aluminum hydride (see procedure under *cis,cis,cis*-1,2,3-trimethylcyclohexane) to obtain 8 g. (36% yield) of *cis*-1,2-dimethylcyclohexane, b.p. 129.5° (uncor.), n^{20}D 1.4361.

trans-**3-Methylcyclohexane**-*cis,cis*-**1,2-dicarboxylic Anhydride**.—Four moles (668 g.) of *cis*-3-methylcyclohexane-*cis,cis*-1,2-dicarboxylic anhydride was distilled (b.p. 94–100° (0.3 mm.)). This material was divided into six equal parts and sealed in glass ampoules together with 3 ml. of diethylaniline per ampoule and was heated at 145° for 22 hours. The tubes were then cooled and opened. The quantitative yield of *trans*-3-methylcyclohexane-*cis,cis*-1,2-dicarboxylic anhydride was not purified further.

A small portion of this anhydride (5 g.) was boiled 30 minutes with water (35 ml.) and the resulting clear solution deposited white crystals of *trans*-3-methylcyclohexane-*cis,cis*-1,2-dicarboxylic acid on standing 2 days at room temperature, m.p. 124–127° (lit.[15] 129°).

The rearranged anhydride (144 g., 0.86 mole) was esterified with ethanol, and the diethyl ester (145 g., 0.6 mole), b.p. 110–111° (1 mm.), n^{20}D 1.4543, was obtained in 70% yield after distillation. *Anal.* Calcd. for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.52; H, 9.07.

3,4,5-Trimethylcyclohexene.—Piperylene and crotonaldehyde were caused to undergo the Diels–Alder reaction by the procedure of Tom.[30] In a typical 5-mole run there was obtained 3.8 moles (a 76% yield) of adduct (b.p. 80–82° (20 mm.), n^{20}D 1.4669). The piperylene–crotonaldehyde adduct (690 g., 5 moles) was then reduced by means of the Huang-Minlon[31] modification of the Wolff–Kishner reaction, except that dihydrazine sulfate was used along with enough additional sodium hydroxide to liberate the hydrazine; thereby there was produced 405 g. (65% of theory) of crude 3,4,5-trimethylcyclohexene. The combined product of several such runs (3160 g.) was distilled at better than 100-plate efficiency to give 1707 g. of *cis,trans,cis*-3,4,5-trimethylcyclohexene (b.p. 144.36° (760 mm.), n^{20}D 1.4484, d^{20}_{4} 0.8114) and 850 g. of *cis,cis,trans*-3,4,5-trimethylcyclohexene (b.p. 148.25° (760 mm.), n^{20}D 1.4511). *Anal.* Calcd. for C_9H_{16}: C, 87.03; H, 12.97. Found for the *cis,trans,cis* isomer: C, 87.24; H, 13.03. Found for the *cis,cis-trans* isomer: C, 87.08; H, 12.89.

cis,trans,cis-**1,2,3-Trimethylcyclohexane**.—The *cis,trans,-cis*-3,4,5-trimethylcyclohexene (1707 g., 13.78 moles) was hydrogenated in a steel bomb at 150° over nickel (Ni(K)) catalyst for a period of 3 hours (1500 p.s.i.g. hydrogen). The catalyst was removed by filtration, and the hydrogenate was treated exhaustively with aqueous potassium permanganate solution to remove any unsaturates. The hydrocarbon material was then steam distilled, dried, and fractionated at about 35-plate efficiency. There was obtained a 60/40 mixture of *cis,trans,cis-/cis,cis,trans*-1,2,3-trimethylcyclohexane (b.p. 151.15° (760 mm.), n^{20}D 1.4394). The physical properties of the *cis,trans,cis*-1,2,3-trimethylcyclohexane were b.p. 145.61, n^{20}D 1.4333, d^{20}_{4} 0.7870, m.p. −66.86°. Its purity was determined cryoscopically as 99.8 ± 0.2 mole per cent. *Anal.* Calcd. for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.50; H, 14.51.

cis,cis,trans-**1,2,3-Trimethylcyclohexane**.—The *cis,cis,-trans*-3,4,5-trimethylcyclohexene was hydrogenated over Raney nickel at 150° for a period of 10 hours (1500 p.s.i.g. hydrogen). The hydrogenate was treated precisely as in the purification of the *cis,trans,cis* isomer, and final distillation at high efficiency gave principally *cis,cis,trans*-1,2,3-trimethylcyclohexane (b.p. 151.21, n^{20}D 1.4401, d^{20}_{4} 0.8029, m.p. −85.73°). Its purity was determined cryoscopically as 96.4 ± 0.5 mole per cent. *Anal.* Calcd. for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.51; H, 14.21.

cis-**3-Methylcyclohexane**-*cis,trans*-**1,2-dicarboxylic Acid**.—*cis*-3-Methylcyclohexane-*cis,cis*-1,2-dicarboxylic acid was prepared by heating anhydride II and water at 100° for 1 hour. An amount of this product (250 g.) was placed in a glass liner within a steel bomb together with 500 ml. of concentrated hydrochloric acid (Baker C.P.), and was heated at 180° for seven hours to effect the desired isomerization.[14] The yield of crude *cis*-3-methylcyclohexane-*cis,-trans*-1,2-dicarboxylic acid was 245 g. (96%). A small sample (4 g.) was recrystallized from water for analysis. This diacid (m.p. 162–163°) when mixed with the "all-*cis*"-diacid (m.p. 165–167°) gave a mixed m.p. of 139–140°, indicating it was a different species. *Anal.* Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.23; H, 7.56.

Acknowledgment.—The authors wish to express their appreciation to Mr. Vincent G. Wiley for his assistance in some of the distillations and physical property determinations. Acknowledgment is also made to the American Petroleum Institute (Research Project 45) and the General Motors Corporation for their financial support of this work.

COLUMBUS 10, OHIO

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(30) T. B. Tom, Doctoral Dissertation, The Ohio State University, 1942.

(31) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

α- *versus* β-Elimination in the Cleavage of Ethers by Organoalkali Metal Compounds

BY ROBERT L. LETSINGER AND DALE F. POLLART

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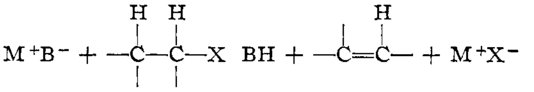
The purpose of this work was to determine whether elimination reactions which occur when ethers are treated with organoalkali metal compounds are α- or β-elimination processes. It was found by use of deuterium labeled compounds that the ethylene obtained from the reaction of propylsodium with ethyl aryl ethers originated by β-elimination. When an α-position of an ether was activated by a phenyl group, as in ethyl benzyl ether, the principal initial step of the elimination was α-metallation. No case could be found, however, in which α-metallation was followed by α-elimination. In the course of this work a new reaction was observed, the cleavage of 2-phenyltetrahydrofuran by organoalkali metal compounds to give high yields of ethylene and acetophenone. Furthermore, it was found that ethyl benzhydryl ether underwent a Wittig rearrangement when treated with propylsodium. Ethyl groups have not previously been observed to migrate in this type of rearrangement.

