onance effects should operate to reduce the rate are unusual. Conversely, the steric effect is very powerful since the *o*-chloro compound which should show the maximum inductive effect is slower than the *p*-chloro compound.

One of the most important corollaries, and indeed evidence for the mechanism, is that the presence of a coördinate covalent bond to phosphorus seemed to be the only intrinsic requirement for catalytic activity in this reaction. On this basis, it could be predicted that other compounds of this type should also be catalytically active. This prediction has been verified.[30]

(30) J. J. Monagle, *J. Org. Chem.*, **27**, 3851 (1962).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO, BUFFALO 14, N. Y.]

The Wittig Rearrangement of the Benzyl Ethers of Cyclobutanol and Cyclopropylcarbinol[1]

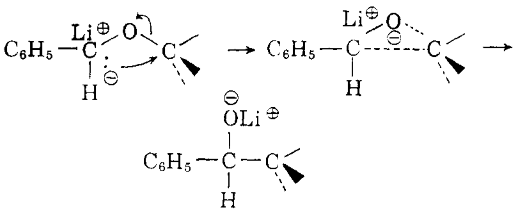
BY PETER T. LANSBURY AND VICTOR A. PATTISON

RECEIVED MAY 17, 1962

The rearrangements of cyclopropylcarbinyl benzyl ether and cyclobutyl benzyl ether in the presence of methyllithium in tetrahydrofuran lead to alcohols in which the migrating group is itself largely or completely unisomerized. The only instance of isomerization was that of the cyclopropylcarbinol anion, which in previous carbanion reactions had been found not to be a stable species. These findings are best rationalized in terms of a cleavage–recombination mechanism, involving the intermediacy of an aldehyde–organolithium ion pair.

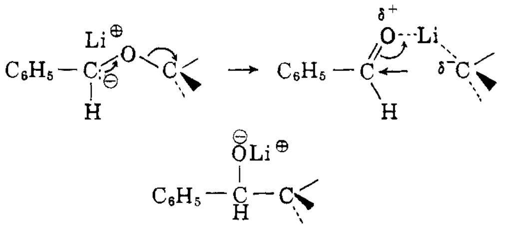
Introduction

The organolithium-induced isomerization of benzyl alkyl ethers to alcohols was considered for some time[2] to be an intramolecular nucleophilic substitution reaction in which a carbanion displaced an alkoxide, the net result being transfer of the migrating group without its bonding electrons.



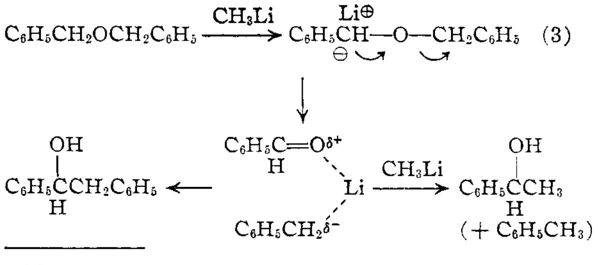
(1)

An alternative mechanism for the rearrangement involves the cleavage of the α-metalated ether into a carbonyl compound and organolithium reagent, followed by recombination of these fragments to give the alkoxide in the usual manner. The earlier workers[2] had rejected this latter mechanism because no evidence for "trapping" of the intermediate carbonyl component by excess metalating base could be obtained. Moreover, the intramolecular substitution mechanism (eq. 1) seemed to find analogy[2b] with the base-induced Stevens rearrangement.[3] The first mechanism predicts that an optically-active migrating group should retain its configuration and in fact a high degree of retention had been observed in an appropriate Stevens rearrangement.[4]



(2)

