on a Beckman Megachrom instrument and were characterized by their infrared and nmr spectra.[28] The ultraviolet spectra did not reveal any maximum above 2100 A, which indicates the absence of conjugated dienes.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found for XIII: C, 88.72; H, 11.05. Found for XIV: C, 88.78; H, 11.19.

(b) **Allyl Bromide.** A solution of 3.21 g (19.9 mmoles) of 1-bromo-3,5-hexadiene in 15 ml of ether was added dropwise to 2.9 g (0.12 mg-atom) of magnesium turnings in 10 ml of ether over 5 hr. The formation and reaction of the Grignard reagent, as usual, were conducted in an atmosphere of prepurified nitrogen at all times. The Grignard solution was stirred for a further hour, then filtered through a sintered-glass disk to remove unreacted magnesium. To the filtrate was added 2.42 g (20 mmoles) of allyl bromide over 10 min. The mixture became warm and turned cloudy owing to formation of magnesium bromide. It was stirred at room temperature for 15 hr, then water was added, the ether layer was separated, washed with water, dried over sodium sulfate, and evaporated. The residue was analyzed by preparative vpc on a Beckman Megachrom instrument at 60°. Three fractions were obtained: nona-1,3,8-triene, $n^{22}\text{D}$ 1.4668 (87%), 1-cyclopropyl-1,5-hexadiene (7%), and 3-cyclopropyl-1,5-hexadiene (6%) which were characterized by their infrared and nmr spectra.[28] The yield of the main product alone was high enough to permit elemental analysis.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.39; H, 11.50.

(c) **Ethanol.** The Grignard reagent was prepared from 3 g (18.6 mmoles) of 1-bromo-3,5-hexadiene in 15 ml of ether and 2.8 g (0.115 g-atom) of magnesium in 10 ml of ether as usual. After 0.5 hr of stirring, 2 ml of absolute ethanol in 5 ml of ether was added dropwise over 15 min. Use of the isolation procedure described in section b gave a hydrocarbon product consisting of 1,3-hexadiene (77%), allylcyclopropane (10%), and probably a mixture of *cis*- and *trans*-propenylcyclopropane (13%). The evidence for the last assignment is not rigorous, however, since the yield of this fraction was very low, and spectra were taken with rather dilute solutions. One of the isomers, it is not known which, predominates in the mixture by a factor of 1.8. The percentages given are for the four main components relative to their total and are not very precise because of difficulties of resolution in the vpc. Several low-retention time products and a small amount of the two cyclopropylallyl coupling products were also present. But no peak corresponding to cyclohexene was detected, indicating that formation of cyclohexenyl Grignard reagent by cyclization of the hexadienyl Grignard reagent does not occur to a detectable extent.

(d) **Oxygen.** The Grignard reagent was prepared using the same quantities and procedure as in section c, except that the bromide was dissolved in 20 ml of ether and the addition period was 7 hr. Dry oxygen was then passed over the surface of the Grignard solution for 3 hr with stirring. Saturated aqueous ammonium sulfate solution, 4 ml in 30 ml of water was added and the products isolated as described in section b by preparative vpc on the Megachrom at 90°. Besides allylcyclopropane, 1,3-hexadiene, and the hydrocarbons XIII and XIV, three carbinols were obtained which were characterized by their spectra:[28] vinylcyclopropylcarbinol (34%), 3,5-hexadien-1-ol, and a mixture of *cis*- and *trans*-γ-cyclopropylallyl alcohol (total 66%). It is not known which isomer predominates in the *cis–trans* mixture, but the relative intensity of the methylene doublets in the nmr indicates that one isomer predominates by a factor of 3. The vpc resolution of the alcohol peaks was not sufficiently good to obtain relative percentages for all the alcohols, but vinylcyclopropylcarbinol was well separated from the others.

(e) **Cobaltous Chloride.** To a refluxing suspension of 1.77 g (13.6 mmoles) of anhydrous cobaltous chloride and 0.332 g (13.6 mg-atoms) of resublimed magnesium in 25 ml of ether was added a solution of 1.99 g (12.3 mmoles) of 1-bromo-3,5-hexadiene in 20 ml of ether over 0.5 hr. The dark mixture was refluxed for 8 hr, then stirred for 15 hr at room temperature. Excess solid carbon dioxide was added, but no carboxylic acid was obtained. The neutral fraction, isolated as usual, was examined by vpc at 142° prior to distillation. Besides several unidentified compounds of lower retention time, we detected 1,6-dicyclopropyl-1,5-hexadiene (XIII, 40%), 1,4-dicyclopropyl-1,5-hexadiene (XIV, 29%), and 7.5% of a compound which after preparative vpc separation on the Megachrom was characterized by its spectra[28] as 1-cyclopropyl-1,6,8-nonatriene (XVI).

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(28) For details see M. E. H. Howden, Ph.D. Thesis, California Institute of Technology, 1962.

Small-Ring Compounds. XLVI. Stabilized Cyclopropylcarbinyl Anions. A Retro Cyclopropylcarbinyl–Allylcarbinyl Rearrangement[1]

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Received October 22, 1965

Abstract: The cyclopropylcarbinyl anion is stabilized by a phenyl group attached to the carbinyl carbon toward ring opening, provided that potassium or sodium is the counterion. Replacement of potassium by lithium or magnesium in ether leads to immediate rearrangement and formation of the corresponding covalent allylcarbinyl organometallic compound. These rearrangements are reversible as can be demonstrated with diphenylcyclopropylcarbinyllithium, which is stable in tetrahydrofuran but completely opened to γ,γ-diphenylallylcarbinyllithium in diethyl ether. The retro rearrangement for this case can be achieved by simply adding tetrahydrofuran to the ether solution. The reaction of γ,γ-diphenylallylcarbinylmercuric bromide with potassium leads to ring closure with the formation of the corresponding cyclopropylcarbinylpotassium derivative.

Cyclopropylcarbinyl Grignard reagents[2] and cyclopropylcarbinyllithium[3] are very labile compounds which rearrange even at −40° to the corresponding allylcarbinyl derivatives.

The reversible character of the rearrangement has been demonstrated starting with α-labeled allylcarbinyl

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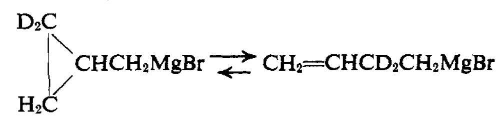
(1) Supported in part by the National Science Foundation.

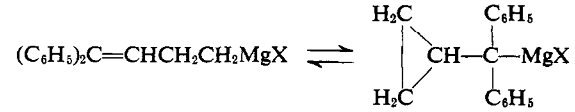
(2) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5144 (1965).

(3) P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. D. Sidler, *ibid.*, **86**, 2247 (1964).

Grignard reagents.[4] Although only open-chain products were obtained, a slow interconversion of the α and β positions in the Grignard reagent was observed, the half-life for equilibration being 30 hr at +27° and 40 min at +55°.[2,4]



This wholly unanticipated rearrangement is highly facilitated by phenyl or vinyl substitution at the 4-positions of the allylcarbinyl Grignard reagent,[5] probably as the result of stabilization of the transition state during the cyclization through delocalization of the partial negative charge on the carbinyl carbon over the phenyl or vinyl groups. However, the cyclopropylcarbinyl Grignard reagent I could not be detected in the equilibrium mixture.

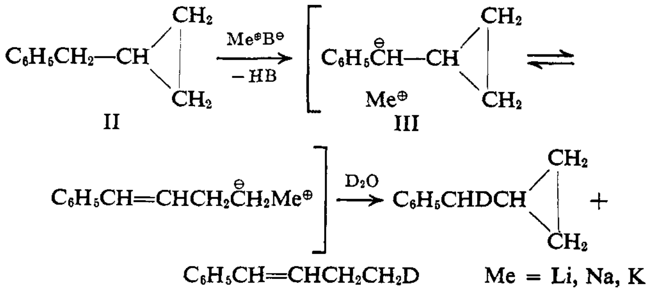


I

In the present study, attempts were made to prepare compounds like I with the largely covalently bonded magnesium replaced by alkali metals. It was anticipated that in making the carbon–metal bond more ionic, the resonance stabilization of the cyclopropylcarbinyl anion would increase so that the cyclic compound might even be favored in the equilibrium with the open-chain isomer.

Results and Discussion

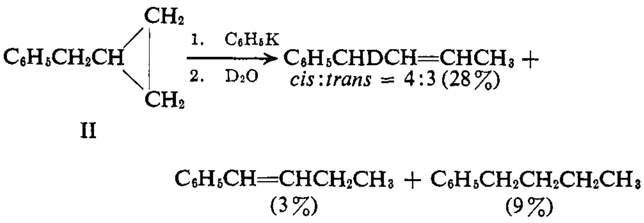
Treatment of Benzylcyclopropane with Bases. The most simple and convenient route for the preparation of the phenylcyclopropylcarbinyl anion (III) seemed to be abstraction of a proton from benzylcyclopropane (II) with a strong base ($Me^{\oplus}B^{\ominus}$, $Me^{\oplus}$ = metal cation). Formation of the anion could then be demonstrated by hydrolysis with deuterium oxide.

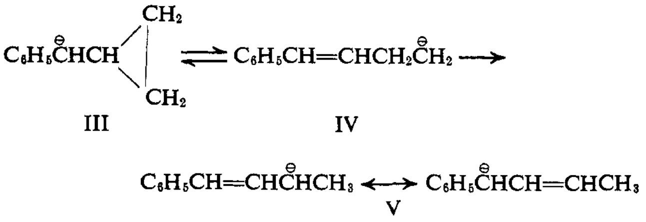


It turned out, however, that, although the benzylic protons in II might be supposed to be fairly acidic, the compound is not readily attacked under normal conditions by butyllithium in ether or benzylpotassium in toluene. This may be due to association of $Me^{\oplus}B^{\ominus}$ in solvents of low polarity so that kinetically controlled reactions occur only very slowly. However, benzylpotassium has been successfully used for metalation of cycloheptatriene.[6] The failure of this reagent with II might, of course, mean that toluene is a stronger acid than benzylcyclopropane, although we expected the opposite because cyclopropyl substituents seem to have an electron-attracting inductive effect.

Attempts to achieve metalation with more powerfully basic reagents were also unsuccessful; even *n*-amylpotassium in heptane did not work although it does react with both ethylbenzene and cumene.[7a] Benkeser and co-workers[8] have found that the first step in this kind of metalation involves removal of an aromatic hydrogen and that the so-formed *m*- and *p*-alkylphenylpotassium derivatives are only converted to the thermodynamically more stable α isomers in the presence of excess hydrocarbon. This suggests the possibility of using phenylpotassium as the metalating agent which would have the advantage of requiring less benzylcyclopropane (II) and thereby making it easier to detect small amounts of deuterium in the benzyl position of the acidolysis product.

At room temperature, benzylcyclopropane (II) did not appear to be attacked by phenylpotassium in heptane, because no deuterium could be detected in the recovered starting material upon hydrolysis with deuterium oxide after 3 hr. A reaction did, however, occur when the mixture was heated at reflux for 46 hr. The main product was 1-phenyl-2-butene with deuterium at the 1-position (the position of deuterium in the other products was not determined). Interestingly, the recovered starting material (60%) was essentially deuterium free. The probable course of this reaction is first formation of the phenylcyclopropylcarbinyl anion (III), reversible formation of the γ-phenylallylcarbinyl anion (IV), and finally an irreversible conversion of IV to the stabilized allylic anion V, which with deuterium oxide should give mostly 1-phenyl-2-butene having deuterium at the 1-position. Similar results were





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(4) M. S. Silver, P. A. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 2646 (1960).