The work described in this paper was undertaken with the object of learning more about the course of reactions in which ethers are converted to olefins by organoalkali metal compounds. These processes are of particular interest since, as formal analogs to the elimination reactions (E2) effected by bases such as sodium alkoxide and sodium amide (see reaction I), they test the limits to which the concepts developed from the homogeneous reactions of the weaker bases can be extended. We have previously reported a stereochemical study which revealed a significant difference in the mech-



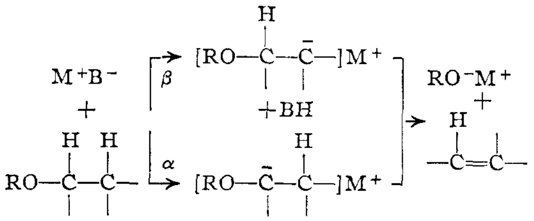
$$\mathrm{M^+B^-} + -\underset{|}{\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{C}}}-\underset{|}{\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{X}\quad \mathrm{BH} + -\overset{|}{\mathrm{C}}=\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{C}}- + \mathrm{M^+X^-}$$

(I)

For ether cleavages B is a carbanion; X, alkoxyl. For E2 reactions B is hydroxide, alkoxide, etc.; X, halide, quaternary ammonium, etc. M is a metal cation.

anism of the ether cleavages and the E2 reactions.[1] The present paper deals with another aspect of these reactions, the question of α- and β-elimination.

The problem is indicated for the ether cleavages by equation II, which represents two possible pathways for the reaction. According to IIα (α-elimination), an α-hydrogen is removed in the initial step from the alkyl group that eventually becomes the alkene; and according to IIβ (β-elimination), initial attack is at the β-hydrogen.[2] Analogous pathways may be postulated for the E2 reactions.



(II)

It is now recognized, however, that the usual, and perhaps exclusive, route for these transformations is β-elimination.[3] By analogy it has been assumed that ether cleavages also follow path IIβ.[1,4] In accordance with this concept, methyl 2-phenylcyclohexyl ether is cleaved by butyllithium more rapidly than methyl cyclohexyl ether[1] and cyclohexene oxide reacts with butyllithium to give appreciable amounts of cyclohexenol.[5] On the other hand, Ziegler and Gellert[6] have suggested that IIα is the general path for reactions of alkyl ethers with organolithium compounds. As such, these reactions would provide examples of the long sought but elusive olefin-forming α-elimination reactions.[3,7] It may be noted that the conditions do appear particularly favorable for such a process since the attacking anion is a very strong base and the carbon–oxygen bond in the ether has relatively little tendency to undergo ionization. As a consequence, the inductive effect of the negative substituent (oxygen), which would labilize the α-hydrogens, should be relatively more important here than in other systems.

Ethyl Aryl Ethers.—As a direct test of the course of an ether cleavage, we investigated the reactions of propylsodium with ethyl-1,1-d_2 phenyl ether and ethyl-1,1-d_2 *p-t*-butylphenyl ether. Cleavage according to IIβ would yield propane, whereas reaction by sequence IIα would give propane-1-*d* as the alkane product.

Preliminary experiments were carried out with deuterium-free compounds. From propylsodium and ethyl phenyl ether at 50° was obtained a low yield of ethylene (12.5%) and a greater than theoretical yield of propane (127%, calculated on the basis of reaction II). The major portion of the propane must have resulted in this case from metallation of the aromatic ring, a reaction known to occur readily with phenyl ethers.[8] One would expect this competing reaction to be less important with ethyl *t*-butylphenyl ether since a *t*-butyl group deactivates the aromatic nucleus toward metallation by ethyl potassium.[9] This proved to be the case; from ethyl *p-t*-butylphenyl ether and propylsodium at 50° was obtained a much more gratifying proportion of ethylene (74% yield of ethylene and 115% yield of propane). In the subsequent work with the deuterium compounds, therefore, the primary effort was directed toward the butyl phenyl ether although a small sample of deuteroethyl phenyl ether also was prepared and studied.

The deuteroethers were allowed to react with propylsodium for a period at 25°; then the temperature was raised to 50° for the remainder of the reaction. From ethyl-1,1-d_2 phenyl ether was obtained propane (152%), deuteroethylene (approximately 28%) and less than 2.5% propane-*d*; and from ethyl-1,1-d_2 *p-t*-butylphenyl ether, propane (112%), deuteroethylene (approximately 42%) and less than 1.3% propane-*d*. The propane-*d* percentages are maximum values which include any higher boiling substances in the gas that could contribute to the mass 45 peak; so the true values may be less. In any event, as they are small relative to the ethylene percentages, it is apparent that propylsodium does not react with these ethers to any significant extent by path IIα.

An alternative course, route III, which could

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[1] R. L. Letsinger and E. Bobko, This Journal, **75**, 2649 (1953).

[2] The cleavages are represented for convenience as two stage ionic reactions, however, it is recognized that this is an over simplification of the actual process. The cation very likely plays a role,[1] and the C–H and C–O bonds may break simultaneously rather than in two steps. Even the strictly ionic character of such reactions has been questioned by Morton and Brachman (A. A. Morton and E. Brachman, This Journal, **76**, 2973 (1954)), who prefer to view the cleavages as ion–radical reactions. We are not concerned here with these aspects of the theory, but only with the position of the hydrogen which is removed from the alkyl group.

[3] For a summary of much of the work in this field, see (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, Chapter VIII; (b) W. E. Doering and H. Meislich, This Journal, **74**, 2099 (1952); (c) D. Y. Curtin and David B. Kellom, *ibid.*, **75**, 6011 (1953); (d) D. Hill, B. Stewart, S. Kantor, W. Judge and C. R. Hauser, *ibid.*, **76**, 5129 (1954). Hauser and co-workers report exclusive β-elimination for the dehydrohalogenation of *n*-octyl-1,1-d_2 bromide by potassium amide (footnote 13 of their paper). As this result is at variance with a previous observation that some α-elimination accompanied the β-elimination of this halide in ether (*ibid.*, **74**, 5599 (1952)), they plan a thorough reinvestigation of the earlier reaction.

[4] (a) D. H. Gould, K. H. Schaaf and W. L. Ruigh, *ibid.*, **73**, 1263 (1951); (b) R. L. Letsinger, A. W. Schnizer and E. Bobko, *ibid.*, **73**, 5708 (1951); (c) R. L. Letsinger, J. G. Traynham and E. Bobko, *ibid.*, **74**, 399 (1952).

