodide ion (S_N2)¹⁵; because the isomerization involves an intramolecular displacement, the kinetics would necessarily be unimolecular. The rearrangement of optically active phenacyl α -phenylethyldimethylammonium bromide by sodium hydroxide solution observed by Campbell, Houston and Kenyon occurs without racemization of the asymmetric carbon (C^* in III and IV).¹⁶ The relative ease of isomerization of the carbanions of ethers,¹⁷ $C_6H_5\bar{C}HOR$, observed by

(15) Bennett and Jones, *ibid.*, 1815 (1935).

(15a) Essentially this mechanism for the Stevens rearrangement has been represented by Watson, "Modern Theories of Organic Chemistry," Oxford University Press, London, England, 1941, p. 205.

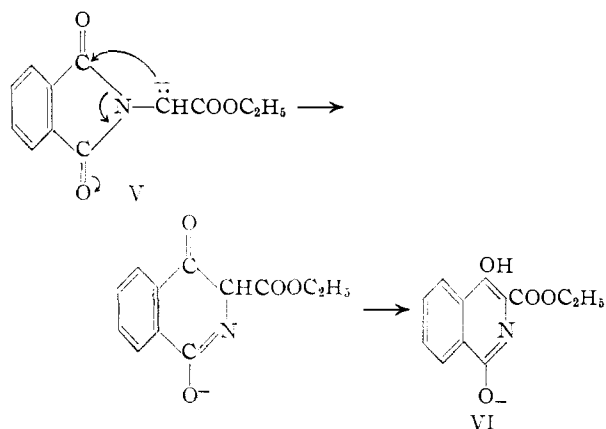
(16) Campbell, Houston and Kenyon, *J. Chem. Soc.*, 93 (1947). They did not determine whether a Walden inversion occurred. In this connection, we are endeavoring to determine whether there is Walden inversion in the similar rearrangement of optically active benzyl s-butyl ether by potassium amide.

(17) The observation of Wittig (ref. 4b) that the ease of isomerization of the alkali metal derivatives of benzohydrilphenyl ether to triphenylcarbinol decrease in the order: $Li > Na > K > Rb > Cs$, might appear to be evidence against the internal displacement mecha-

us (Table I), decrease as R is varied in the order: $C_6H_5CH_2$, $CH_2=CHCH_2$ > $CH_3CH_2C_2H_5$ > $CH_2C(CH_3)_2$, C_6H_5 ; this order would presumably be related directly to the relative ease of bimolecular displacement of the corresponding halides by basic anions.

We recognize that the simulation of change III to IV using Fisher-Hershfelder-Taylor molecular models indicates that the carbanion portion of the molecule would have to attack the starred carbon atom in III at the front or side, in relation to A (S_Ni), instead of at the rear as is usually the case. However, frontward or sideward displacements are not without precedent.¹⁸ Indeed, this difference in the manner of displacement might account for certain of the discrepancies observed between the relative rates of isomerization of the series of I and of bimolecular displacements of the corresponding benzyl chlorides.

In the cases considered above, A in III is positively charged nitrogen or sulfur¹⁹ or neutral oxygen. A search of the literature revealed a special case in which A in III is neutral nitrogen. This example, reported many years ago without a mechanism, involves the ring enlargement of ethyl α -phthalimidoacetate by sodium ethoxide to form an isoquinoline (VI).²⁰ Presumably intermediate carbanion V isomerizes accompanied by enolization, to form anion VI.



Such intramolecular displacements produce bases weaker than the intermediate carbanions. How-

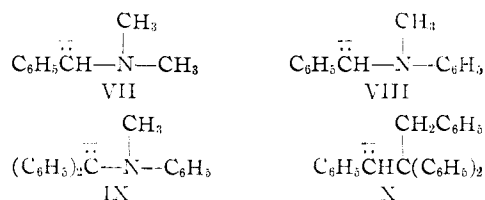
ever, since the relative availability (basicity) of the free pair of electrons of the carbanion might be expected to decrease in the reverse order. However, these metallic derivatives were not prepared by an acid-base reaction. Instead, they were prepared by the cleavage of the diphenyl ether of benzopinacol by means of the alkali metals. Under these conditions free radicals might be expected; indeed, diphenylmethane and tetraphenylethane, which must have arisen from free radicals, were reported to be formed. Since the carbanion of benzyl phenyl ether does not rearrange (see Table I), it seems doubtful that the carbanion of benzohydryl phenyl ether was the intermediate in the rearrangement to triphenylcarbinol.