Recently, Schollkopf and Fabian[5] showed that optically-active *sec*-butyl benzyl ether rearranges when treated with *n*-butyllithium in a variety of solvents to give phenyl-*sec*-butylcarbinol in which the migrated group is largely racemized. This stereochemical evidence was interpreted as favoring the cleavage–recombination mechanism, wherein carbanion racemization could occur, rather than the intramolecular nucleophilic substitution path.[6] Although not an exact analogy, the SNi reaction of alcohols with thionyl chloride has been shown[7] to give variable stereochemical results and therefore one cannot exclude the SNi mechanism for the Wittig rearrangement wholly on this basis. We have, however, provided confirmation of Schollkopf's interpretation by the isolation of varying amounts of methylphenylcarbinol from the methyllithium-induced isomerization of benzyl ether in a series of solvent mixtures.[8] Polar solvents which are good cation solvators, such as tetrahydrofuran,



(3)

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(1) Presented in part at the 141st Meeting of the American Chemical Society, March, 1962, Washington, D. C.

(2) (a) G. Wittig and E. Stahnecker, *Ann.*, **605**, 69 (1957), and earlier papers; (b) C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.*, **73**, 1437 (1951).

(3) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 55 (1932).

(4) J. H. Brewster and M. W. Kline, *J. Am. Chem. Soc.*, **74**, 5179 (1952).

(5) U. Schollkopf and W. Fabian, *Ann.*, **642**, 1 (1961).

(6) We hesitate to call this the "SNi" mechanism since this terminology has generally been applied to chlorosulfite decompositions which usually involve a two-step process with intermediate ion pair formation (ref. 7), analogous to SN1 reactions. One may speak, however, of a graded series of SNi reactions, in which the other extreme is an intramolecular substitution with concerted bond making and breaking, similar to the SN2 mechanism. Our use of the term "SNi" will be in this more general sense.

(7) C. E. Boozer and E. S. Lewis, *J. Am. Chem. Soc.*, **75**, 3182 (1953).

(8) P. T. Lansbury and V. A. Pattison, *J. Org. Chem.*, **27**, (1962).

gave the largest proportion of "trapped" product. Unfortunately, when the migrating group was an *n*-alkyl or *sec*-alkyl group, rather than benzyl, no methylphenylcarbinol resulting from trapped benzaldehyde could be detected[9] and therefore we cannot infer unambiguously that cleavage–recombination occurs in all of these benzyl alkyl ether rearrangements, although this is a reasonable assumption. It is noteworthy that very recent stereochemical studies of the Stevens rearrangement support the contention that this reaction is also best considered a cleavage–recombination process.[10]

We previously studied the Wittig rearrangement of several benzyl *t*-alkyl ethers, since it appeared rather unlikely that the cleavage mechanism (eq. 2) involving the expulsion of highly basic tertiary carbanions would be operative here. The alternative intramolecular nucleophilic substitution mechanism (eq. 1), in which the *t*-alkyl group could accommodate cationic character, the exact amount depending on the relative extent of bond making and breaking in the transition state, seemed a reasonable expectation in this case. Preliminary evidence for such a postulate was found in a comparison of the reactivities of three *t*-alkyl benzyl ethers. *t*-Butyl and 1-adamantyl benzyl ethers isomerized to the alcohols in high yield under conditions where 1-apocamphyl benzyl ether did not,[8] as expected for an SNi reaction. Thus, it is conceivable that the major, but not necessarily exclusive, path for isomerization depends on the structure of the migrating group.[11]

From a consideration of the above situation, it appeared of interest to study the reactions of benzyl cyclobutyl ether and benzyl cyclopropylcarbinyl ether in order to see which mechanism was involved in their isomerizations. Cyclopropylcarbinyl and cyclobutyl systems, particularly the former, are exceedingly reactive in cationic processes and such reactions always lead to a mixture of cyclobutyl, cyclopropylcarbinyl and allylcarbinyl derivatives, the proportions depending on whether or not the reaction is reversible.[12] On the other hand, if such ethers were to react *via* carbanionoid intermediates, the above interconversions of the migrating group would not occur. Indeed, in the latter case one would expect[12a,13] no isomerization of the cyclobutyl group but extensive if not complete rearrangement of cyclopropylcarbinyl anion to allylcarbinyl.[14] This paper reports an investigation of the behavior of the benzyl ethers of cyclobutanol and cyclopropylcarbinol toward organolithium reagents, with the intention of elucidating the mechanistic course of their rearrangements to alcohols.