[5] With cyclohexene oxide the abstraction of an α-hydrogen should lead to the formation of the enolate of cyclohexanone, whereas abstraction of a β-hydrogen should result in the formation of the anion of cyclohexenol. Both processes compete with a displacement reaction which produces the anion of 2-butylcyclohexanol. The products actually isolated were: cyclohexanone, less than 3%; cyclohexenol, more than 26%; and butylcyclohexanol, 15% (reference 4c). The relatively high yield of cyclohexenol indicates that β-elimination competes favorably with the other processes.

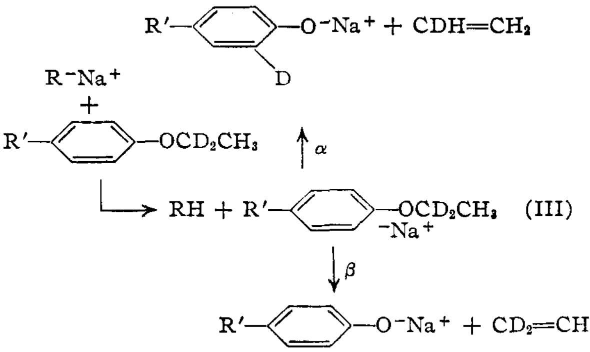
[6] K. Ziegler and H. G. Gellert, *Ann.*, **567**, 185 (1950).

[7] Other types of α-elimination have been observed. Thus, a number of reactions of chloroform with bases (J. Hine, This Journal, **72**, 2438 (1950); J. Hine and A. M. Dowell, *ibid.*, **76**, 2688 (1954); W. E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954); W. E. Parham, H. E. Reiff and P. Zwartzentruber, *ibid.*, **78**, 1437 (1956)) and some cases of dehydrohalogenation of 1-haloalkenes (G. H. Coleman and R. D. Maxwell, *ibid.*, **56**, 132 (1934); S. J. Cristol and W. P. Norris, *ibid.*, **76**, 3005 (1954)) clearly involve the elimination of hydrogen halide from a particular carbon atom. The existence of such reactions has stimulated interest in the possibility that alkenes might also be formed by a base initiated α-elimination process.

[8] (a) A. A. Morton, *Chem. Revs.*, **35**, 28 (1944); (b) A. A. Morton and E. Brachman, This Journal, **76**, 2973 (1954).

[9] D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

involve α-elimination remains to be considered. Morton and Brachman[8b] have demonstrated that in the cleavage of alkyl aryl ethers at 75° some olefin may arise from successive metallation and elimination reactions of this type.

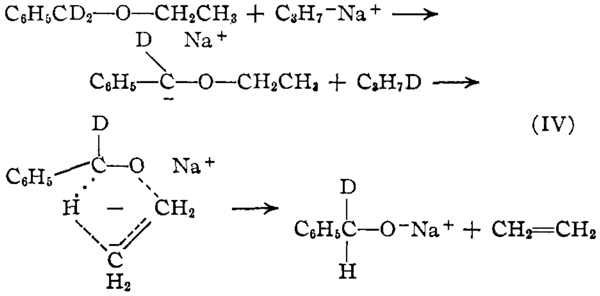


(III)

As applied to the deuteroethyl aryl ethers, this means that α-elimination would be signified by the formation of a deuterated phenoxide, and β-elimination by the formation of a deuterium-free phenoxide; no deuteropropane would be produced in either case. It seems rather unlikely the ethylene was produced in this way in our case (see Experimental portion); nevertheless, we hydrolyzed the residues from the reaction of deuteroethyl *t*-butylphenyl ether and isolated the phenol. The infrared spectrum of this substance was identical with the spectra of ordinary *p*-*t*-butylphenol; there was no evidence for any absorption characteristic of carbon–deuterium bonds. Reaction IIIα may therefore be excluded as a possible reaction path.[10]

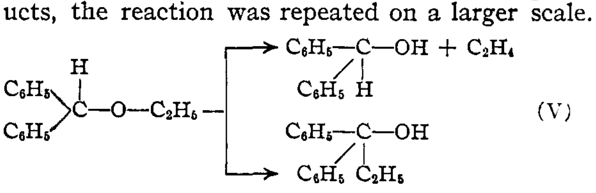
These experiments can be rationalized only on the basis that the cleavage of ethyl aryl ethers by propylsodium involves the preferential removal of a β- rather than an α-proton from the ethyl group. The next task was to determine whether α-attack could play a role in elimination reactions of ethers that were especially activated in the α-position. For this purpose we investigated the reactions of ethyl benzyl ether, ethyl benzhydryl ether and 2-phenyltetrahydrofuran with propylsodium.

Ethyl Benzyl and Benzhydryl Ethers.—Wittig and Lohmann[11] discovered that methyl benzyl ether and dibenzyl ether rearranged when treated with phenyllithium to give, after hydrolysis, 1-phenylethanol and 1,2-diphenylethanol, respectively; but ethyl benzyl ether decomposed under similar conditions to ethylene and benzyl alcohol. They explained these results on the assumption that the initial step was α-metallation in all cases, and the terminal step was either intramolecular displacement (which yielded the rearrangement product) or elimination (which yielded ethylene). It seems clear that the rearrangements proceed as proposed; however, although the suggestion is a very reasonable one, convincing evidence that the ethyl benzyl ether reaction involves an α-elimination is not available.[12] To obtain data on this point, we subjected ethyl benzyl-α,α-d_2 ether to the action of propylsodium. This ether reacted readily at 0°, in contrast to the ethyl aryl ethers which decomposed slowly only at higher temperatures (25°), to give a 91% yield of ethylene, 81% yield of propane-*d* and a 21% yield of non-deuterated propane.[13] The recovered benzyl alcohol contained both hydrogen and deuterium on the α-carbon atom (by infrared). These results show that the principal primary step in this cleavage is the removal of a deuterium ion from the benzyl α-position by the propyl group of the metallic reagent. The subsequent decomposition can be formulated conveniently as an intramolecular *cis* elimination.[14] This transition state is similar to that proposed by Curtin and Kellom[3c] to account for the elimination of acetate in the reaction of 2-deutero-1,2-diphenylethyl acetate with potassium amide.



(IV)

In contrast to ethyl benzyl ether, ethyl benzhydryl ether reacted with propylsodium to give only a 24% yield of ethylene, although the propane yield was 110%. For isolation of the solid products, the reaction was repeated on a larger scale.