(5) M. E. H. Howden, A. Maercker, J. Burdon, and J. D. Roberts, *ibid.*, **88**, 1732 (1966).

(6) H. J. Dauben and M. R. Rifi, *ibid.*, **85**, 3041 (1963).

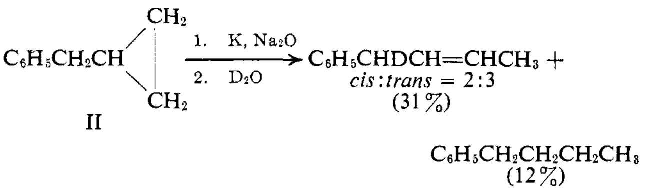
(7) (a) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1636 (1958); (b) C. E. Claff and A. A. Morton, *ibid.*, **20**, 440, 981 (1955).

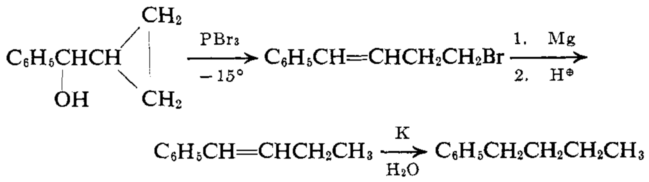
(8) (a) R. A. Benkeser, A. E. Tevillyan, and J. Hooz, *J. Am. Chem. Soc.*, **84**, 4971 (1962); (b) R. A. Benkeser, J. Hooz, T. V. Liston, and A. E. Trevillyan, *ibid.*, **85**, 3984 (1963).

obtained using a different metalation procedure known to be effective for metalation of the side chain of toluene.[7b]

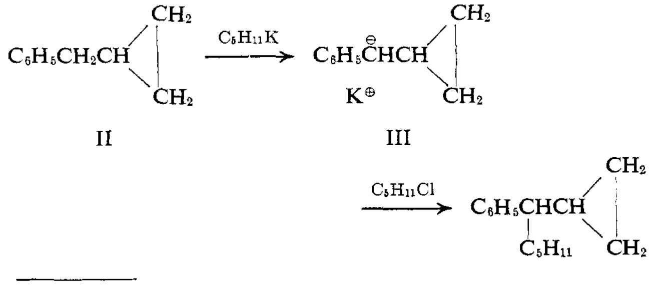
$$2C_6H_5CH_3 + 2K + Na_2O \longrightarrow 2C_6H_5\overset{\ominus}{C}H_2K^{\oplus} + NaH + NaOH$$

Benzylcyclopropane (II), stirred at high speed for 22 hr at 80-85° in heptane containing liquid potassium and sodium monoxide as hydrogen acceptor, then treated with deuterium oxide, gave recovered starting material (57%) which was deuterium free. No trace of 1-phenyl-1-butene could be detected and the *cis*:*trans* ratio of 1-phenyl-2-butene was somewhat different from that obtained with phenylpotassium. It is possible, however, that in both this, and the preceding experiment, substantial amounts (12%) of 1-phenyl-1-butene were actually formed but were reduced to *n*-butylbenzene by the metallic excess potassium during hydrolysis. This hypothesis for the origin of the *n*-butylbenzene present in the products is supported by the finding that 1-phenyl-1-butene, but not 1-phenyl-2-butene, is reduced by potassium and water to *n*-butylbenzene under the hydrolysis conditions. The 1-phenyl-1-butene used for comparison purposes in this work was obtained by hydrolysis of the Grignard reagent prepared from 4-bromo-1-phenyl-1-butene, the latter having been synthesized in 80% yield by treating phosphorus tribromide with phenylcyclopropylcarbinol at −15°. This reaction under the same conditions has been erroneously reported to yield pure phenylcyclopropylcarbinyl bromide.[9] However, the nmr spectrum of the product, identical in boiling point and index of refraction with that reported, is in complete agreement with that expected for 4-bromo-1-phenyl-1-butene.

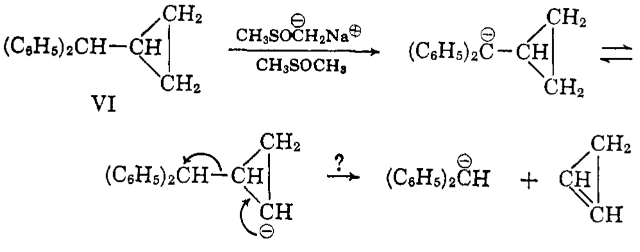




That the phenylcyclopropylcarbinyl anion (III) is actually an intermediate in the metalations which lead to open-chain products is indicated by an experiment in which *n*-amyl chloride was added with high-speed stirring to potassium sand in the presence of benzylcyclopropane (II) at −10°. 1-Phenyl-1-cyclopropylhexane was obtained in about 50% yield and no rearrangement products were formed; the only substance isolated besides starting materials was *n*-decane from the reaction of amyl chloride with *n*-amylpotassium. In an attempt to avoid coupling of the initially formed anion III with alkyl halides, *n*-butylpotassium was prepared from di-*n*-butylmercury and potassium in the presence of benzylcyclopropane (II). However, after hydrolysis with deuterium oxide, the starting material was recovered essentially unchanged, the ratio of phenyl protons to benzyl protons being 2.7 according to the nmr spectrum.



Other proton-abstraction experiments were carried out in dimethyl sulfoxide which is a reasonably polar solvent but one in which potassium *t*-butoxide is a very strong base especially in the absence of the corresponding alcohol.[10] It is also possible to use the sodium salt of the methylsulfinyl carbanion[11a] (dimsyl sodium) as a strong base in dimethyl sulfoxide, and this combination has been found to abstract a proton from diphenylmethane.[11b] With benzylcyclopropane (II), however, no salt formation was observed with either potassium *t*-butoxide or dimsyl sodium; we therefore turned to diphenylcyclopropylmethane (VI) which was expected to be much more reactive. A reaction did occur with dimsyl sodium in dimethyl sulfoxide at room temperature, but after hydrolysis with deuterium oxide the recovered starting material (56%) was found to be deuterium free and the only isolable product was diphenylmethane (44%), the cyclopropyl group having for practical purposes disappeared.



Since the elements of cyclopropene were lost in the reaction, the possible formation of cyclopropene or other similar gaseous products was checked by passing nitrogen over the reaction mixture and condensing the exit gases in a trap cooled in a Dry Ice–acetone bath, but the results were negative. The mechanism of this reaction is as yet unknown. That benzylcyclopropane (II) does indeed react with potassium *t*-butoxide was demonstrated using deuterated solvents. While no exchange occurred in *t*-butyl alcohol-O-*d* or in a mixture of this alcohol with dimethyl sulfoxide, in perdeuteriodimethyl sulfoxide, 50% of the benzylic protons of II were replaced by deuterium after 5 hr at room temperature. The product mixture, II (25%), VII (25%), and VIII (50%), when allowed to stand for an additional 20 hr in deuterated dimethyl sulfoxide–

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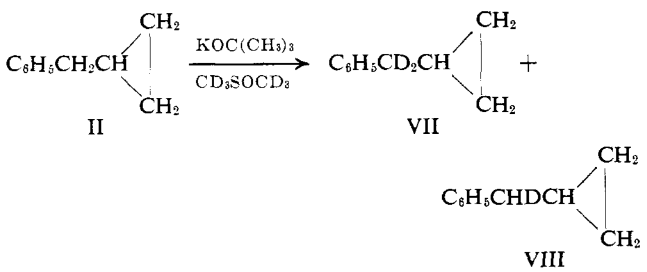
(9) J. G. Bennett and S. C. Bunce, *J. Org. Chem.*, **25**, 73 (1960).

(10) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **85**, 3054 (1963).

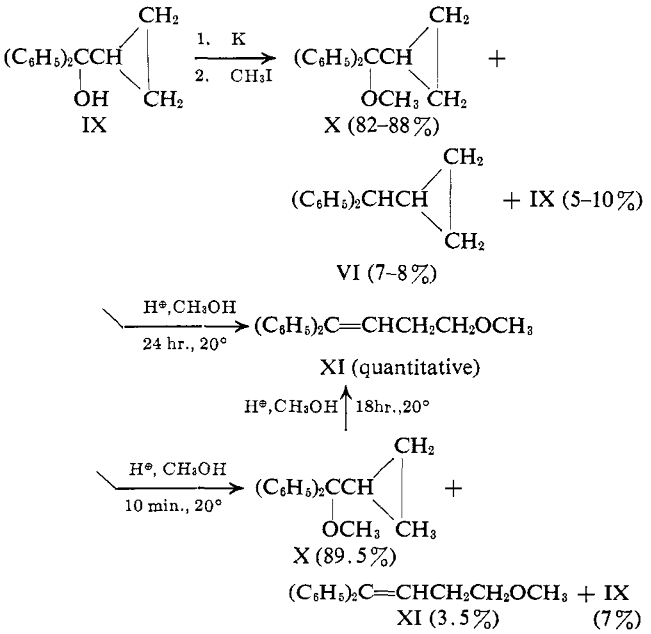
(11) (a) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962); (b) G. Price and M. C. Whiting, *Chem. Ind.* (London), 775 (1963).



potassium t-butoxide, became almost completely deuterated in the benzyl position without undergoing any ring opening. Only a trace of the monodeuterated product VIII was still present. Cram and co-workers[12] have found that in base-catalyzed hydrogen–deuterium exchange reactions run under these conditions, the carbanion is a relatively long-lived discrete intermediate. If this is true in our case also, then in dimethyl sulfoxide, the phenylcyclopropylcarbinyl anion (III) may be stable to rearrangement. Clearly, however, a less acidic solvent will be necessary if isolation of the anion is to be achieved.

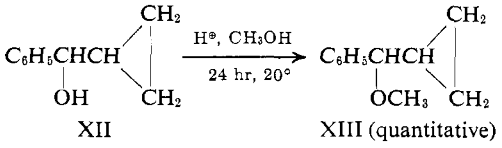
The nmr spectrum of the monodeuterated compound VIII with its two equal-intensity triplets for the benzylic proton ($J_{\mathrm{HD}} = 2.2$ cps) permitted calculation of J_{HH} for benzylcyclopropane as 14.4 cps, which is reasonable for a tetrahedral C atom of the type $\mathrm{RR'CH_2}$; J_{HH} normally falls between 12 and 15 cps.[13] For α-deuteriotoluene[14] J_{HD} is reported to be 2.38 cps. The benzylic proton in VIII shows a 1.3 cps isotope effect on its chemical shift, being more shielded than those in deuterium-free benzylcyclopropane.

Preparation of Phenyl-Substituted Cyclopropylcarbinylpotassium Derivatives. Ether cleavage is often a highly effective method for preparation of tertiary carbanions stabilized by at least one phenyl group.[15]

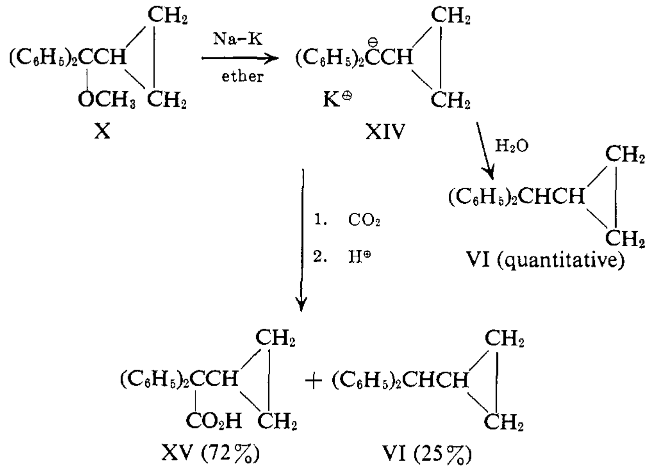


We therefore investigated the cleavage of diphenylcyclopropylcarbinyl methyl ether (X) with sodium–potassium alloy as a possible route for preparation of diphenylcyclopropylcarbinylpotassium under milder conditions than appear to be necessary for the abstraction of a proton from diphenylcyclopropylmethane (VI). For the preparation of the starting material X, the Williamson method[16] was preferred because treatment of diphenylcyclopropylcarbinol (IX) with acidic methanol leads to formation of the rearranged ether XI. That this rearrangement occurs in two steps was demonstrated by stopping the reaction after 10 min.; only 3.5% of the rearranged ether XI had been formed, the main product being diphenylcyclopropylcarbinyl methyl ether (X) which was converted quantitatively to the ring-opened ether XI when treated again with acidic methanol.