Results and Discussion

The preparation of the requisite ethers involved the reactions of the sodium salts of cyclopropylcarbinol and cyclobutanol[12b] with benzyl chloride. Spectral and analytical data confirmed the structures of cyclopropylcarbinyl benzyl ether (I) and cyclobutyl benzyl ether (II). Isomerizations of I and II were performed by treating the ether with two equivalents of halide-free methyllithium in tetrahydrofuran. In addition to small scale reactions, which were analyzed by vapor phase chromatography (v.p.c.) with the aid of authentic samples, the rearrangements were carried out on a larger scale in order to isolate pure samples of product(s) for comparison with specimens prepared by independent routes. Cyclobutylphenylcarbinol (III) was prepared by the Friedel–Crafts reaction of cyclobutane carbonyl chloride with benzene, followed by lithium aluminum hydride reduction of the resultant ketone. The synthesis of cyclopropylcarbinylphenylcarbinol (IV) involved the reaction of allylphenylcarbinol with methylene iodide and zinc–copper couple (the Simmons–Smith cyclopropane synthesis). Interestingly, this latter synthesis worked much better than one utilizing the acetate of allylphenylcarbinol.[15] Alcohols III and IV could not be separated on a variety of v.p.c. columns, nor were the infrared spectra sufficiently different in the fingerprint regions for unambiguous quantitative analysis of mixtures of the two. The nuclear magnetic resonance spectra of III and IV were clearly different, however. Cyclopropylcarbinylphenylcarbinol showed a multiplet centered at *ca.* 9.7 τ (cyclopropyl H's), another multiplet at 8.5–8.6 τ (–CH_2–) and a triplet centered at 5.45 τ (benzylic H), whereas cyclobutylphenylcarbinol showed a broad absorption envelope at *ca.* 8.25 τ (cyclobutyl H's) and a doublet at 5.72 τ (J, 8 c.p.s.) attributable to the benzylic hydrogen. The third possible rearrangement product, allylcarbinylphenylcarbinol (V), was prepared from benzoylacetic ester by alkylation with allyl bromide, followed by hydrolysis and decarboxylation, then hydride reduction of the unsaturated ketone. Carbinol V had shorter retention time in v.p.c. than III and IV and was thus easily identified and isolated from reaction mixtures.

Cyclopropylcarbinyl benzyl ether (I) rearranged in tetrahydrofuran in almost quantitative yield during forty-eight hours, yielding 94% of IV and 6% of V. Infrared and n.m.r. spectroscopy showed

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(9) P. T. Lansbury and V. A. Pattison, unpublished observations.

(10) E. F. Jenny and J. Druey, *Angew. Chem. Internat. Edit.*, **1**, 155 (1962).

(11) Additional evidence for the duality of mechanism arises from a study of "α',β-elimination" products which sometimes appear as by-products; *e.g.*, benzyl isobutyl ether gives benzyl alcohol and isobutylene (62%). The "elimination" products may actually result from *hydride* transfer within the carbonyl–organolithium complex, since benzyl *t*-butyl ether gives no elimination product, although one would expect hydride transfer if the cleavage process occurred in this ether. Thus, one is led to the possibility that benzyl *t*-butyl ether isomerizes by the SNi route and, as a corollary, that α',β-elimination does not occur in ether reactions of this sort, because the above initial α-metalated ether would have every opportunity to attack one of the nine *primary* β-C-H bonds and thus give *more* elimination than the isobutyl ether, where only a single *tertiary* β-C-H bond is present. The actual results are entirely contrary and thus support the alternative hydride transfer mechanism for the formation of olefin and benzyl alcohol (P. T. Lansbury and V. A. Pattison, to be published).