(18) Such displacements evidently occur in the reactions of thionyl chloride with certain optically active alcohols (Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1267 (1937)) and of nitrosyl chloride with apocamphanol-1 (Bartlett and Knox, *This Journal*, 61, 3184 (1939)).

(19) In contrast to dibenzyl ether, dibenzyl sulfide has been found not to undergo a 1,2-shift in the presence of potassium amide; instead, rearrangement involving the benzene ring occurs. Similar rearrangements have been observed also with certain quaternary ammonium ions. These entirely different types of rearrangements will be described later.

(20) Gabriel and Colman, *Ber.*, 33, 980, 2630 (1900).

ever, not in all cases which might form weaker bases has the rearrangement been realized. Thus, we have found that, although weaker bases would presumably be formed if carbanions VII, VIII, IX and X were to isomerize (involving 1,2-shifts of methyl or benzyl), they failed to do so under the conditions employed in the rearrangement of dibenzyl ether (see experimental) and the corresponding amines and hydrocarbon were recovered. That the carbanions were formed was indicated by the production of red colored reaction mixtures.²¹



Experimental

Dibenzyl ether (b.p. 163–164° at 15 mm. and 158–160° at 10 mm.), benzyl methyl ether (b.p. 60–62° at 12 mm.), benzyl ethyl ether (b.p. 70–71.5° at 12 mm.) and diallyl ether (b.p. 94–95°) were redistilled Eastman Kodak Co. products.

The following benzyl ethers were prepared from benzyl chloride and the sodium salt of the appropriate alcohol: benzyl phenyl ether,²² b.p. 283–287° (reported b.p. 286–287°),²³ 162–165° at 19 mm., yield 66%; benzyl *s*-butyl ether, b.p. 210–212°, 94–95° at 13 mm. (reported b.p. 108–109° at 29 mm.),¹⁴ yield 80%; benzyl allyl ether,²⁴ b.p. 204–206° (reported b.p. 204–205°),²⁵ 87–90° at 12 mm., yield 50%.

Benzyl Neopentyl Ether.—To a stirred solution of 7.82 g. (0.2 mole) of potassium metal in 300 ml. of liquid ammonia was added slowly a solution of 18.5 g. (0.2 mole) of neopentyl alcohol²⁶ in 200 ml. of anhydrous dioxane. The blue color of the solution was discharged. The ammonia was removed on the steam-bath. To the stirred suspension in dioxane was added rapidly 25.3 g. (0.2 mole) of benzyl chloride in 150 ml. of dioxane and the resulting mixture was stirred and refluxed for 18 hours. The dioxane was removed under reduced pressure and the residue taken up in water and ether. After saturating the mixture with sodium chloride and shaking thoroughly, the aqueous layer was drawn off. The ether layer was washed with salt solution, dried over Drierite and the solvent distilled. The residue was distilled at atmospheric pressure. The fraction boiling at 212–220° was redistilled yielding pure benzyl neopentyl ether, b.p. 217–219°, in 68% yield. A redistilled sample, b.p. 92° at 10 mm., was analyzed.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.70; H, 10.09.

Dibenzohydryl Ether.—The method of Knoevenagel and Heckel²⁷ which involves heating benzohydrol with copper powder at 210–220° was attempted several times but in each case the greater portion of the product was tetraphenylethane, m.p. 210–212° (reported m.p. 211°).²⁸ The method of Linnemann²⁹ in which benzohydrol reacts with phosphorus trichloride was also unsatisfactory. Dibenzohydryl ether was obtained as described by Nef³⁰ by

(21) With the amines, the color persisted until the mixtures were acidified but, with the hydrocarbon, the color was discharged when the ammonia was replaced by ether. Similar reconversions of carbanions to hydrocarbons have been observed previously with sodium diphenylmethide and sodium triphenylmethide; see Yost and Hauser, *This Journal*, 69, 2325 (1947).

(22) Peacock, *Proc. Chem. Soc.*, 30, 247 (1914).

(23) Sintenis, *Ann.*, 161, 337 (1872).

(24) Van Duzee and Adkins, *This Journal*, 57, 147 (1935).

(25) Braun, *Ber.*, 43, 1352 (1910).

(26) Conant, Webb and Mendum, *This Journal*, 51, 1246 (1929).