It is interesting to note that the corresponding monophenyl-substituted cyclopropylcarbinyl methyl ether (XIII) is stable in acidic methanol and can be prepared conveniently by treating phenylcyclopropylcarbinol (XII) with sulfuric acid in methanol.



Diphenylcyclopropylcarbinyl methyl ether (X) was found to be readily cleaved by sodium–potassium alloy in diethyl ether using a high-speed stirrer. Within a few minutes, a deep-red precipitate was formed which was instantly decolorized upon reaction with water or solid carbon dioxide. Hydrolysis yielded exclusively and quantitatively diphenylcyclopropylmethane (VI), while after carbonation, diphenylcyclopropylacetic acid (XV) was isolated in 72% yield, the only byproduct being the corresponding cyclic hydrocarbon VI. No rearranged products could be detected.



That these cyclic reaction products are formed *via* the stable cyclopropylcarbinylpotassium derivative XIV was demonstrated with tetrahydrofuran as solvent. Deep-red solutions of the salt were obtained in concentrations up to 1 N (20%), which made possible taking nmr spectra. For these measurements, the

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(12) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961).

(13) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

(14) G. V. D. Tiers, *ibid.*, **29**, 963 (1958).

(15) (a) K. Ziegler and F. Thielmann, *Ber. Deut. Chem. Ges.*, **56**, 1740 (1923); (b) K. Ziegler and B. Schnell, *Ann.* **437**, 227 (1924).

(16) P. Lipp, J. Buchkremer, and H. Seeles, *ibid.*, **499**, 16 (1932).

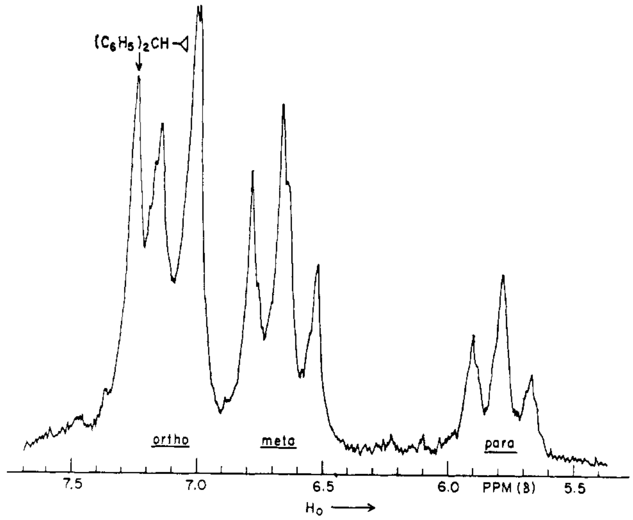

Figure 1. Proton nmr spectrum of diphenylcyclopropylcarbinylpotassium (XIV) in tetrahydrofuran (aromatic region).

excess of sodium–potassium alloy was removed by stirring the solution with metallic mercury.

The phenyl region of the nmr spectrum (Figure 1) showed a nearly first-order spectrum for the *ortho*, *meta*, and *para* protons indicating a high degree of charge delocalization over the aromatic rings. The spectrum also showed the presence of about 25% of diphenylcyclopropylmethane (VI). The large amount of VI in the solution of the anion was unexpected and indicates that the relatively low yield of acid on carbonation reaction may not be due to moisture introduced with the solid carbon dioxide. Indeed, carbonation of a tetrahydrofuran solution gave a similar low yield of acid. We believe that the hydrocarbon VI is probably formed by side reactions during the cleavage of the ether X with sodium–potassium alloy, possibly involving diphenylcyclopropylcarbinyl radicals abstracting hydrogen from the solvent. It is not likely that water in the solvents is the source of protons for VI, because extremely dry solvents were used, and furthermore the yield of hydrocarbon was found to be independent of the amount of solvent used. The diphenylcyclopropylmethane was not formed by reaction of the potassium compound XIV with the solvent because the nmr spectrum of the tetrahydrofuran solution did not change with time, and even after 3 weeks the ratio XIV:VI was still 3:1.

The nmr spectrum of the aromatic protons in XIV (Figure 1) has some interesting features. There are three discrete multiplets with chemical shifts of 7.06, 6.66, and 5.78 ppm for the *ortho*, *meta*, and *para* protons, respectively. The extreme downfield peak at δ 7.26 ppm is due to the aromatic protons of diphenylcyclopropylmethane (VI). The shielding and coupling parameters of the five-spin system of the aromatic protons in XIV were obtained with the aid of computed spectra,[17] the final values giving excellent agreement with the observed spectrum (Figure 2) (ν in ppm, J in cps): $\nu_0 = 7.06$, $\nu_m = 6.66$, $\nu_p = 5.78$; $J_{o-m} = 8.75$, $J_{o-m'} = 0.3$, $J_{o-p} = 1.3$, $J_{m-p} = 7.0$, $J_{o-o'} = 2.0$, and $J_{m-m'} = 1.7$.

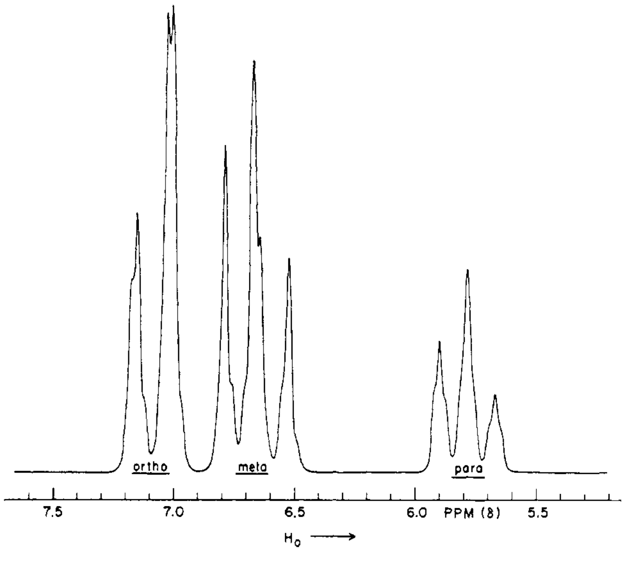

Figure 2. Calculated nmr spectrum for aromatic protons in diphenylcyclopropylcarbinylpotassium (XIV), using $\nu_0 = 7.06$ ppm.

The chemical shift of an aromatic proton, in general, is often assumed to be approximately proportional to the π-electron density on the carbon atom to which it is attached. The diphenylcyclopropyl carbanion (XIV) is particularly interesting in that the *meta* ring positions apparently bear more negative charge than do the *ortho* positions, while classical resonance theory predicts delocalization of the negative charge to the *ortho* and *para* positions only. An analogous situation has been reported for the triphenylmethyl anion,[18] which shows an nmr spectrum very similar to ours.

The cyclopropane region of the spectrum was not investigated in detail because it was complicated by ^{13}C satellite lines of the solvent, but sizable peaks centered about 16 cps upfield of TMS show that the cyclopropyl hydrogens must also be influenced by the negative charge in the anion since diphenylcyclopropylmethane (VI) shows no resonance lines upfield of TMS.

The diphenylcyclopropylcarbinyl anion (XIV) with potassium as the counterion does not seem to rearrange, apparently because the two phenyl groups provide substantial stabilization through delocalization of the negative charge. The gain in stabilization energy relative to the corresponding allylcarbinyl derivative must be sufficient to compensate for the strain of the cyclopropane ring. An important question at this point was whether a single phenyl group attached to the negative center would also be able to provide sufficient stabilization to prevent ring opening. One of the phenyl groups was therefore replaced by a methyl group. The starting material XVIII was best prepared by the Williamson method because cyclopropylmethylphenylcarbinol (XVI) in acidic methanol afforded a mixture of 1-phenyl-1-cyclopropylethylene (XVII), cyclopropylmethylphenylcarbinyl methyl ether (XVIII), and the corresponding rearranged ether XIX. The cyclopropylmethylphenylmethane (XX) formed as a by-product in the Williamson method was found to be easily removed by distillation.

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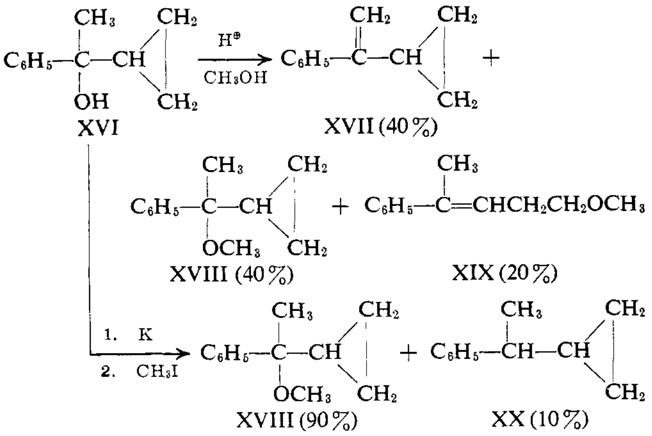
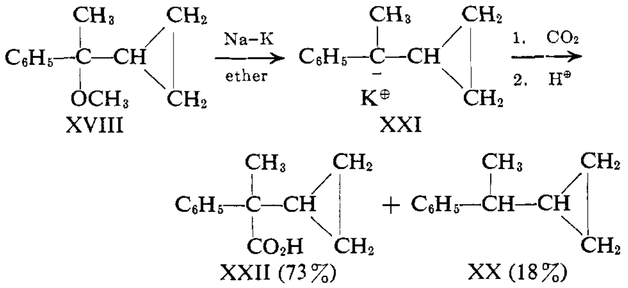
(17) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

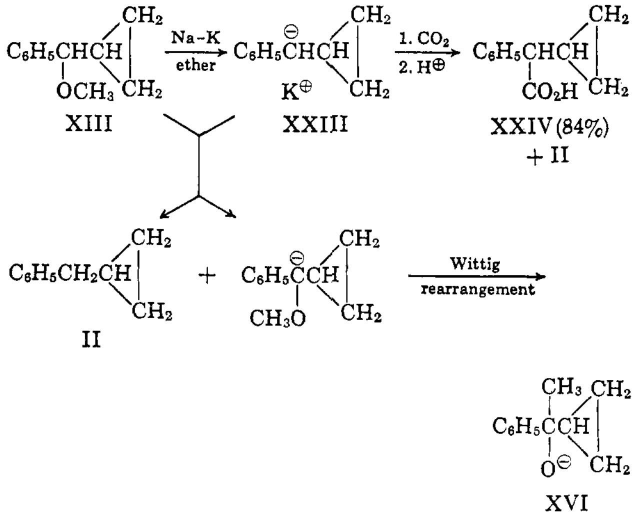
(18) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).