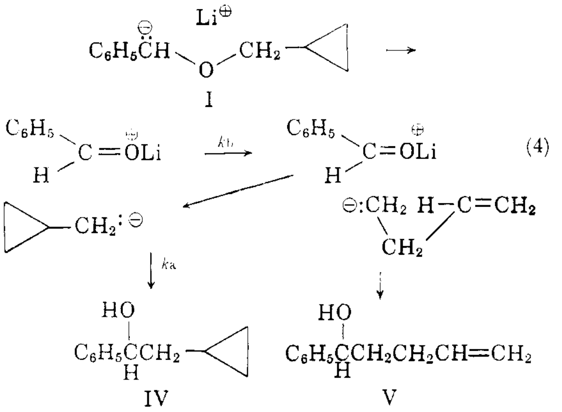
(12) (a) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); (b) M. C. Caserio, W. H. Graham and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960); (c) D. B. Denney and E. J. Kupchik, *J. Am. Chem. Soc.*, **82**, 859 (1960).

(13) J. D. Roberts, Abstracts of 16th Organic Chemistry Symposium, June, 1959, p. 1.

(14) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 2646 (1960).

(15) A similar observation was made with Δ^3-cyclopentenol in its conversion to the bicyclo[3.1.0]hexanol system (S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961)).

that no detectable quantities of III were present. These results are not explainable by an SNi mechanism[12a,b] (see below) but are readily accounted for by a carbanionoid cleavage–recombination mechanism, the last step being essentially irreversible under the conditions used.[16] The formation of IV is the first example wherein a product



resulting from cyclopropylcarbinyl carbanion has been obtained ($k_a > k_b$). Previously,[8] products derived from the latter Grignard reagent were shown to contain only the allylcarbinyl structure and n.m.r. evidence has shown that the freshly-prepared Grignard reagent from cyclopropylcarbinyl bromide has the allylcarbinyl structure. Roberts has also shown[14] that the interconversion of C_1- and C_2-labeled (C^{14} or D) allylcarbinylmagnesium bromide is quite slow, with an activation energy of *ca.* 23 kcal./mole. These data do not establish whether the cyclopropylcarbinyl Grignard reagent is an intermediate or transition state in the interconversion. In the present case, cleavage or I generates the carbanion[5,8] in close proximity to the electrophilic carbonyl group present in the resultant ion pair,[5] so that recombination (k_a) apparently occurs faster than isomerization. This does not appear unreasonable since the addition of lithium reagents to ketones has been shown to be extremely rapid.[17] Put in qualitative energy terms, the cyclopropylcarbinyl carbanion may be considered a reactive intermediate with the activation energy for skeletal isomerization of the anion in the ion pair ($\Delta F_b^{\ddagger}$) apparently exceeding that for carbonyl addition ($\Delta F_a^{\ddagger}$). The ratio of IV to V might be expected to vary with the cation-solvating ability of the solvent, since complexing of lithium ion by solvent lowers the electrophilicity of the carbonyl group, thus decreasing k_a without affecting k_b comparably.[5] Actually, when the metalation of I was performed in hexane with *n*-propyllithium the reaction was much slower (>50% recovery of I after four days) and IV/V was essentially the same as above, within experimental error. Similarly, Schollkopf had observed only a small change in the degree of racemization during the Wittig rearrangement of benzyl *sec*-butyl ether in a variety of solvents ranging from tetrahydrofuran to pentane.[5]