(V)

In addition to benzhydrol (24%), there was obtained 1,1-diphenyl-1-propanol (44%), the product of a Wittig rearrangement.[11] This reaction is of interest since it is the first case in which an ethyl group has been observed to move in a rearrangement of this type. It seems clear that the initial step must have been α-metallation since the α-hydrogen of benzhydryl is more acidic than the α-hydrogen of benzyl. The extra phenyl group, however, must have decreased the tend-

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(10) A reaction sequence in which propylsodium metallates the ether, and the metallated ether functions as the base to cause an α-elimination from another ether molecule, should likewise lead to the formation of some, though perhaps less, deuterated phenol.

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

(12) Potassium amide will effect similar transformations of these ethers. Hauser and Kantor consider that such rearrangements involve α-metallation, but that ethyl benzyl ether reacts by a typical β-elimination in which amide ion attacks the ethyl group directly (C. R. Hauser and S. W. Kantor, THIS JOURNAL, **73**, 1437 (1951)). A good indication, however, that α-metallation may indeed be involved in the eliminations effected by both potassium amide and phenyllithium is provided by the fact that ethyl benzyl ether is decomposed by these agents more readily than is ethyl ether (see footnote 11 for discussion of the phenyllithium reaction).

(13) The lithium aluminum deuteride used in making the deuteroether contained at least 92.5% of the theoretical deuterium. The amount of ordinary propane is greater than can be accounted for on the basis of the amount of hydrogen in the lithium aluminum deuteride. It may be that the propane resulted from metallation of the aromatic ring, from traces of moisture, or possibly from some direct β-elimination of the ether.

(14) Professor Wittig has suggested the same type of transition state; private communication.

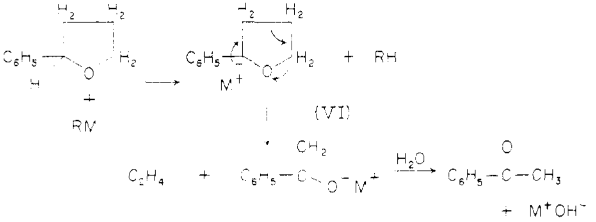
ency for the intermediate carbanion to displace on hydrogen (basicity) relative to the tendency for it to displace on carbon (nucleophilicity). This effect of a phenyl group on the reactions of carbanions has been noticed previously.[15]

Phenyltetrahydrofuran.—The work on the ethyl deuterobenzyl ether demonstrated that α-metallation could precede the elimination of an ethyl group. It was now of interest to see if a case could be found in which α-metallation would be followed by α-elimination of the same alkyl group (*i.e.*, a case that followed path IIα). A compound for which this might be possible is 1-phenylethyl ethyl ether; however, as preliminary experiments indicated that the decomposition of this ether was complicated by numerous side reactions, it was apparent that definitive results would be very difficult if not impossible to obtain for this substance. We therefore turned to the reaction of 2-phenyltetrahydrofuran with propylsodium. This cyclic ether appeared to be an ideal compound on which to observe α-elimination for the following reasons: (a) the α-position was activated by a phenyl group, so initial attack should occur at this place, (b) intramolecular β-elimination was unlikely since a proton would have to be transferred 1,3 across the tetrahydrofuran ring, and (c) conditions were unfavorable for a Wittig rearrangement, which would yield a highly strained cyclobutane ring. Furthermore, the elimination product, sodium 4-phenyl-3-buten-1-oxide, would have less tendency to undergo subsequent polymerization or metallation than alkenes which did not bear a negative charge.

2-Phenyltetrahydrofuran was prepared by an acid-catalyzed cyclodehydration of 1-phenyl-1,4-butanediol, which in turn was obtained by the reduction of methyl β-benzoylpropionate with lithium aluminum hydride. It was found to react readily with propylsodium (gas evolution began when the reactant was stirred at −40°); however, no 4-phenyl-3-butenol could be isolated from the products. Instead, there was obtained acetophenone (56%), 1-phenylethanol (3%), 2,3-diphenyl-2,3-butanediol (26%) and unreacted phenyltetrahydrofuran (5.5%); which altogether account for 90.5% of the starting ether. When the reaction was repeated on a smaller scale for a quantitative analysis of the gas that was evolved, a 95.5% yield of ethylene and 98.2% yield of propane was obtained.

From the nature of the products, it appears that the reaction of phenyltetrahydrofuran with the alkali metal reagent was probably a simple one which produced equimolar amounts of ethylene, propane and acetophenone (after hydrolysis). The diol and phenylethanol can best be explained as products of reduction of acetophenone (by sodium) which were formed during hydrolysis. No doubt some metallic sodium was present in all of the propylsodium mixtures. To test this idea, we examined the reaction of 2-phenyltetrahydrofuran with a metal-free solution of propyllithium in ether. As expected, acetophenone (85–92%) was isolated, but none of the reduction products could be found. Phenyllithium also cleaved phenyltetrahydrofuran to give acetophenone.

The products of these reactions are accommodated satisfactorily by sequence VI.



(VI)

Initial attack at an α-position, suggested by the course of cleavage of ethyl benzyl ether, is further indicated by the fact that tetrahydrofuran itself is relatively unreactive (less than 5% of the theoretical gas volume was obtained from a two-hour reaction of propylsodium with tetrahydrofuran in hexane at 50°). The second (or possibly concomitant) step is 1,4-elimination accompanied by carbon–carbon scission. While such reactions are not common, several examples have recently been reported.[16] Sequence VI also has the virtue of yielding the enolate of acetophenone directly. Any process that would produce acetophenone in the original reaction mixture must be excluded since the ketone would certainly undergo further reaction with the organometallic compound. It may be noted that ethylene is formed in this reaction by *cis* elimination. This fact is of interest in light of our previous observation that *cis* elimination occurs readily, in fact more readily than *trans* elimination, when butyllithium reacts with the stereoisomeric methyl 2-phenylcyclohexyl ethers.[1]

In this reaction of 2-phenyltetrahydrofuran, a substance that appeared ideally constituted for the observation of α-elimination in that known competing reactions were minimized, we observed a new type of ether cleavage rather than α-elimination. It is apparent from this and the work previously described that α-elimination, if possible, is at least an unfavorable process relative to the numerous other reactions that can occur. In this regard, therefore, the ether cleavages must be classed with the E2 reactions.

Experimental Part

All reactions which were conducted with the intention of obtaining a quantitative measure of the gaseous products were carried out in a small reaction flask fitted by a standard taper joint to an all glass vacuum system. Gas samples were collected and transferred by conventional techniques, and were analyzed with a modified L-V mass spectrometer.

Infrared spectra were taken of most of the compounds prepared in this work; a Baird recording spectrophotometer with sodium chloride optics was used. The deuterated compounds all showed strong absorption in the 4.5–4.8 μ region.

Melting points were determined with a Fisher–Johns block and are uncorrected. Carbon and hydrogen analyses were carried out by Miss Hilda Beck.