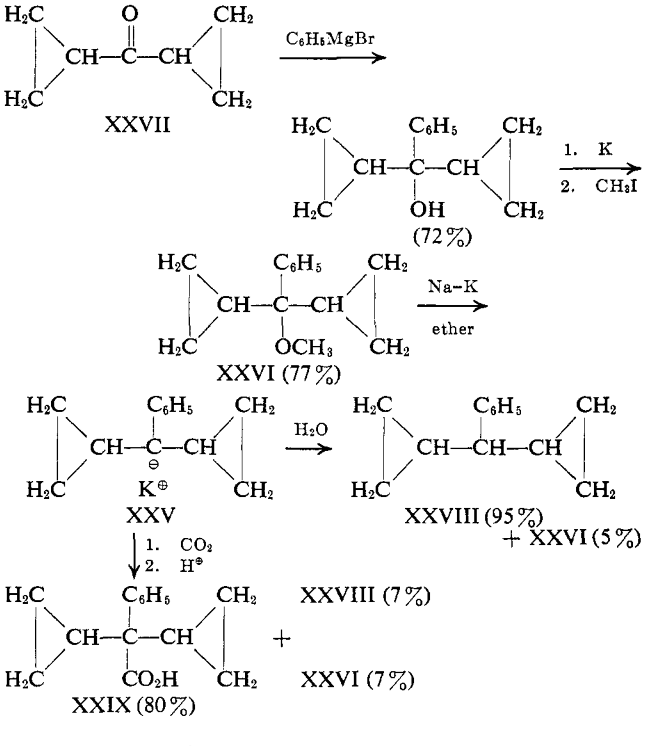
Cleavage of the ether XVIII with sodium–potassium alloy in diethyl ether produced a deep-red precipitate of phenylmethylcyclopropylcarbinylpotassium (XXI) which was decolorized upon reaction with solid carbon dioxide. Besides phenylmethylcyclopropylacetic acid (XXII) (73% yield), considerable amounts of the corresponding hydrocarbon XX were isolated, which was probably formed during the preparation of the anion. However, not even a trace of open-chain products could be detected, and therefore we can conclude that a single phenyl group is sufficient to stabilize a cyclopropylcarbinyl anion even in the presence of an electron-releasing group, like the methyl group, which should have a destabilizing effect. However, the fact that hydrolysis after 2 hr at room temperature gave only about 50% of the cyclic hydrocarbon XX and olefinic compounds shows that the anion XXI is less stable than the diphenylcyclopropylcarbinyl anion (IV) which gave no decomposition products even after several hours at room temperature.



Secondary benzylic ethers like XIII usually cannot be used for the preparation of carbanions by ether cleavage, because the first-formed anion attacks the starting material with the formation of a new anion which, as an α-metalated ether, undergoes a Wittig rearrangement.[19] It was therefore expected that phenylmethylcyclopropylcarbinol (XVI) would be the product from the reaction of phenylcyclopropylcarbinyl methyl ether (XIII) with sodium–potassium alloy. However, carbonation of the deep-red reaction mixture afforded phenylcyclopropylacetic acid (XXIV) in 84% yield, and no phenylmethylcyclopropylcarbinol (XVI) could be detected in the neutral fraction which consisted mainly of benzylcyclopropane (II). Apparently under the conditions used (sodium–potassium alloy in combination with a high-speed stirrer), the starting material XIII reacts with the metal faster than with the anion XXIII, so that the Wittig product was not formed.



We have also found that the single phenyl group of the phenyldicyclopropylcarbinyl anion (XXV) suffices to stabilize the anion against ring opening. The starting material XXVI for the preparation of the anion was made from dicyclopropyl ketone (XXVII) in the usual way, and its reaction with sodium–potassium alloy led within a few minutes to the formation of the deep-red dicyclopropylphenylcarbinylpotassium (XXV) which after 0.5 hr at 0° was characterized by hydrolysis and carbonation. Again no rearranged products were found; about 5% of starting material XXVI was isolated and it appears as though XXVI reacts with sodium–potassium alloy more slowly than the other ethers used, because with the other ethers cleavage seemed to be complete in 0.5 hr at 0°. The high net yield of dicyclopropylphenylacetic acid (XXIX), however, indicates that with XXVI radical side reactions during the cleavage are less important.



The nmr spectrum of dicyclopropylphenylmethane (XXVIII) is of particular interest because of the high diamagnetic shift of the benzylic proton 82 cps upfield

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(19) G. Wittig and L. Löhmann, *Ann.*, **550**, 260 (1942).

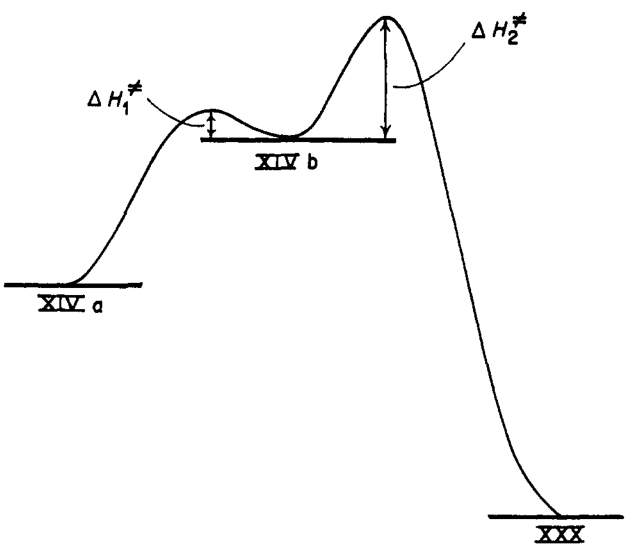
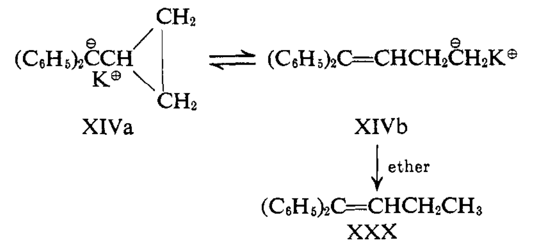


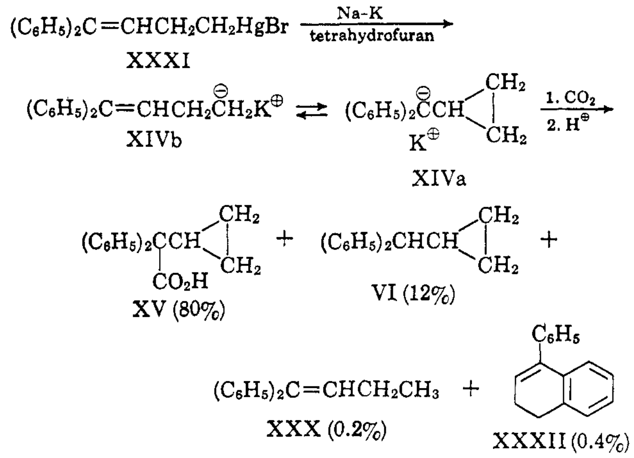
Figure 3. Schematic energy diagram for equilibration of potassium anion and formation of 1,1-diphenyl-1-butene.

from the corresponding proton in cumene. Although magnetic anisotropy of the C–C bonds may be a factor in determining the shielding,[20] the cyclopropane ring-current effect is likely to be more important. The ring current is expected to produce a paramagnetic effect on a hydrogen nucleus near the equatorial plane of a cyclopropane ring, while inside the ring, or somewhat above it, a diamagnetic effect is expected. A Stuart model of dicyclopropylphenylmethane (XXVIII) shows that the rotation of the cyclopropyl groups is highly restricted and, in the most favored conformation, the benzylic proton is located just above both of the cyclopropane rings close to their perpendicular axes. For this conformation a diamagnetic shift of +92 cps is calculated assuming four electrons to be involved in the ring current.[21]

The considerable stability of diphenylcyclopropylcarbinylpotassium (XIVa) in ether and tetrahydrofuran raises the question whether it is really in equilibrium with its ring-opened counterpart XIVb, which as an aliphatic organopotassium compound is expected to react irreversibly with the solvent by proton abstraction.

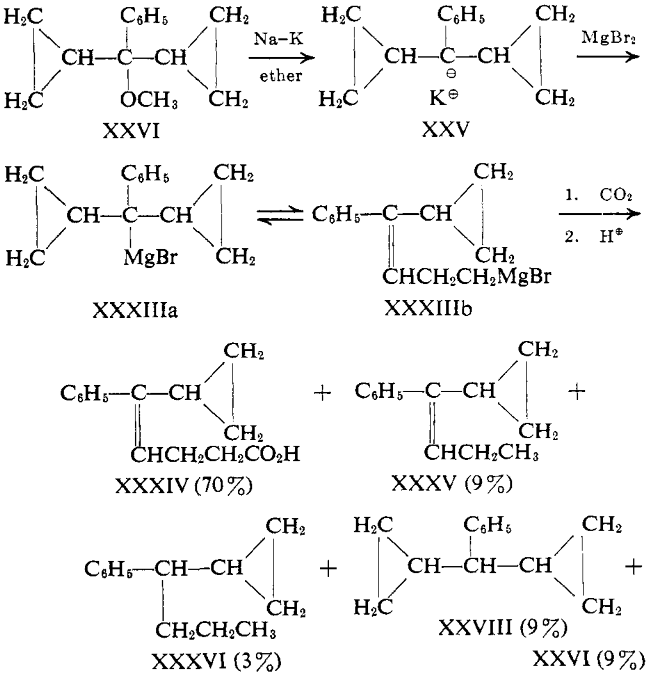


Clearly, if equilibration occurs, the activation energy for cleavage of the solvent must be larger than for ring closure (*cf.* Figure 3). Some information on this point was obtained by an independent synthesis of the open-chain anion XIVb from γ,γ-diphenylallylcarbinylmercuric bromide (XXXI).[5]



Addition of XXXI to sodium–potassium alloy in tetrahydrofuran immediately produced a deep-red solution of the cyclic anion XIVa, which upon carbonation gave diphenylcyclopropylacetic acid (XV) in 80% yield. No trace of γ,γ-diphenylallylacetic acid could be detected. Among the neutral products were found about 12% of diphenylcyclopropylmethane (VI) and about 0.2% of 1,1-diphenyl-1-butene (XXX). The mode of formation of these products will be discussed later. The retro cyclopropylcarbinyl–allylcarbinyl rearrangement observed here is, of course, consistent with the reaction profile shown in Figure 3.