Cyclobutyl benzyl ether (II) underwent rearrangement under the same conditions as I to give only cyclobutylphenylcarbinol (III).[18] This result is an accord with expectations for a carbanionoid mechanism, although the SNi path is not entirely excludable. Other SNi reactions in the cyclobutyl–cyclopropylcarbinyl series, *e.g.*, reaction of the alcohols with thionyl chloride[12a,13] and "internal return" in the ethanolysis of the above chlorides,[13] always occur with extensive skeletal rearrangement, but bond breaking is probably more extensive in the transition state for these reactions than in the ether rearrangements, if they were to follow this mechanism, since the latter reaction would involve a relatively poor leaving group (alkoxide) and a strong attacking nucleophile. Thus it is not inconceivable that ethers I and II may be rearranging by a concerted SNi process[6] in which very little, if any, positive charge develops in the migrating group. However, it should be remembered the Schollkopf observed extensive racemization in the rearrangement of optically-active 2-butyl benzyl ether under the same conditions as those used here.[5] This means that if an SNi mechanism were in operation, some *cationic* character in the migrating group would be required to account for the loss of configuration. This argument should apply equally to ethers I and II, meaning that cyclopropylcarbinyl–cyclobutyl interconversion should have been observed if this were the correct mechanistic path for their rearrangement. The above results thus are in contrast to this expectation but clearly support the carbanion mechanism.

In conclusion, we tend to favor the cleavage–recombination mechanism as the preferred one for most Wittig rearrangements, although the SNi mechanism may be more favorable for the rearrangement of the *t*-alkyl ethers.[8]

Acknowledgment.—We are grateful to the U. S. Army Research Office (Durham) for financial support (Grant DA-ORD-19). The assistance of Dr. Stephen Proskow in obtaining several of the n.m.r. spectra is also greatly appreciated.

Experimental[19]

Cyclopropylcarbinyl Benzyl Ether (I).—To 11.0 g. (0.15 mole) of cyclopropylcarbinol[20] in 250 ml. of benzene was

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(16) The cleavage of lithium alkoxides (reversal of organolithium addition to ketones) requires temperatures >100° and preferably solvents of high ionizing power (*cf.* H. D. Zook, *et al.*, *J. Am. Chem. Soc.*, **81**, 1617 (1959); D. J. Cram, *et al.*, *ibid.*, **81**, 5740 (1959)). In the present work, cyclopropylcarbinylphenylcarbinol (IV) was shown to be unaffected under the reaction conditions.

(17) C. G. Swain and L. Kent, *J. Am. Chem. Soc.*, **72**, 518 (1950).

(18) The cyclobutanol used in preparing II was obtained by acid-catalyzed rearrangement of cyclopropylcarbinol (ref. 6b) and hence contained some of the latter. Consequently, the sample of II had a small amount of I present (by n.m.r. spectroscopy). However, the rearrangement product contained essentially the same low concentration (probably less than 10%) of cyclopropylcarbinylphenylcarbinol (IV) as the amount of I in starting material, as indicated by the still weak cyclopropyl proton signal in the n.m.r. spectrum. Furthermore, no detectable amounts of the unsaturated alcohol V were found (v.p.c.), thus further verifying that little I was initially present.

(19) Elemental analyses were performed by Dr. Alfred Bernhardt, Mulheim (Ruhr), Germany. Melting points (taken on a Mel-temp capillary m.p. apparatus) and boiling points are uncorrected. Nuclear magnetic resonance spectra were measured in carbon tetrachloride solution, using tetramethylsilane as internal standard. Most of the spectra were obtained on the Varian A-60 spectrometer, although several were taken in a 40 mc. instrument. Infrared spectra were measured on either a Beckman IR-5 or Perkin–Elmer 21 spectrophotometer, using smears or CCl_4 solutions. Vapor phase chromatography analyses were performed on an F & M model 300 apparatus.

gradually added 7.2 g. (0.15 mole) of a 50% dispersion of sodium hydride in mineral oil. The stirred mixture was refluxed for 30 minutes (no more hydrogen evolution), then cooled and 22.1 g. (0.18 mole) of benzyl chloride added slowly. After 3 hours reflux, the reaction mixture was kept overnight, then hydrolyzed with concentrated ammonium chloride solution. The benzene layer was washed with salt solution and dilute sodium bicarbonate, then dried over sodium sulfate. After removal of solvent, two distillations under reduced pressure through a 25-cm. Vigreux column yielded 6.0 g. (25%) of the ether, b.p. 92–94° (3 mm.). The infrared spectrum of I showed no O–H absorption and v.p.c. showed no impurities (any allylcarbinyl benzyl ether would have been detected).