Octane was purified for use as a solvent by successive treatments with concentrated sulfuric acid and sodium, then it was fractionally distilled. Petroleum hexane (b.p. 63–69°) was purified in a similar manner.

Propane-1-*d*.—This gas was prepared for use as a mass spectrometric standard from propylmagnesium bromide and

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[15] (a) A. A. Morton and F. Fallwell, THIS JOURNAL, **60**, 1429 (1938); (b) R. L. Letsinger, *ibid.*, **70**, 406 (1948).

[16] C. A. Grob and W. Baumann, *Helv. Chem. Acta*, **38**, 594 (1955).

deuterium oxide[17] (1.0 g.). The oxide was distilled onto the Grignard reagent which was at liquid nitrogen temperature in the vacuum system. When the mixture was allowed to warm, a vigorous reaction ensued. The evolved gases were condensed in a trap at −78° and subsequently redistilled.

The propane and ethylene used as standards were Matheson extrapure grade.

Propylsodium.—Propylmercury, b.p. 74° (13 mm.), was prepared in 80% yield from propylmagnesium bromide and mercuric chloride essentially by the procedure of Gilman and Brown,[18] and converted to propylsodium by stirring with sodium in octane as directed by Whitmore and Zook.[19]

It is well known that organometallic compounds decompose on heating to give gaseous products. To check the stability of propylsodium, a sample of this substance (prepared from 0.16 g. (7 mmoles) of sodium and 1.0 g. (3.5 mmoles) of propylmercury) was heated with stirring as a suspension in octane under nitrogen at one atmosphere of pressure. The volume of evolved gas was measured at intervals, then the temperature increased rapidly to a definite value and maintained there while more gas was evolved. The data are summarized in Table I. The maximum amount of C-3 hydrocarbon obtainable from the propyl groups present would be 173 ml. This experiment shows that the propylsodium suspensions could be heated for short periods of time to 50° without yielding gaseous decomposition products.

TABLE I

PYROLYSIS OF PROPYLSODIUM

Time of heating (hr.)	Temp. of heating bath, °C.	Vol. of gas (ml. at 26°)
1	40	0
1	50	0
3	56	4
3	69	34
2.5	84	30
10.5 (total)		68 (total)

Preparation of 1-Iodoethane-1,1-d_2.—The deuterated alcohol was prepared by reduction of purified phenyl acetate with lithium aluminum deuteride.[20] In a typical experiment 1 g. (24 mmoles) of lithium aluminum deuteride was warmed with an ether solution of 5.5 g. (40 mmoles) of the acetate at reflux temperature for 90 minutes, then cooled and hydrolyzed by successive additions of 3.5 ml. of 10% sodium carbonate solution and 10 ml. of 20% sodium hydroxide. This hydrolytic procedure was more satisfactory in our hands than that suggested by Amundsen and Nelson.[21] The resulting clear supernatant ether solution was then decanted from the solid inorganic residue, dried and distilled to give 0.9 g. (50%) of ethyl-1,1-d_2 alcohol, b.p. 75–78°. The infrared spectrum was taken with an arsenic sulfide cell.

For preparation of the iodoethane, it was found to be advantageous yieldwise to convert the deuterated ethanol to the halide without prior isolation of the pure alcohol. Thus, 40 mmoles of phenyl acetate was reduced with a 20% excess of lithium aluminum deuteride as described above. Following hydrolysis, the organic layer was dried and the major portion of the ether removed by distillation. The residue was then taken up in octane and added dropwise to a slurry of red phosphorus and iodine in octane. After the addition was complete, the mixture was stirred for 75 minutes on a steam-bath under an efficient reflux condenser. The octane solution was decanted from the unused phosphorus, washed successively with 5% sodium hydroxide, dilute sodium thiosulfate, 5% sodium hydroxide and distilled water. After drying over potassium carbonate, the solution was distilled to give 4.4 g. of 1-iodoethane-1,1-d_2, b.p. 72–73°. The over-all yield, based on phenyl acetate, was 70%.

Preparation of the Aryl Ethyl Ethers.—As directed by Senkowski,[22] a sodium ethoxide solution, prepared from 6 g. of sodium in excess ethanol, was added to 30 g. (0.2 mole) of *p*-*t*-butylphenol. The solution was warmed until all the phenol had dissolved, then cooled and allowed to react with 40 g. (0.26 mole) of ethyl iodide. After five hours refluxing, it was distilled to remove most of the alcohol and excess ethyl iodide, diluted with water, extracted with ether and the ether solution extracted with dilute sodium hydroxide solution. Distillation of the dried ether portion yielded 33 g. (93%) of *p*-*t*-butylphenyl ethyl ether, b.p. 113° (15 mm.).

The deuterated sample, 0.55 g. (48%), b.p. 113° (15 mm.), was similarly prepared from 1.5 g. (10 mmoles) of *p*-*t*-butylphenol and 1.0 g. (6.4 mmoles) of 1-iodoethane-1,1-d_2. The yield would have been higher except for an untimely accident that resulted in the loss of some material. The infrared spectra of this substance and the non-deuterated sample were similar, the major differences being the strong bands at 4.55, 4.8 and 8.8 μ and a weak band at 10.3 μ in the deuterated sample.

A similar preparation yielded 0.1 g. of phenyl ethyl-1,1-d_2 ether, b.p. 81° (25 mm.), which gave strong absorption at 4.55, 4.8, 8.8 and 10.33 μ.

Reactions of Phenetole and Ethyl *p*-*t*-Butylphenyl Ether with Propylsodium.—Phenetole (0.37 g., 3.0 mmoles) was stirred with excess propylsodium (prepared from 0.16 g. of sodium and 1.0 g. of propylmercury in 15 ml. of octane) at 50° for three hours. From this reaction was obtained 96 ml. (S.T.P.) of gas which analyzed as 89.3 ± 0.4% propane and 8.8 ± 0.4% ethylene. On the basis of a simple elimination reaction of phenetole, this corresponds to a 12.5% yield of ethylene and 127% yield of propane.

The reaction of propylsodium with ethyl *p*-*t*-butylphenyl ether (0.90 g., 5.05 mmoles) was carried out similarly at 50° for two hours, during which 214 ml. (S.T.P.) of gaseous products were collected. This analyzed as 39.1 ± 0.5% ethylene and 60.8 ± 0.5% propane, which is a 74% yield of ethylene and 115% yield of propane from the reaction.

Reactions of Ethyl-1,1-d_2 Phenyl Ether and Ethyl-1,1-d_2 *p*-*t*-Butylphenyl Ether with Propylsodium.—These reactions were carried out in the same manner as the corresponding reactions of the non-deuterated ethers with one variation. Gas samples were collected from reactions which were carried out first at 25° and then warmed to 50°.