Replacement of the Potassium by Other Metals. The stability of substituted cyclopropylcarbinylpotassium derivatives compared with the corresponding Grignard reagents[5] can be ascribed to the high degree of ionic character of the carbon–metal bond and the concomitant possibilities for stabilization by delocalization of the electron pair of carbon over the phenyl ring(s). Replacement of potassium by metal ions which form more strongly covalent bonds to carbon might then be expected to lead to rearrangement. This was found to be the case. The deep-red color of dicyclopropylphenylcarbinylpotassium (XXV) disap-



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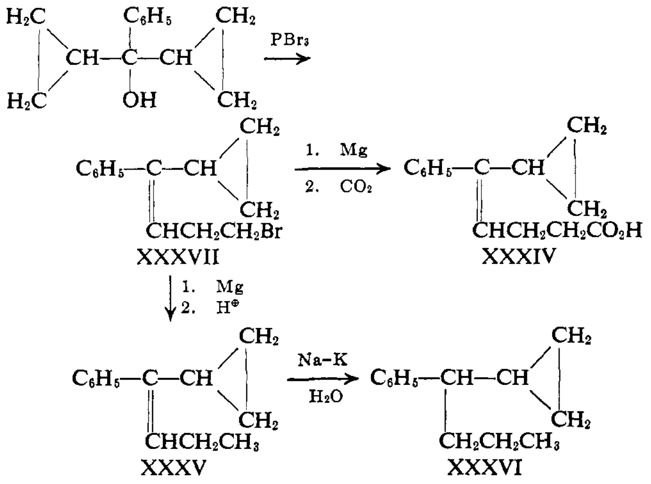
[20] *Cf.* K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

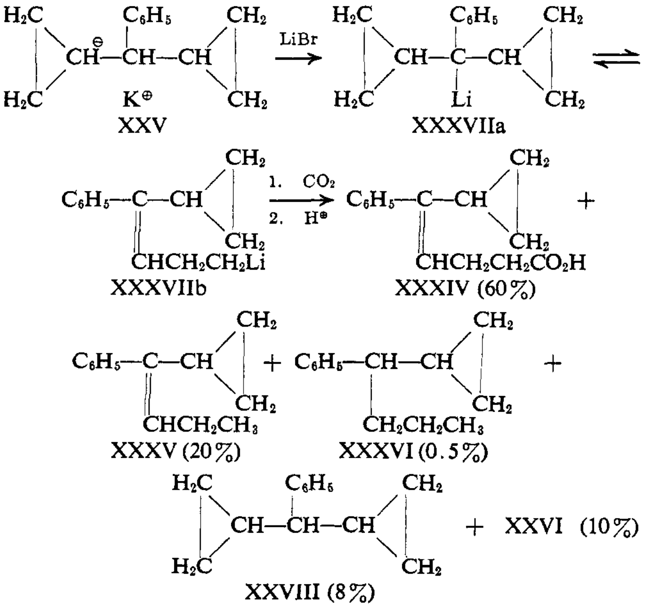
[21] D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963).

peared immediately on mixing with an ethereal solution of magnesium bromide, and carbonation gave 5-phenyl-5-cyclopropyl-4-pentenoic acid (XXXIV) in 70% yield. The neutral fraction contained besides starting material (XXVI) and dicyclopropylphenylmethane (XXVIII) (already present before the magnesium bromide was added), some 1-phenyl-1-cyclopropyl-1-butene (XXXV) and 1-phenyl-1-cyclopropylbutane (XXXVI), these being formed during hydrolysis by reduction of some XXXV with the excess potassium. Authentic samples of all these products were obtained *via* the Grignard reagent prepared independently from the rearranged halide XXXVII.



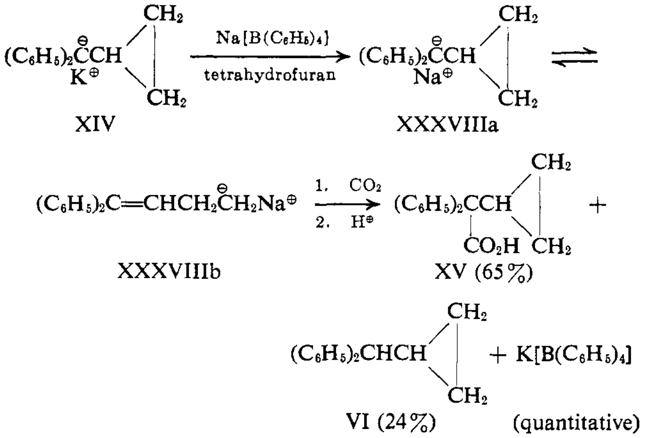
XXXVII XXXIV XXXV XXXVI

The fact that with potassium as the cation, the equilibrium lies on the cyclopropylcarbinyl side, while the Grignard reagent prefers the allylcarbinyl structure, prompted a search for a metal, which might make the two forms nearly equal in stability. Lithium, a metal with electropositivity between potassium and magnesium, was tried next, but again equilibrium appeared to lie in favor of the open-chain compound XXXVIIb.



XXV XXXVIIa XXXVIIb XXXIV (60%) XXXV (20%) XXXVI (0.5%) + XXVI (10%) XXVIII (8%)

The reactions of diphenylcyclopropylcarbinylpotassium (XIV) were studied in rather more detail. To obtain the sodium derivative XXXVIII, XIV was treated with Kalignost[22] (sodium tetraphenylboride), which has the advantage over the sodium halides of being quite soluble in tetrahydrofuran and of reacting with potassium ions with the formation of a nearly insoluble precipitate of potassium tetraphenylboride, thus providing an indicator for formation of the sodium derivative XXXVIII. Prompt carbonation of the reaction mixture gave exactly the same products as were obtained with the potassium derivative XIV; no open-chain products could be detected. However, this was true only if carbonation was carried out within a few hours. In contrast to diphenylcyclopropylcarbinylpotassium (XIV), which is stable in tetrahydrofuran for weeks, considerable amounts of rearranged products were obtained from the sodium compound XXXVIII after 63 hr at room temperature in tetrahydrofuran. The neutral fraction from the carbonation product gave 1,1-diphenyl-1-butene (XXXIX) and 1,1-diphenylbutane (XL) in 16 and 5% yield, respectively, while the yield of diphenylcyclopropylmethane (VI) remained unchanged (24%). Apparently, with sodium, the concentration of the open-chain sodium compound XXXVIIIb in the equilibrium mixture is somewhat higher than with potassium, so that the reaction with the solvent is detectable. As before, the 1,1-diphenylbutane (XL) is formed by reduction of XXXIX during hydrolysis.



XIV XXXVIIIa XXXVIIIb XV (65%) VI (24%) (quantitative)

Essentially the same result was obtained when attempts were made to prepare diphenylcyclopropylcarbinylsodium (XXXVIIIa) directly from diphenylcyclopropylcarbinyl methyl ether (X) and sodium metal in ether. As expected, the reaction was very slow, 40% of the starting material (X) being recovered after 65 hr at room temperature, and no acid was obtained by carbonating the reaction mixture. The relatively high yield of the open-chain hydrocarbons XXXIX and XL (45%) is considered to be the result of ether clavage by open-chain sodium compound XXXVIIIb. In an attempt to prepare XXXVIIIa from diphenylcyclopropylmethane (VI) with sodium hydride in tetrahydrofuran the reaction was found to be very slow and, after 48 hr at room temperature and an additional 6 hr at reflux, carbonation gave only a very small amount of an unknown acidic fraction. Much of the starting material (57%) was recovered and the main products were the ring-opened hydrocarbons XXXIX and XL which again shows that diphenylcyclopropylcarbinylsodium over long periods of time reacts with the solvent.

Although there is a marked difference between the potassium and the sodium derivatives in the diphenyl-

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[22] G. Wittig and P. Raff, *Ann.*, **573**, 195 (1950).

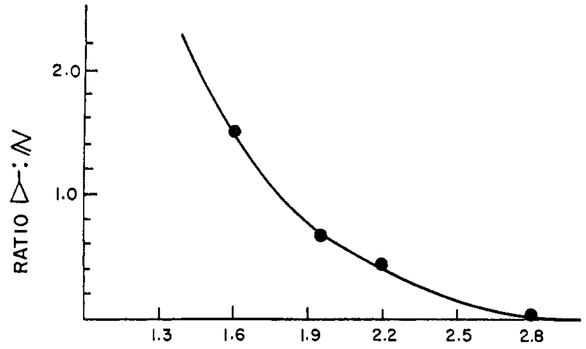
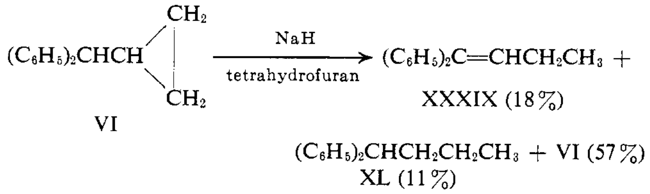
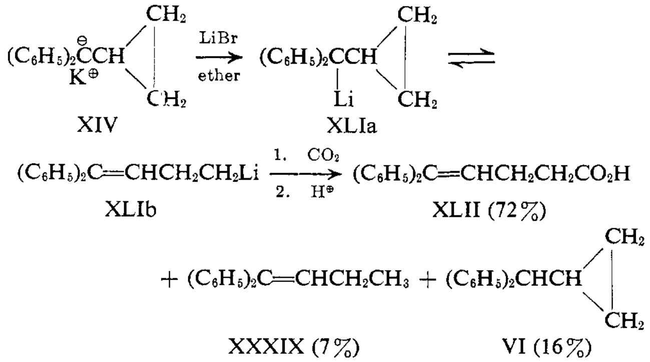


Figure 4. Ratio of cyclopropylcarbinyl to allylcarbinyl products as a function of moles of lithium bromide added to diphenylcyclopropylcarbinylpotassium in ether.



cyclopropylcarbinyl system, the presence of the open-chain form with sodium as the metal was detected only indirectly by its irreversible reaction with the solvent. With sodium and potassium the equilibrium in both seems to lie far on the ring-closed side. Although replacement of potassium by lithium in dicyclopropylphenylcarbinylpotassium (XXV) led to complete rearrangement, it was expected that diphenylcyclopropylcarbinyllithium (XLIa) would be more stable than dicyclopropylphenylcarbinyllithium (XXXVIIa) so that it might be detected in equilibrium with its ring-opened counterpart XLIb.



However, on treatment of diphenylcyclopropylcarbinylpotassium (XIV) with lithium bromide, the deep-red color disappeared, and carbonation afforded pure γ,γ-diphenylallylacetic acid (XLII) in 72% yield (not even a trace of cyclopropyl protons could be detected by nmr spectroscopy). The diphenylcyclopropylmethane (VI) detected in the neutral fraction was formed as a by-product during the preparation of diphenylcyclopropylcarbinylpotassium (XIV). This was confirmed by quenching the organolithium compound with deuterium oxide. Deuterium was found exclusively in the 4-position of 1,1-diphenyl-1-butene (XXXIX), while the diphenylcyclopropylmethane (VI) was deuterium free; the diphenylcyclopropylcarbinyllithium (XLIa) is not the source of the cyclic hydrocarbon VI.

For complete conversion of the potassium derivative XIV to the lithium compound XLI, more than a twofold excess of lithium bromide is necessary. The first mole of lithium bromide reacts with the potassium methoxide formed in the ether cleavage to give practically insoluble potassium bromide. The second mole is used in the metathesis of XIV, and some lithium bromide may react with the excess sodium of the sodium–potassium alloy.

With less than 2 moles of lithium bromide, the carbonation products seemed to be derived from a mixture of forms. Thus, with 1.6 moles of lithium bromide, carbonation yielded 35% of diphenylcyclopropylcarbinylacetic acid (XV) and only 25% of γ,γ-diphenylallylacetic acid (XLII). The ratio of cyclic products to open-chain products decreases further when more lithium bromide is used as shown in Figure 4.