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.30; H, 8.64.

Cyclobutyl Benzyl Ether (II).—Using the same procedure as above, equimolar amounts (0.10 mole) of cyclobutanol[12b] and sodium hydride were allowed to react in toluene, then treated with excess benzyl chloride (0.15 mole) and refluxed briefly before keeping overnight (under nitrogen). Hydrolysis and work-up as above gave 8.7 g. (54%) of ether II, b.p. 109–110° (10 mm.), which was gas chromatographically pure.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.37; H, 8.71.

Cyclobutylphenylcarbinol (III).—Cyclobutyl phenyl ketone was prepared by acylation of benzene with cyclobutanecarbonyl chloride in the presence of aluminum chloride, according to the procedure of Mariella and Roule,[21] yield 84%. A solution of this ketone (6.7 g., 0.042 mole) in 50 ml. of ether was gradually added to a slurry of 1.9 g. (0.05 mole) of lithium aluminum hydride in 100 ml. of ether. After stirring for 2 hours at room temperature, the reaction mixture was hydrolyzed with 5% hydrochloric acid and the ether layer washed with salt solution and 5% sodium bicarbonate, then dried over sodium sulfate. Removal of the ether, followed by distillation under reduced pressure, afforded 5.5 g. (81%) of the carbinol III, b.p. 121–122° (5 mm.), whose infrared spectrum (neat) showed O–H at 3.0μ and no carbonyl absorption. The n.m.r. spectrum (in CCl_4 with tetramethylsilane as internal standard) at 60 mc. had resonance signals at 8.25, 6.45 (-O–H), 5.72 (doublet) and 2.82 τ, whose assignments are in the discussion.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.40; H, 8.53.

Cyclopropylcarbinylphenylcarbinol (IV).—Allylphenylcarbinol was prepared from allylmagnesium bromide and benzaldehyde (0.3 mole) by the usual Grignard technique. The yield of product, b.p. 106–108° (10 mm.) (reported[22] b.p. 228–229° (atm.)), was 25.0 g. (56%). The infrared spectrum showed O–H absorption 2.8–3.0 μ, alkene at 6.1 μ, and no carbonyl band.

The reaction of allylphenylcarbinol with methylene iodide in the presence of zinc–copper couple was used to prepare the cyclopropylcarbinol. To a slurry of 12.4 g. of zinc–copper couple[23] in 30 ml. of ether, contained in a 200-ml. flask equipped with magnetic stirrer, reflux condenser and addition funnel, was added a mixture of 26.8 g. (0.10 mole) of methylene iodide and 7.4 g. (0.05 mole) of allylphenylcarbinol. The reaction mixture was stirred for 2 hours, then cooled and filtered through Celite on a büchner funnel. The filtrate was washed with water and then dried over sodium sulfate. After distillation of ether at atmospheric pressure, the solution was distilled under reduced pressure, yielding a dark colored fraction having b.p. 125–130° (12 mm.). Chromatography of this material over alumina gave, with ether as eluent, 2.7 g. (33%) of the desired alcohol, slightly contaminated with starting material. Further purification by preparative v.p.c. gave a pure sample of IV, m.p. 37–40°, whose infrared spectrum (neat) showed no double bond absorption at 6.1 μ.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.60; H, 8.63.