From 0.085 g. (0.67 mmole) of ethyl-1,1-d_2 phenyl ether and excess propylsodium there was obtained after 0.5 hour of stirring at 25° 5.4 ml. (S.T.P.) of gas which analyzed as 83.0 ± 0.5% propane and not more than 0.5% propane-1-*d*. The amount of deuterated ethylene could not be determined absolutely since a standard was unavailable; however, the intensity of the mass 30 peak indicated that dideuterated ethylene was present in the mixture. After collection of the first sample, the reaction mixture was cooled rapidly with a Dry Ice bath, the system evacuated and the reaction mixture warmed quickly to 50°. It was stirred for an additional hour, by which time all visible gas evolution had ceased. In this case 22.0 ml. (S.T.P.) of gas was collected, and it analyzed as 83.1 ± 0.5% propane and not more than 1.6% propane-1-*d*. As before, ethylene-1,1-d_2 was indicated to be present. The total gaseous products represented a 152% yield of propane and not more than 2.5% yield of propane-*d*. The amount of deuterated ethylene, calculated on the assumption that it is the only other gas present in more than trace amounts, represented a 28.2% yield.

The reaction of 0.491 g. (2.72 mmoles) of ethyl-1,1-d_2 *p*-*t*-butylphenyl ether was carried out similarly with an excess of propylsodium for 2 hours at 25°, yielding 62.2 ml. (S.T.P.) of gas which was 71.8 ± 0.5% propane and not more than 0.72% propane-1-*d*. Subsequently there was produced in one hour at 50° 31.7 ml. (S.T.P.) of gas which was 72.5 ± 0.5% propane and not more than 1.1% propane-1-*d*. The total gas collected corresponded to a 112% yield of propane, not more than 1.3% yield of propane-*d*, and 42% yield of ethylene-1,1-d_2, the last component again being calculated on the assumption that it is the only other component present in more than trace amounts.

It is interesting that the gas samples collected at 25 and 50° checked very well in both cases. This result suggests

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[17] Obtained from Stuart Oxygen Company; specified to be greater than 99.5% pure deuterium oxide.

[18] H. Gilman and R. E. Brown, THIS JOURNAL, **52**, 3314 (1930).

[19] F. C. Whitmore and H. D. Zook, *ibid.*, **64**, 1783 (1942).

[20] Obtained from Metal Hydrides, Inc., and specified as containing at least 92.5% of the theoretical deuterium.

[21] L. H. Amundsen and L. S. Nelson, THIS JOURNAL, **73**, 242 (1951).

[22] M. Senkowski, *Ber.*, **23**, 2419 (1890).

that metallation and elimination were competing reactions with about the same temperature coefficient, and that ethylene did not result from an initial metallation followed by an intramolecular elimination. Morton and Brachman[8b] have evidence that alkyl ethers which are metallated in the *ortho* position do undergo elimination when heated to 75°. Their data were derived from the liquid reaction products, and ours from the gases; however, the difference is probably ascribable to the higher temperature at which they operated.

The problem of removal of propane from the octane solvent is pertinent here. In later work reaction mixtures were generally heated to 50° for a few minutes to ensure removal of all propane; however, the data indicated that a period of stirring at 25° was probably sufficient. The analyses of the gas obtained at 25 and 50°, therefore, should give a fairly reliable indication of the composition of gas actually produced at the two different temperatures.

Preparation of Benzyl-α,α-d_2 Alcohol.—To a cooled, stirred, ether slurry of 1.12 g. (26 mmoles) of lithium aluminum deuteride was added an ether solution of 6.5 g. (43 mmoles) of freshly distilled ethyl benzoate over a period of about 20 minutes. The solution was refluxed gently for two hours after the addition was complete, cooled and hydrolyzed with 6 ml. of 5% sodium hydroxide. The organic layer was decanted from the solid inorganic residue, the residue washed well with ether, the ether layers combined and dried over potassium carbonate. Distillation of the dried solution gave 3.2 g. (68%) of benzyl-α,α-d_2 alcohol, b.p. 88° (10 mm.).

Preparation of Benzyl-α,α-d_2 Bromide.—Anhydrous hydrogen bromide was bubbled through a solution of 3.2 g. (29 mmoles) of benzyl-α,α-d_2 alcohol in a mixed hydrocarbon solvent for two hours. The organic layer was separated from the aqueous layer which had formed in the reaction flask, the aqueous layer extracted with ether, and the non-aqueous layers combined and dried over potassium carbonate. Distillation gave 4.0 g. (80%) of benzyl-α,α-d_2 bromide, b.p. 80–81° (14 mm.).

Preparation of Ethyl Benzyl-α,α-d_2 Ether.—To 10 ml. of absolute ethanol in which 0.6 g. (26 mmoles) of sodium had been dissolved was added over a period of 15 minutes 4.0 g. (23 mmoles) of benzyl-α,α-d_2 bromide. After the addition was completed, the mixture was refluxed on a steam-bath for 30 minutes. The cooled solution was extracted with water, the aqueous layer extracted with ether and the organic phases then dried over potassium carbonate and distilled. There was obtained 2.25 g. (70%) of the ether, which was halide free; b.p. 68–69° (13 mm.); $n^{20}\mathrm{D}$ 1.4903. A sample of non-deuterated ether prepared similarly boiled at 65° (10 mm.); $n^{26}\mathrm{D}$ 1.4900; the literature values[23] are: b.p. 78° (18 mm.), $n^{20}\mathrm{D}$ 1.4955.

Reaction of Ethyl Benzyl-α,α-d_2 Ether with Propylsodium.—A suspension of propylsodium (from 0.16 g. of sodium and 1.0 g. of propylmercury) in 15 ml. of octane was stirred with 0.50 g. (3.6 mmoles) of ethyl benzyl-α,α-d_2 ether for 15 minutes at 0°, then 10 minutes at 25° and finally, after a rapid warming, at 48° for five minutes. Gas evolution could no longer be discerned by this time. There was obtained a total of 156 ml. (S.T.P.) of gas, which analyzed as 47.2 ± 0.4% ethylene, 41.8 ± 0.4% propane-1-*d* and 11 ± 0.5% propane. These amounts of gas correspond to a 91% yield of ethylene, 81% yield of propane-*d* and a 21% yield of propane.

To demonstrate the presence of a deuterobenzyl alcohol, the residue was hydrolyzed with water, the organic layer dried, filtered and warmed for 10 minutes on a steam-bath with 0.5 g. of 3,5-dinitrobenzoyl chloride. The derivative was washed with 5% sodium carbonate and recrystallized repeatedly from ethanol–water and carbon tetrachloride. There was obtained 0.2 g. of white crystals, m.p. 111–112°; m.p. reported for benzyl 3,5-dinitrobenzoate, 112°. The infrared spectrum of this substance was taken in carbon tetrachloride solution with a Beckman IR2T spectrophotometer with lithium fluoride optics, which resolved the bands due to aliphatic and aromatic C–H very well. The spectra showed strong absorption at both 3.46 μ (characteristic of aliphatic C–H) and 4.51 μ (characteristic of aliphatic C–D).