The results here have general significance. They indicate beyond doubt that the open-chain lithium compound is truly covalent and the cyclic lithium compound (as judged from its color) is largely if not wholly ionic. The thermodynamics of these processes are of interest although there are so many unknown quantities that a detailed analysis is quite impossible. There are four principal equilibrium constants.

$$\begin{tikzcd}
\text{cyclic anion}\cdot\text{solvated cation} \arrow[r, shift left, "K_3"] \arrow[d, shift left] & \text{open-chain anion}\cdot\text{solvated cation} \arrow[l, shift left] \arrow[d, shift left] \\
\text{covalent cyclic organometallic} \arrow[u, shift left, "K_1"] \arrow[r, shift left, "K_4"] & \text{covalent open-chain organometallic} \arrow[l, shift left] \arrow[u, shift left, "K_2"]
\end{tikzcd}$$

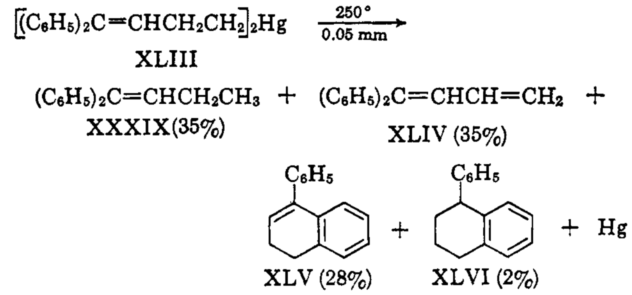
Of these, we can estimate from heats of combustion of other compounds that K_4 is probably such that ring opening is favorable by some 4–7 kcal. The results with sodium and potassium compounds indicate that K_3 must be quite small, especially if the open-chain potassium and sodium organometallics exist largely in the covalent form. The magnitude of K_1 is clearly dependent on the nature of the metal. If the carbon–metal bond is weak and the solvation energy of the cation reasonably large, then ionization occurs with assistance from the delocalization energy supplied by the aromatic and cyclopropane rings. Clearly, K_2 will always be smaller than K_1, because steric hindrance will be less in the covalent open-chain forms and the open-chain anion will hardly be expected to derive any substantial stabilization from delocalization of the electron pair at the primary position. The actual pathway for ring-opening and closing are of course unknown, but it seems likely that equilibrium would be established more readily by K_3 than by K_4.

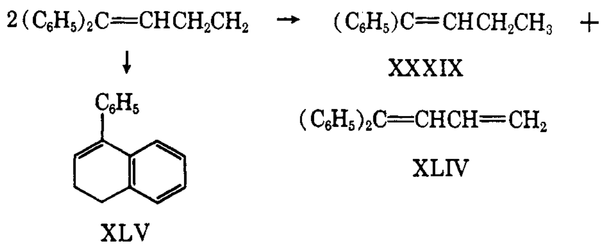
When an attempt was made to remove the excess sodium–potassium alloy before adding the lithium bromide by stirring the mixture with mercury metal, it was found that instead of γ,γ-diphenylallylcarbinyllithium (XLIb), the corresponding mercury compound XLIII was formed. This reaction is just the inverse of the usual procedure for preparation of salt-free organolithium compounds from organomercury compounds. Apparently exothermic formation of lithium amalgam

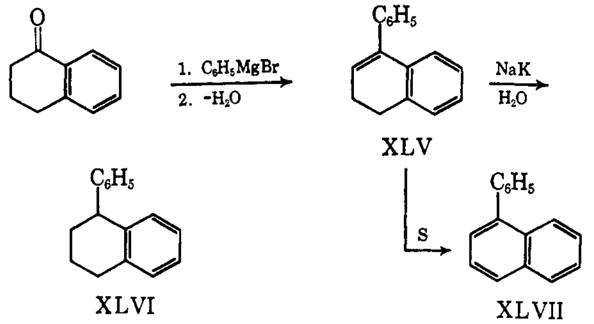
$$\underset{\text{XLIb}}{2(C_6H_5)_2C{=}CHCH_2CH_2Li} + Hg \rightleftharpoons \underset{\text{XLIII}}{[(C_6H_5)_2C{=}CHCH_2CH_2]_2Hg} + 2Li(Hg)$$

shifts the equilibrium toward the mercury compounds. Support for this hypothesis was obtained by treating *n*-butyllithium in ether with metallic mercury. Di-*n*-butylmercury was obtained in more than 90% yield based on *n*-butyl bromide. Since this is about the yield of *n*-butyllithium prepared from *n*-butyl bromide,[23] the second step must nearly be quantitative. Diphenylmercury was prepared similarly from phenyllithium and metallic mercury.

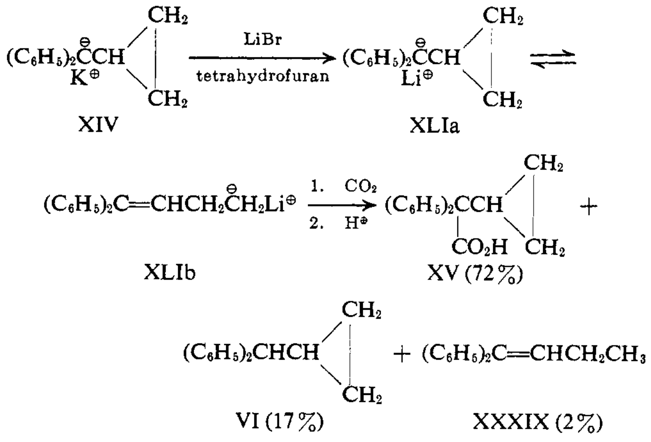
The mercury compound XLIII decomposed during an attempt to distil it under reduced pressure to give metallic mercury and a 1:1 mixture of 1,1-diphenyl-1-butene (XXXIX) with a compound which according to its nmr spectrum was tentatively identified as 1,1-diphenyl-1,3-butadiene (XLIV). These compounds as well as a third, 1-phenyl-3,4-dihydronaphthalene (XLV), appear to be due to a radical-cleavage mechanism, the initially formed γ,γ-diphenylallylcarbinyl radicals[24] undergoing disproportionation or ring closure. The naphthalene derivatives XLV, XLVI, and XLVII were synthesized independently.



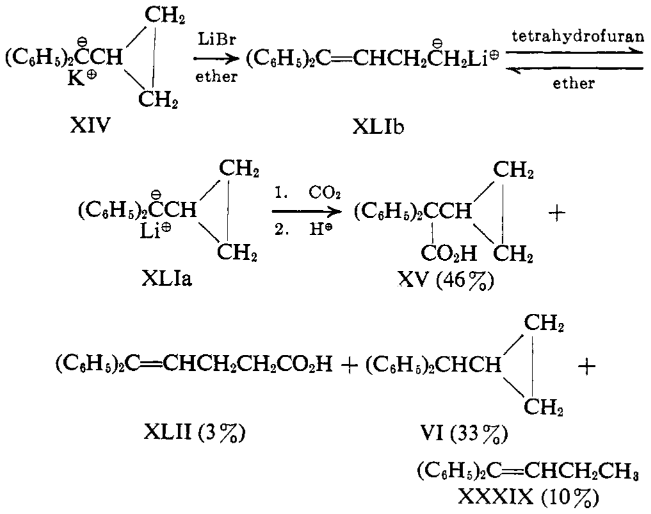




The preparation of the lithium organic compound XLI in tetrahydrofuran, using the same method as was used for diethyl ether, gave no color change, and, on carbonation of the deep-red reaction mixture, diphenylcyclopropylacetic acid (XV) was obtained in 72% yield. Only about 2% of the rearranged hydrocarbon XXXIX could be detected in the neutral fraction. Essentially the same result was obtained using a 1:1 mixture of tetrahydrofuran and diethyl ether as the solvent. Again, no rearranged acid could be found, but this time about 7% of 1,1-diphenyl-1-butene (XXXIX) was detected in the hydrocarbon fraction.



When the colorless open-chain lithium compound was prepared in diethyl ether as the solvent and then tetrahydrofuran added, the deep-red color of the cyclic anion immediately reappeared. Carbonation yielded a mixture of cyclic and ring-opened products with the former strongly predominating. Here, for the first time, a retro cyclopropylcarbinyl–allylcarbinyl rearrangement was achieved simply through a solvent change. Apparently, in ether–tetrahydrofuran (2:1), the equilibrium between the closed and open forms lies more than 90% on the side of the cyclic anion XLIa. The relatively high percentage of ring-opened hydrocarbon XXXIX is probably due to reaction of the aliphatic organolithium compound XLIb with the solvent, particularly tetrahydrofuran.



Diphenylcyclopropylcarbinylpotassium (XIV) with magnesium bromide in tetrahydrofuran gave on carbonation exclusively open-chain acid. This result is in agreement with studies of the same Grignard reagent XLVIII prepared from γ,γ-diphenylallylcarbinyl bromide.[5]

The reaction of mercuric bromide with diphenylcyclopropylcarbinylpotassium (XIV) took an unexpected course. The expectation was that the product might be the covalent ring-opened mercury compound XXXI if the reaction were subject to thermodynamic

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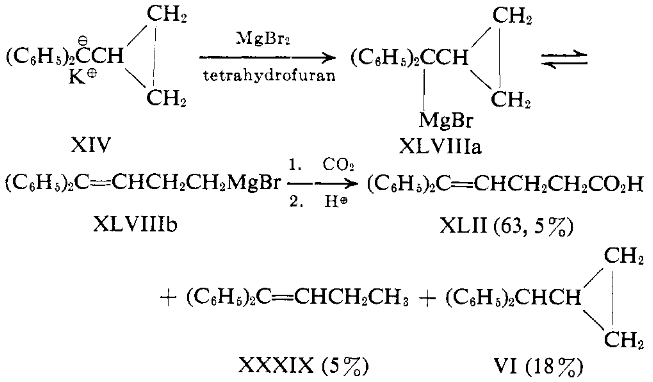
(23) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 353 (1951).

(24) A number of studies on this interesting radical were made by M. E. H. Howden, Ph.D. Thesis, California Institute of Technology, 1962, and are being continued by Mr. T. A. Halgren.



XIV XLVIIIa

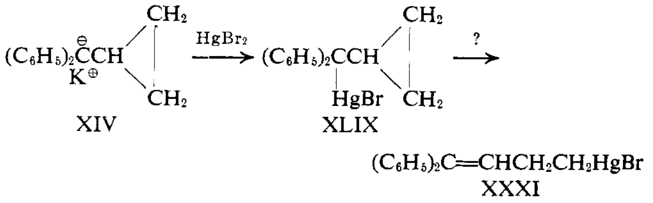
$(C_6H_5)_2C{=}CHCH_2CH_2MgBr \xrightarrow[2.\ H^{\oplus}]{1.\ CO_2} (C_6H_5)_2C{=}CHCH_2CH_2CO_2H$

XLVIIIb XLII (63, 5%)

$+ (C_6H_5)_2C{=}CHCH_2CH_3 + (C_6H_5)_2CHCH(CH_2)_2$

XXXIX (5%) VI (18%)

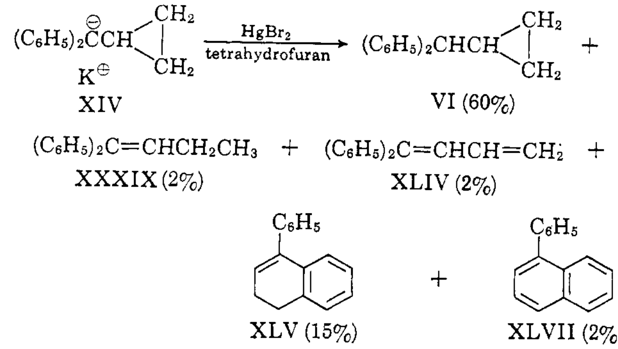
control, but the cyclic compound XLIX if subject to kinetic control. But none of the expected compounds were formed. On addition of a solution of mercuric bromide in tetrahydrofuran to diphenylcyclopropylcarbinylpotassium (XIV) in tetrahydrofuran, the deep-red color turned to black and a mixture of hydrocarbons typical of free-radical intermediates was formed. The principal product was diphenylcyclopropylmethane (VI). Apparently the mercury compound XLIX seems to decompose spontaneously with the formation of diphenylcyclopropylcarbinyl free radicals (La) which may either react with the solvent to form VI or rearrange to γ,γ-diphenylallylcarbinyl radicals (Lb), giving rise to the same end products of disproportionation and ring closure as was obtained previously upon the thermal decomposition of bis(γ,γ-diphenylallylcarbinyl)mercury (XLIII).