(27) Knoevenagel and Heckel, *Ber.*, 36, 2827 (1903).

(28) Biltz, *Ann.*, 296, 221 (1897).

(29) Linnemann, *ibid.*, 133, 13 (1865).

(30) Nef, *ibid.*, 298, 232 (1897).

refluxing benzohydril bromide (45 g. 0.178 mole) with 250 ml. of water. The crude ether, m.p. 94–102° (32 g.), was recrystallized twice from ethanol to obtain the pure product, m.p. 108.5–109.5° (reported m.p. 110°)³⁰ in 68% yield. More pure product could probably have been obtained from the mother liquors.

Anal. Calcd. for C₂₆H₂₂O: C, 89.10; H, 6.33. Found: C, 89.10, 89.23; H, 6.43, 6.37.

Reaction of Dibenzyl Ether with Lithium Butyl.—To a stirred solution of 0.26 mole of lithium butyl in 240 ml. of anhydrous diethyl ether, prepared from 0.88 mole of lithium metal and 0.40 mole of butyl bromide³¹ (most of the excess lithium being removed), was added 0.1 mole of dibenzyl ether in 50 ml. of anhydrous diethyl ether. The resulting red solution was stirred for 40 hours at room temperature. Methanol was added to destroy the excess lithium butyl and lithium metal. The mixture was decomposed with water and finally acidified. The ether layer was washed with water, dried over Drierite and the solvent distilled. The residual oil was fractionated at 12.5 mm. through a 30-cm. Vigreux column yielding the following fractions: (1) 2.5 g., b.p. 87–115°; (2) 0.5 g., b.p. 115–176°; (3) 9.1 g., b.p. 176–188°; (4) 1.8 g., b.p. 188–245°. Fraction (3) solidified on cooling in an ice-bath. It was essentially pure benzylphenylcarbinol (44%), melting at 57–60° and, after one recrystallization from ethanol-water, at 66–67° (reported m.p. 66–67°).³² Obviously, there was no appreciable amount of butylphenylcarbinol, b.p. 132° at 14 mm. (see next experiment) which would have appeared in fraction (2).

In a similar experiment using 0.13 mole of lithium butyl and 0.1 mole of dibenzyl ether, the yield of benzylphenylcarbinol was 51%; there was no indication of the presence of butylphenylcarbinol.

Reaction of Benzaldehyde with Lithium Butyl and Lithium Benzyl.—A solution of lithium benzyl (0.106 *N*), prepared from benzylmagnesium chloride and lithium metal, was filtered through glass wool and standardized.³³ To a mixture of 0.0392 mole of lithium benzyl and 0.0594 mole of lithium butyl in 500 ml. of anhydrous diethyl ether was added a solution of 4.2 g. (0.0392 mole) of benzaldehyde in 50 ml. of ether. After stirring for 40 hours, the mixture was worked up as described in the preceding experiment yielding the fractions: (1) 0.95 g., b.p. 103–132° at 12 mm.; (2) 1.8 g., b.p. 132–137° at 12 mm.; (3) 2.2 g., b.p. 137–177° at 12 mm.; (4) 2.6 g., b.p. 177–181° at 12 mm. Fraction (2) was essentially pure butylphenylcarbinol (34%) (reported b.p. 132° at 14 mm.).³⁴ On oxidation with chromic acid, it gave *n*-valerophenone; semicarbazone, m.p. and mixed m.p. 164–165° (reported m.p. 166°).³⁵ Fraction (4) was essentially pure benzylphenylcarbinol (34%), m.p. 66–67° after one recrystallization from alcohol-water.

Reactions of Various Ethers with Potassium Amide.—To a stirred solution of 0.2 mole of potassium amide in 200 ml. of liquid ammonia³⁶ was added 0.1 mole of dibenzyl ether in 200 ml. of anhydrous diethyl ether. The red colored mixture was stirred until all the ammonia had evaporated (about 1.5 hours) and the resulting ethyl ether suspension was refluxed on a steam-bath for 15 hours. The mixture was cooled in an ice-bath and decomposed with 200 ml. of water. The ether layer was separated, washed with water, dried over Drierite and the solvent distilled. The residue was distilled *in vacuo* yielding toluene (1.5 g., 16%), b.p. 110° (2,4-dinitro derivative, m.p. 70–71°),³⁷ and a fraction (13.2 g.), b.p. 169–172° at 10 mm., which solidified in the receiver. This fraction, consisting mostly of benzylphenylcarbinol (reported b.p. 167–170° at 10 mm.)³⁸ and partly of benzamide, was refluxed with 100 ml. of 2 *N* NaOH