Reaction of Ethyl Benzhydryl Ether with Propylsodium. (**a**).—Propylsodium (from 0.2 g. of sodium and 0.9 g. of propylmercury) and 0.52 g. (2.5 mmoles) of ethyl benzhydryl ether were stirred in the gas collection system at 10°. The mixture soon began to turn brown and to generate a gas. The temperature was raised to about 25° and maintained there for 20 minutes. During this time the color changed from light brown to a dark violet, almost black, and gas evolution ceased. Further warming of the mixture to 50° increased the gas volume only very slightly. A total of 75.5 ml. (S.T.P.) of gas was collected, and it analyzed as 82 ± 1% propane and 18 ± 0.5% ethylene. On the basis of the ether, this is a 110% yield of propane and 24% yield of ethylene. In other similar reactions duplicate results were obtained.

(**b**).—A somewhat larger scale reaction was carried out with excess propylsodium and 2.1 g. (10 mmoles) of benzhydryl ethyl ether for 15 minutes at 25° and 25 minutes at 50°. The total gas yield (not analyzed) was 253 ml. (S.T.P.), or 11.3 mmoles. The reaction mixture was cooled and poured onto solid carbon dioxide. An equal volume of water was added and the aqueous and organic layers separated. Distillation of the organic neutral fraction yielded 0.78 g. of solid material, which after recrystallization from ethanol gave a first crop of crystals melting at 85–90°, and a second crop of crystals melting at 45–48°. Recrystallization of the first crop six times from ethanol yielded pure white, cubical crystals that melted sharply at 95°. These were identified as 1,1-diphenyl-1-propanol by a mixed melting point determination and infrared spectra comparison with an authentic sample of this alcohol prepared by the method of Tuot and Guyard.[24] Six recrystallizations of the lower melting crystals from ligroin resulted in a mixture of cubical and needle-shaped crystals which could be separated mechanically. The cubes were 1,1-diphenyl-1-propanol and the needles (m.p. 62–63°) were benzhydrol.

(**c**).—To approximately 50 mmoles of propylsodium suspended in hexane at 0° was added a hexane solution of 5.3 g. (25 mmoles) of ethyl benzhydryl ether over a period of about 25 minutes. On removal of the cooling bath the temperature of the stirred mixture was observed to rise to 33° over a period of 30 minutes. After all gas evolution had ceased, the reaction mixture was poured onto solid carbon dioxide, hydrolyzed and separated into neutral and acid portions. The acidic fraction weighed 1.4 g. after it had stood for 48 hours at 0.3 mm. pressure to remove volatile materials; however, all attempts to obtain a crystalline material were fruitless.

Excess ether and hexane were distilled from the neutral products, and the resulting semi-solid residue washed with pentane to give 3.4 g. of crystalline solid; m.p. 45–50°. This material was analyzed by infrared spectra for benzhydrol and 1,1-diphenyl-1-propanol. For this purpose the 8.82 μ band of 1,1-diphenyl-2-propanol was useful since benzhydrol does not absorb in this region. By comparison with the spectra of standard mixtures of diphenylpropanol and benzhydrol, it was determined that the reaction product consisted of a mixture of 68% diphenylpropanol (by weight) and 32% benzhydrol (or 44 and 24% yields, respectively). The analysis was confirmed by preparing a known mixture of this composition, and comparing its spectrum from 2 to 16 μ with the spectrum of the reaction product.

Reaction of Ethyl 1-Phenylethyl Ether with Propylsodium.—1-Phenylethyl ethyl ether, b.p. 70° (14 mm.), (reported b.p., 67° at 14 mm.),[25] was prepared in 60% yield by a Williamson synthesis from sodium 1-phenylethoxide and ethyl bromide in benzene. This ether (3.76 g., 25 mmoles) was stirred in octane with approximately 30 mmoles of propylsodium at room temperature until all gas evolution had ceased, then the mixture was hydrolyzed with wet ether. Distillation of the organic portion yielded some 1-phenylethanol (hydrogen phthalate derivative, m.p. 105–106°) and 1.0 g. of tarry residue which could not be crystallized. The spectrum of this residue was very similar to that of polystyrene.

Preparation of 1-Phenyl-1,4-butanediol.—β-Benzoylpropionic acid[26] was esterified with methanol in the presence of sulfuric acid to give methyl β-benzoylpropionate, b.p. 105° (0.4 mm.). An ether solution of this ester (57.6 g., 0.30

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[23] V. Chelintzev and B. V. Parlor, *J. Russ. Phys. Chem. Soc.*, **45** 289 (1913).

[24] M. Tuot and M. Guyard, *Bull. soc. chim.*, [5] **14**, 1091 (1947)

[25] J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1676 (1930).

[26] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 81.

mole) was added slowly to a stirred ether slurry of 10.3 g. (0.26 mole) of lithium aluminum hydride. The solution was warmed over a steam-bath for 15 minutes after the addition was complete, then cooled and carefully hydrolyzed with 25 ml. of 10% sodium carbonate followed by sufficient 20% sodium hydroxide to precipitate the inorganic salts. The ether solution was decanted, the residue washed well with ether, and the ether layers combined and dried. Evaporation of the ether yielded 42.3 g. (85%) of crude product, m.p. 60–63°. A small sample was recrystallized from benzene–petroleum hexane to give pure 1-phenyl-1,4-butanediol,[27] m.p. 65–66°; reported value, m.p. 65–66°.

Preparation of 2-Phenyltetrahydrofuran.—To 41.5 g. (0.25 mole) of 1-phenyl-1,4-butanediol dissolved in about 250 ml. of benzene was added 19 g. (0.1 mole) of *p*-toluenesulfonic acid monohydrate. The solution was refluxed until 6.3 ml. of water had been collected (about two hours), then washed with water and with 10% sodium carbonate. Distillation yielded 32 g. (85%) of 2-phenyltetrahydrofuran, b.p. 96° (8 mm.), n^{25}D 1.5278; reported b.p. 105° (14 mm.).[28] The infrared spectrum was that expected of an ether containing a phenyl group.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.05; H, 8.16. Found: C, 81.14; H, 7.85.

The higher boiling residue was distilled from a semi-micro apparatus, yielding 0.35 g. of 4-phenyl-3-butenol, b.p. 102° (1.5 mm.); m.p. 36°; reported values[29] b.p. 140° (12 mm.) and m.p. 36°.