XIV XLIX

$(C_6H_5)_2C{=}CHCH_2CH_2HgBr$

XXXI

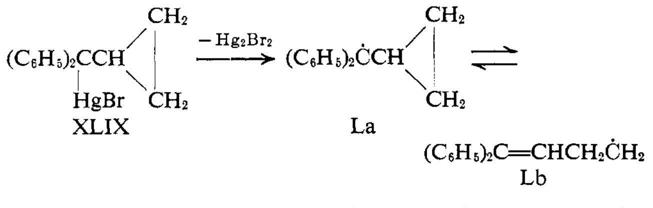


XIV VI (60%)

$(C_6H_5)_2C{=}CHCH_2CH_3 + (C_6H_5)_2C{=}CHCH{=}CH_2 +$

XXXIX (2%) XLIV (2%)

XLV (15%) XLVII (2%)



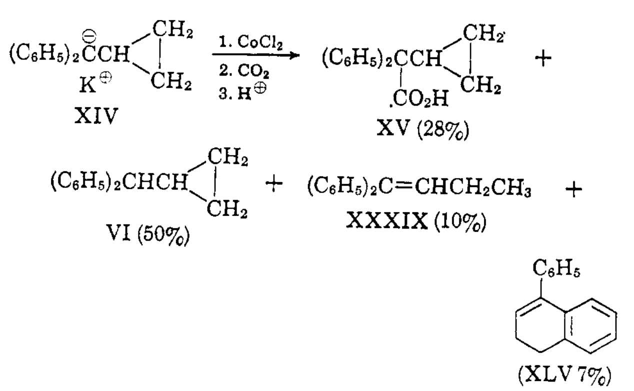
XLIX La

$(C_6H_5)_2C{=}CHCH_2\dot{C}H_2$

Lb

It might be argued that the formation of radical could have been induced by mercurous bromide formed from mercuric bromide with the excess of sodium–potassium alloy. However, the same result was obtained when the excess of sodium–potassium alloy was destroyed by stirring with metallic mercury, the mercury phase removed, and the deep-red organometallic solution added to a solution of mercuric bromide.

Additional evidence for the character of these reactions was obtained by adding cobaltous chloride, a well-known initiator for radical reactions, to diphenylcyclopropylcarbinylpotassium (XIV). The reaction was much slower than with mercuric bromide and even after 2 hr not complete. The unreacted starting material XIV was removed by carbonation, and it was found that neutral products were essentially the same as those found with mercuric bromide. The principal difference was in the absence of 1,1-diphenyl-1,3-butadiene (XLIV) which may have been due to the long reaction time, since LXIV is expected to be susceptible to polymerization, especially in the presence of the potassium compound XIV. The postulated instability of the mercury compound XLIX is consistent with the fact that the corresponding potassium and lithium compounds XIV and XLIa are not attacked by metallic mercury, while the open-chain γ,γ-diphenylallylcarbinyllithium (XLIb) reacts with mercury metal with the formation of the dialkylmercury compound XLIII. Also it may be noted that the carbon–mercury bond in dibenzylmercury is broken easily enough homolytically to initiate polymerization at moderate temperatures.[25]



XIV XV (28%)

VI (50%)

$+ (C_6H_5)_2C{=}CHCH_2CH_3 +$

XXXIX (10%)

(XLV 7%)

A summary of the most important reactions carried out with the diphenylcyclopropylcarbinyl-γ,γ-diphenylallylcarbinyl organometallics is shown in Figure 5.

Experimental Section

All melting and boiling points are uncorrected. Microanalyses are by Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were run on a Beckman infrared spectrometer, Model IR-7. All nmr spectra were obtained using the Varian A-60 instrument. Mass spectra were run on a CEC 21-103C mass spectrometer. Most of the vapor-phase chromatograms were obtained with a Perkin-Elmer Model 800 gas chromatograph in connection with a Perkin-Elmer Model 194 printing integrator. Some of the vpc work analyses were performed with the Perkin-Elmer fractometer, Model 154-C.

Benzylcyclopropane with Organopotassium Compounds. A. **Benzylpotassium** was prepared[26] from 11.2 g (0.1 mole) of chlorobenzene, 8.5 g (0.22 g-atom) of freshly prepared potassium sand, and 150 ml of toluene. Benzylcyclopropane (1.32 g, 0.01 mole) was added to the suspension, and the mixture was stirred under nitrogen for 18 hr at room temperature. After hydrolysis with 4 ml of deuterium oxide, the starting material was recovered unchanged, the ratio of cyclopropyl to benzyl protons being 2.5 as judged by integration of the corresponding peaks in the nmr spectrum.

B. *n*-**Amylpotassium** was prepared in the usual manner[7a] by the dropwise addition of 12.1 g (0.1 mole) of *n*-amyl chloride to 8.2 g

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[25] M. M. Koton, *Dokl. Akad. Nauk SSSR*, **88**, 991 (1953).

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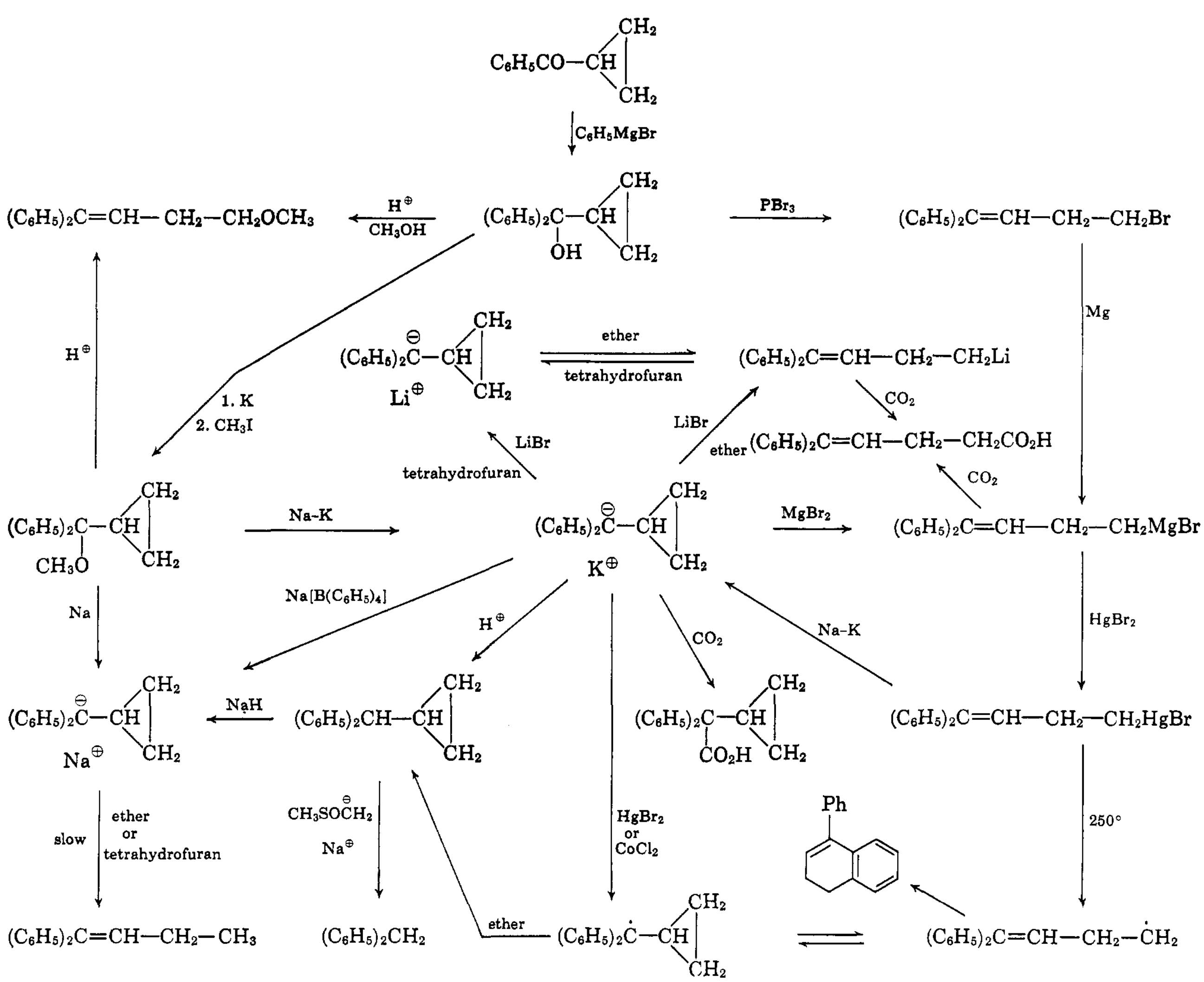

Figure 5. Summary of observed rearrangements of diphenylcyclopropylcarbinyl–γ,γ-diphenylallylcarbinyl organometallic compounds.

(0.21 g-atom) of potassium sand in 200 ml of heptane at −10° over a period of 1 hr. After the addition of 5.3 g (0.04 mole) of benzylcyclopropane, the mixture was stirred for 15 min at −10°. Hydrolysis with 12 ml of deuterium oxide afforded essentially unchanged starting material (ratio of phenyl to benzyl protons = 2.7) together with some *n*-decane. Only a trace of *n*-butylbenzene could be detected by vpc analysis.

C. ***n*-Amylpotassium** *in Situ.* Potassium sand (8.2 g, 0.21 g-atom) was prepared with a high-speed stirrer in 200 ml of heptane under nitrogen at 90°. After addition of 10 g (0.075 mole) of benzylcyclopropane, 12.1 g (0.1 mole) of freshly distilled *n*-amyl chloride was added dropwise over a period of 1 hr, the temperature being maintained at −10°. The black suspension was stirred for an additional 0.5 hr and hydrolyzed by the dropwise addition of 12 ml of deuterium oxide at 0°. Water was added, the aqueous layer was extracted several times with ether, and the combined organic layers after washing with sodium chloride solution were dried over sodium sulfate. The residue obtained after evaporation of the solvent was shown by vpc analysis to contain *n*-decane and a 1:1 mixture of benzylcyclopropane and 1-phenyl-1-cyclopropyl-*n*-hexane. The latter was purified by distillation, bp 85° (0.5 mm), $n^{25}\text{D}$ 1.4943, and characterized by infrared and nmr spectroscopy. The benzyl resonance in the nmr spectrum was overlapped with part of the methylene resonances due to an extraordinary diamagnetic shift of the benzylic proton. The assigned structure was in agreement with the mass spectrum.

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89.02; H, 10.86.

The recovered benzylcyclopropane was essentially deuterium free, the ratio of phenyl to benzyl protons being 2.6 according to nmr spectroscopy.

D. ***n*-Butylpotassium** *in Situ.* To 7.8 g (0.2 g-atom) of potassium sand, prepared in the usual manner under nitrogen in 50 ml of heptane using a high-speed stirrer, was added 5.3 g (0.04 mole) of benzylcyclopropane. Then 15.8 g (0.05 mole) of di-*n*-butylmercury in 50 ml of heptane was added over a period of 2 hr, the temperature being maintained at 0 to 5°. After 24 hr at room temperature, the black mixture was hydrolyzed by the dropwise addition of 12 ml of deuterium oxide. The same isolation procedure used for previous experiments afforded mainly unchanged benzylcyclopropane and di-*n*-butylmercury as shown by vpc and nmr spectroscopy. Only traces of *n*-butylbenzene and 1-phenyl-2-butene could be detected.

E. **Phenylpotassium.** To 8.1 g (0.208 g-atom) of potassium sand, prepared under nitrogen in 200 ml of heptane using a high-speed stirrer, was added 10.8 g (0.1 mole) of anisole dropwise over a period of 1 hr, the temperature being maintained at 25 to 30° by occasionally cooling with ice–water. After an additional hour, 1.32 g (0.01 mole) of benzylcyclopropane was added and the mixture was stirred for 3 hr at room temperature. Hydrolysis with 12 ml of deuterium oxide afforded essentially unchanged starting material somewhat contaminated by anisole. Only traces of *n*-butylbenzene and 1-phenyl-2-butene were detected by vpc analysis and nmr spectroscopy.