until ammonia ceased to be evolved. After cooling, the resulting mixture was extracted with ether. The alkaline solution gave, on acidification, benzoic acid (14%), m.p. and mixed m.p. 122°. The ether extract gave, on evaporation, benzylphenylcarbinol (61%), m.p. 66–67°, after one recrystallization from ethanol-water. A mixed melting point with an authentic sample (m.p. 64–66°) was 66.5–67°. The hydrogenphthalate derivative melted at 130–131° (reported m.p. 131°).³⁹

In a similar experiment, the residue obtained on removing the solvent was cooled and scratched until it mostly solidified. The oily solid was stirred with 50 ml. of petroleum ether and the mixture filtered. There was obtained benzylphenylcarbinol (13.2 g., 67%), m.p. 63–65°. One recrystallization from ligroin (b.p. 70–90°) containing 5% benzene raised the melting point to 65–66°.

In another experiment, equivalent amounts of dibenzyl ether and potassium amide were used and the ether suspension was refluxed for 19 hours. There was obtained benzylphenylcarbinol (58%), toluene (13%) and benzamide (7.4%), determined as benzoic acid.

The reaction was also allowed to proceed to completion in liquid ammonia using 0.1 mole of potassium amide in 350 ml. of liquid ammonia and 0.1 mole of dibenzyl ether in 75 ml. of diethyl ether. After 3.25 hours under a Dry Ice condenser, excess solid ammonium chloride (*ca.* 10 g.) was added carefully and the ammonia allowed to evaporate. The residue was stirred with water and ether and the layers separated. Acidification of the aqueous layer yielded benzoic acid (3%), m.p. and mixed m.p. 122°. The ether layer was washed with water, dried over sodium sulfate and the solvent removed. The residue was distilled *in vacuo* yielding toluene (22%), b.p. 47° at 85 mm., benzaldehyde (28%), b.p. 77–78° at 25 mm., (2,4-dinitrophenylhydrazine, m.p. 238–239°) and benzylphenylcarbinol (51%), b.p. 168–172° at 10 mm. The carbinol was not contaminated with any benzamide and melted at 66.5–67.5° after one recrystallization from alcohol-water. The reactions of various other ethers with potassium amide were carried out essentially as described above for the first experiment with dibenzyl ether. The results are summarized in Table I.

Reaction of Dibenzohydril Ether with Potassium Amide.—To a stirred solution of 0.105 mole of potassium amide in 250 ml. of liquid ammonia was added a solution of benzohydril ether (17.52 g., 0.05 mole) in 300 ml. of anhydrous diethyl ether. The red solution was stirred until all the liquid ammonia had evaporated, and the resulting red ether suspension was refluxed on a steam-bath for 3.5 hours. Powdered Dry Ice (400 g.) was added carefully and the mixture stirred until the Dry Ice disappeared. The ethereal mixture was shaken with 300 ml. of water and the layers were separated. The aqueous layer was acidified to litmus with concentrated hydrochloric acid and, after saturating with sodium chloride, the solid diphenylacetic acid was collected on a funnel. The acid, m.p. and mixed 146–147°, was obtained in yields of 60–68%.

Anal. Calcd. for C₁₄H₁₂O₂: C, 79.22; H, 5.70; neut. equiv., 212.2. Found: C, 79.46; H, 5.60; neut. equiv., 212, 213.

The ether layer was washed with water, dried over sodium sulfate and the solvent removed. Methanol was added to the residue and after cooling, 11% of the dibenzohydril ether was recovered in two crops. The combined methanol filtrate was evaporated yielding 6.2 g. of residue which partially solidified. To a portion of the residue was added an excess of 2,4-dinitrophenylhydrazine reagent precipitating benzophenone-2,4-dinitrophenylhydrazine (15–20%), m.p. and mixed m.p. 236.5–238°. The remainder of the residue was again taken up in methanol and, after filtering off a trace of unidentified solid (m.p. 200–222°), the solution was mostly evaporated yielding, on the addition of a little diethyl ether, solid benzamide. This product was collected on a funnel and more of it (total yield 41%) obtained by adding petroleum ether to the filtrate. It was identified by mixed melting point and by hydrolysis to benzoic acid.

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