Reaction of Propylsodium with 2-Phenyltetrahydrofuran. (**a**).—To a cold (−60°), stirred hexane slurry of propylsodium prepared from 28.3 g. (0.1 mole) of dipropylmercury and 6.9 g. (0.3 mole) of sodium, was added all in one portion a cold (−50°) hexane solution of 29.6 g. (0.2 mole) of 2-phenyltetrahydrofuran. No immediate reaction was evident. When the stirred reaction mixture had warmed to about −40°, vigorous gaseous evolution was observed and the temperature of the reaction mixture rose rapidly to 0°. The reaction temperature was maintained at 0 to 3° for 15 minutes, by which time gas evolution had ceased. The dark gray slurry was stirred at room temperature for two hours, then hydrolyzed with water, and the non-aqueous layer separated and dried. Distillation through a Piros–Glover spinning band column yielded 13.5 g. (56.5%) of acetophenone (b.p. 96° at 20 mm.), 0.76 g. (3.1%) of 1-phenylethanol (b.p. 106–107° at 20 mm.) and 1.6 g. (5.5%) of unreacted starting material. The acetophenone was characterized by the identity of its infrared spectra to that of a known sample, by quantitative microhydrogenation of the carbonyl group, by its ultraviolet spectra, and by derivatives (2,4-dinitrophenylhydrazine, m.p. 248°; semicarbazone, m.p. 196–197°). The carbinol gave an α-naphthylurethan which melted at 104°, and the mixed melting point with an authentic sample of the derivative of 1-phenylethanol was not depressed. The residue from the distillation amounted to 6.29 g. After one recrystallization from benzene it melted at 122° and a small sample recrystallized several times from ligroin melted at 124°. This was shown to be 2,3-diphenyl-2,3-butanediol (acetophenone pinacol) by a mixed melting point determination with a sample of the pinacol prepared by reduction of acetophenone with magnesium amalgam.[30]

(**b**).—The reaction was repeated on a smaller scale to obtain a quantitative measure of the gaseous products. To a sample of propylsodium in octane at −78° was added 0.746 g. (5.05 mmoles) of 2-phenyltetrahydrofuran. The Dry Ice bath was removed and the reaction mixture allowed to warm slowly with stirring. Gas evolution started well below room temperature and was complete in about 10 minutes; however, the reaction mixture was subsequently stirred at 40° for 90 minutes, and finally at 50° for 90 minutes to assure total propane recovery. The final gaseous yield was 224 ml. (S.T.P.) and was found to consist of 49.5 ± 0.2% propane and 48.1 ± 0.3% ethylene. These percentages of 224 ml. of gas represent a 98% yield of propane and a 95% yield of ethylene. The reaction mixture was hydrolyzed. On treatment of the organic layer with an acidified alcoholic solution of 2,4-dinitrophenylhydrazine (1.5 g. of the hydrazine), there was obtained 0.481 g. (32%) of acetophenone phenylhydrazone, m.p. 245°. No attempt was made to recover the pinacol which was undoubtedly present in the reaction mixture.

Reaction of Propyllithium with 2-Phenyltetrahydrofuran. (a).—A solution of 8.1 g. (75 mmoles) of 2-phenyltetrahydrofuran in 100 ml. of 1.085 molar propyllithium–ether solution was refluxed for approximately 16 hours, then cooled and hydrolyzed. Isolation of the products in the manner previously described yielded 3.1 g. (35%) of acetophenone, b.p. 81–82° (9 mm.); 1.1 g. of a mixture of acetophenone and phenyltetrahydrofuran; and 2.7 g. of a yellow, amorphous residue, which exhibited only a weak carbonyl absorption (at 5.99 μ) and decolorized neither bromine in carbon tetrachloride nor dilute, aqueous permanganate. It seemed likely that the gummy residue resulted from reaction of the excess propyllithium with the acetophenone enolate. Subsequent reactions were therefore carried out with less propyllithium. In accordance with expectations, more acetophenone and less of the residue was then obtained (b and c).

(**b**).—Reaction (a) was repeated using 100 ml. of 0.93 molar propyllithium (93 mmoles) and 13.3 g. (90 mmoles) of 2-phenyltetrahydrofuran. A reaction started even at room temperature, as evidenced by gas evolution; nevertheless, the solution was refluxed overnight (approximately 11 hours) before hydrolysis. In this case there was obtained 9.2 g. (85%) of acetophenone (b.p. 80° at 8 mm.) which contained a very small amount of unreacted phenyltetrahydrofuran (by infrared) and 1.5 g. of non-crystalline residue.

(**c**).—This time 100 ml. of 0.77 molar propyllithium (77 mmoles) and 13.3 g. (90 mmoles) of 2-phenyltetrahydrofuran were refluxed for 24 hours. Distillation of the hydrolyzed reaction products gave 11.3 g. of distillable liquid products, b.p. 86° (10 mm.) to 95° (8 mm.), and less than 0.2 g. of residue in the distillation flask. Ten grams of the distillate were fractionated through a Piros–Glover spinning band column, giving 7.5 g. of acetophenone, b.p. 95° (20 mm.), 1.3 g. of unreacted phenyltetrahydrofuran, b.p. 115° (20 mm.), 0.1 g. of a fraction intermediate between these two fractions and 0.85 g. of residue from holdup in the column (mainly 2-phenyltetrahydrofuran by infrared). An extrapolation of the composition of the 10 g. which was fractionated to the 11.3 g. of initial product gives a 92% yield of acetophenone (based on propyllithium). The infrared spectra of the intermediate fraction (0.1 g.) showed the absence of 1-phenylethanol (previously observed to boil at 106° at 20 mm.).

Reaction of 2-Phenyltetrahydrofuran with Phenyllithium.—A mixture of 50 ml. of 0.72 molar phenyllithium (36 mmoles) in ether was refluxed with 5.0 g. (34 mmoles) of 2-phenyltetrahydrofuran on a steam-bath overnight, then hydrolyzed and worked up as in the previous reactions. The products were 2.0 g. of acetophenone (b.p. 88–89° at 12 mm.; 2,4-dinitrophenylhydrazone, m.p. 248°), 1.5 g. of unreacted phenyltetrahydrofuran (b.p. 108° at 12 mm.) and 1.0 g. of solid residue identified as biphenyl, m.p. 69° (no doubt the biphenyl arose during the preparation of the phenyllithium). The yield of acetophenone calculated on the basis of the phenyltetrahydrofuran that was not recovered was 71%.

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EVANSTON, ILLINOIS

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(27) M. Gouge, *Ann. chim.*, **6**, 648 (1951).

(28) H. Normant, *Compt. rend.*, **226**, 1734 (1948).

(29) H. Normant, *ibid.*, **226**, 733 (1948).

(30) The standard procedure for preparing pinacol was used: L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, p. 62.