Allylcarbinylphenylcarbinol (V).—A solution of sodium ethoxide (0.10 mole) was prepared from 4.8 g. of 50% sodium hydride in mineral oil and 200 ml. of ethanol. To this was added 19.2 g. (0.10 mole) of ethyl benzoylacetate, and after a short time, 12.1 g. (0.10 mole) of allyl bromide. The mixture was refluxed for 6 hours, during which a copious precipitate formed. The ethanol was then largely removed by distillation and a solution of 25 g. of potassium hydroxide in 100 ml. of H_2O was added. Reflux was resumed for 2 hours and then 50 ml. of 50% sulfuric acid was added slowly, with a final additional 1-hour reflux period. The cooled solution was extracted with several portions of ether and the combined extracts washed with sodium bicarbonate solution, then water and finally dried over Na_2SO_4. Fractionation of the crude product gave some acetophenone and 9.2 g. (58%) of the desired phenyl allylcarbinyl ketone, b.p. 137–140° (25 mm.) (reported[24] 135–138° (24 mm.)), which was >98% pure by v.p.c.

The above ketone was reduced with excess lithium aluminum hydride in ether, and the mixture worked-up in the usual manner. A 77% yield (7.2 g.) of V was obtained, b.p. 121–124° (10 mm.). (reported[24] b.p. 144–144.5° (28 mm.)). The infrared spectrum (neat) showed bands at 3.0 μ (O–H), 6.1 μ (>C=C<) and no carbonyl absorption.

Wittig Rearrangement of Cyclopropylcarbinyl Benzyl Ether.—The procedure was similar to that used earlier[8] involving the use of halide-free methyllithium and tetrahydrofuran solvent in a nitrogen atmosphere.

A tetrahydrofuran solution (100 ml.) of methyllithium (0.04 mole) and ether I (3.29 g., 0.02 mole) was kept at room temperature for 24 hours (under nitrogen), then hydrolyzed with saturated ammonium chloride solution and the product extracted into ether. The ether solution was dried over sodium sulfate and evaporated to dryness. Vapor phase chromatography, using a 1.5-m. 20% Tide on Chromosorb-P column at 150° (helium flow, 60 cc./min.) showed no I, 6% of V and 94% of IV. In addition, no benzyl alcohol was detected. Fractions of IV and V, collected by prep scale v.p.c., were shown to be identical with authentic samples by infrared. Furthermore, column chromatography of the reaction mixture on alumina yielded 2.19 g. (67% yield) of IV, whose n.m.r. spectrum (60 mc.) was identical with that of pure IV and showed no indication of any III.

Treatment of authentic IV with excess methyllithium in tetrahydrofuran for 24 hours, followed by the usual work-up, resulted in the recovery of unchanged starting material and no V (by v.p.c.).

A small scale reaction of I (100 mg.) with two equivalents of *n*-propyllithium in hexane was kept for 96 hours, then hydrolyzed and worked up; v.p.c. analysis indicated 59% recovered I, 37% IV and 4% V.

Rearrangement of Cyclobutyl Benzyl Ether (II).—Using the above procedure, 3.06 g. (0.019 mole) of II[18] and 0.038 mole of methyllithium in 125 ml. of tetrahydrofuran were kept for 24 hours under nitrogen, then hydrolyzed and worked up as before. Vapor phase chromatography showed that no II remained and that *ca.* 13% benzyl alcohol and 75% cyclobutylphenylcarbinol (III) were formed, together with a small quantity of unknown material. Chromatography of the product mixture on alumina led to the isolation of benzyl alcohol and III (1.90 g., 68%), which were identified by infrared comparison with authentic samples. Nuclear magnetic resonance spectra of II and III at 40 mc. in CCl_4 showed that small amounts of I and IV were present as impurities in the samples of II and III, respectively, as indicated by low intensity absorption at 9.6–9.7 τ. The source of this impurity is considered in footnote 18.

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(20) C. G. Bergstrom and S. S. Siegel, *J. Am. Chem. Soc.*, **74**, 145 (1952).

(21) R. P. Mariella and R. R. Roule, *ibid.*, **74**, 521 (1952).

(22) M. H. Fournier, *Bull. soc. chim. France*, **9**, 600 (1893)

(23) R. S. Schank and H. Schecter, *J. Org. Chem.*, **24**, 1825 (1959).

(24) B. Helferich and O. Lecher, *Ber.*, **54**, 930 (1921).