Phenylpotassium prepared from chlorobenzene or diphenylmercury gave the same result.

In another experiment, a solution of 11.25 g (0.1 mole) of chlorobenzene in 25 ml of heptane was added dropwise over a period of 1 hr to 10.2 g (0.26 g-atom) of potassium sand prepared in 50 ml of heptane under nitrogen with high-speed stirring. The temperature was maintained at 30° or below. After the addition of 6.6 g (0.05 mole) of benzylcyclopropane, the mixture was refluxed for 46 hr. Hydrolysis with 12 ml of deuterium oxide afforded a dark brown viscous material insoluble in water as well as in heptane. After the addition of water, the mixture was extracted several times with benzene and with ether, and the dark brown organic layers were dried over sodium sulfate. The solvents were evaporated, and the residue was distilled at 20 mm giving three fractions: (a) 0.9 ml, bp 79–80°; (b) 2.65 ml, bp 80–84°; (c) 0.9 ml, bp >84°. Analysis by vpc at 100° (TCEP column) showed that all fractions consisted of five different components, the composition of the main fraction b being: *n*-butylbenzene (9%), *trans*-1-phenyl-2-butene (12%), *cis*-1-phenyl-2-butene (16%), benzylcyclopropane (60%), and 1-phenyl-1-butene (3%). Each compound was identified by comparison with authentic samples through vpc and nmr spectroscopy. Distinction between *cis*- and *trans*-1-phenyl-2-butene was possible by the strong absorption of the latter at 970 cm^{-1} in the infrared spectrum. The benzylcyclopropane was deuterium free by nmr spectroscopy, while one of the benzyl protons in 1-phenyl-2-butene was replaced by deuterium. The position of deuterium in the by-products could not be determined.

F. **Potassium and Sodium Monoxide.**[7b] Potassium sand (4.6 g, 0.12 g-atom) was prepared in the usual manner in 60 ml of heptane under nitrogen using a high-speed stirrer, and 13.3 g (0.21 mole) of sodium monoxide[27] and 6.6 g (0.05 mole) of benzylcyclopropane were added. The mixture was stirred for 22 hr at 80 to 85°. During the first 0.5 hr the color turned to brown. Finally more heptane (50 ml) was added to the thickened mixture which was then hydrolyzed by the dropwise addition of 20 ml of deuterium oxide, whereby the mixture became colorless. After the addition of water, the aqueous layer was extracted once more with ether, and the combined organic layers were dried over sodium sulfate. The solvents were evaporated and the residue was distilled at 16 mm. Three fractions were obtained: (a) 3.4 ml, bp 74–75°; (b) 1.0 ml, bp 75–77°; (c) 0.4 ml, bp >77°. Vpc analysis (TCEP column, 100°) and nmr spectroscopy showed that the products were the same as in the previous experiment, except that no trace of 1-phenyl-1-butene could be detected. Thus, the main fraction a consisted of *n*-butylbenzene (12%), *trans*-1-phenyl-2-butene (19%), *cis*-1-phenyl-2-butene (12%), and benzylcyclopropane (57%). The accuracy of integration of the vpc peaks was standardized by analysis of an authentic 2:1 mixture of benzylcyclopropane and 1-phenyl-2-butene, which gave nearly the same ratio by integration as fraction a. The same ratio was also obtained from the nmr spectrum which gave the additional information that benzylcyclopropane was essentially deuterium free while one of the hydrogens at the 1-position of 1-phenyl-2-butene was replaced by deuterium.

4-Bromo-1-phenyl-1-butene. Phosphorus tribromide, 38.4 g (0.139 mole), was cooled to −15° and 14.82 g (0.1 mole) of freshly distilled phenylcyclopropylcarbinol was added under nitrogen over a period of 0.5 hr. The mixture was stirred for 15 min at −15°, then poured over ice, and extracted with ether. The ether layer was washed with saturated sodium bicarbonate and saturated sodium chloride solutions and dried over potassium carbonate. The ether was evaporated and the residue on distillation yielded 16.8 g (80%) of 4-bromo-1-phenyl-1-butene, bp 79–81° (0.2 mm), n^{20}D 1.5883. The product reacted with potassium permanganate and with bromine in acetic acid. The nmr spectrum showed phenyl protons, olefinic protons, and alkyl protons in the ratio 5:2:4; no cyclopropyl protons could be detected.[9]

1-Phenyl-1-butene from 4-Bromo-1-phenyl-1-butene. The Grignard reagent prepared under nitrogen from 8.44 g (0.04 mole) of 4-bromo-1-phenyl-1-butene and 1.2 g (0.05 g-atom) of magnesium in 50 ml of ether was refluxed for 2 hr. After hydrolysis with 25 ml of saturated ammonium chloride solution, the phases were separated and the aqueous layer was extracted once more with ether. The combined organic layers were washed with water and dried over sodium sulfate. The solvent was evaporated and the residue on distillation yielded three fractions: (a) 0.7 ml, bp 87.5–88° (21 mm); (b) 1.55 ml, bp 88–88.5° (21 mm); (c) 0.8 ml, bp 88.5–89° (21 mm). All three fractions were better than 99% pure by vpc. The total yield was 2.77 g (52%), n^{19}D (fraction b) 1.5413, lit[28] n^{25}D 1.5401. Fraction a showed traces (less than 1%) of *n*-butylbenzene, *trans*-1-phenyl-2-butene, and benzylcyclopropane by vpc analysis (TCEP column, 100°).

1-Phenyl-1-butene with Potassium and Water. A mixture of 2 g (0.05 g-atom) of potassium cut into small pieces, 1 ml (0.01 mole) of 1-phenyl-1-butene, and 20 ml of heptane was stirred under nitrogen while water was added dropwise. When the reaction was complete, the aqueous layer was extracted with ether; the combined organic layers were washed with sodium chloride solution and dried over sodium sulfate. Evaporation of the solvents and distillation of the residue at 23 mm yielded 0.43 ml of a colorless liquid which consisted of *n*-butylbenzene (56%), *trans*-1-phenyl-2-butene (4.5%), *cis*-1-phenyl-2-butene (1.5%), benzylcyclopropane (0.5%), and 1-phenyl-1-butene (37.5%) according to vpc analysis (TCEP column, 100°). An authentic sample of *n*-butylbenzene was prepared from bromobenzene, *n*-butyl bromide, and sodium by the Wurtz–Fittig synthesis.[29]

Diphenylcyclopropylmethane with Dimsyl Sodium in Dimethyl Sulfoxide. In a 100-ml, three-necked flask equipped with a high-speed stirrer, dropping funnel, and a nitrogen inlet, 5 g of sodium hydride (55% in mineral oil, 0.1 mole) was washed twice with pentane in order to remove the mineral oil and then heated under nitrogen in 50 ml of dimethyl sulfoxide at 75 to 80° for 45 min.[11a] The solution of dimsyl sodium was allowed to cool to room temperature; then a solution of 1.5 g (7.2 mmoles) of diphenylcyclopropylmethane[5] in 5 ml of dimethyl sulfoxide was added dropwise, whereby a deep-red color appeared immediately After 5 hr of stirring at room temperature, the mixture was hydrolyzed by the dropwise addition of 10 ml of deuterium oxide, whereby the color disappeared After the addition of water, the mixture was extracted three times with pentane. The combined organic layers were washed with water and dried over sodium sulfate. Evaporation of the solvent yielded 1.9 g of a crude product which on distillation at 0.2 mm gave three fractions: (a) 0.5 g, bp 59–89°; (b) 0.85 g, bp 89–105°; (c) 0.2 g, bp >105°. These fractions were investigated by vpc analysis (silicone column, 200°) and nmr spectroscopy. Besides diphenylmethane and starting material (ratio in the crude product 44:56) mainly mineral oil from the sodium hydride was detected, the latter especially in the last fraction (c). The diphenylmethane did not contain a significant amount of deuterium.

In another run, a slow stream of nitrogen was passed continually over the reaction mixture, and the exit gases were passed through a trap cooled in a Dry Ice–acetone bath. The material condensed in the trap (*ca.* 0.2 ml of a colorless liquid) was transferred into an nmr tube *via* a vacuum line, but no cyclopropene could be detected. The volatile material seemed to be a complex mixture of decomposition products of the dimsyl sodium in dimethyl sulfoxide since the same products were obtained when the procedure was repeated without adding diphenylcyclopropane to the dimsyl sodium solution.

Benzylcyclopropane with Potassium *t*-Butoxide in Perdeuteriodimethyl Sulfoxide. In a small Schlenk tube equipped with a dropping funnel and a magnetic stirrer, 1.12 g (10 mmoles) of potassium *t*-butoxide was dissolved under nitrogen in 2 ml of pure perdeuteriodimethyl sulfoxide. A solution of 1.32 g (10 mmoles) of benzylcyclopropane in 1 ml of perdeuteriodimethyl sulfoxide was added over a period of 15 min. The yellow solution was stirred at room temperature for 5 hr during which time the color turned to dark brown. Then petroleum ether (bp 30–60°) and 0.5 ml of deuterium oxide were added, the precipitate thus formed dissolving on further treatment with water. The yellow aqueous layer was extracted once more with petroleum ether; the combined organic phases were washed with water and dried over sodium sulfate. Vpc analysis showed only starting material; no rearranged products could be found. The solvent was evaporated and the residue on distillation at 25 mm gave 0.95 ml of benzylcyclopropane, bp 84°, which contained more than 50% deuterium at the benzyl position by nmr spectroscopy. The ratio of phenyl protons to benzyl protons was determined by integration of the corresponding peak areas and was found to be 6.1. The benzyl doublet of the starting material partly overlapped the two equal-intensity triplets of the monodeuterated compound. The concentration of the latter was about twice that of the deuterium-free benzylcyclopropane; the dideuterated compound was judged to have about the same concentration as the starting material (25%).

The partly deuterated compound was treated once more with potassium *t*-butoxide in perdeuteriodimethyl sulfoxide. After 20 hr of stirring at room temperature, the same isolation procedure afforded 0.55 ml of benzylcyclopropane which was nearly 100% deuterated at the benzyl position. No deuterium-free starting material could be found, and only a trace of the monodeuterated compound was detectable by nmr spectroscopy.

Diphenylcyclopropylcarbinyl Methyl Ether (X). A solution of 6 g (0.04 mole) of diphenylcyclopropylcarbinol[16] in 50 ml of methanol containing 1 ml of concentrated sulfuric acid was allowed to stand for 24 hr at room temperature. Two layers formed on addition of water and the organic portion was removed by ether extraction. The combined ether extracts were washed with a

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(27) The authors wish to thank E. I. du Pont de Nemours and Co., Wilmington, Del., for a generous gift of sodium monoxide.

(28) C. G. Overberger and D. Tanner, *J. Am. Chem. Soc.*, 77, 371 (1955).

(29) R. R. Read and L. S. Foster, *ibid.*, **48**, 1606 (1926).

sodium bicarbonate solution and water and then dried over sodium sulfate. The ether was evaporated and the residue distilled at 0.3 mm. Three fractions were obtained: (a) 0.6 g, bp 122–123°; (b) 7.2 g, bp 123–125°; (c) 2.8 g, bp >125°. Fractions a and b were shown to be better than 99% pure by vpc. Only fraction c showed even a trace of impurity. The nmr spectrum of the product showed phenyl peaks, vinyl triplet, allyl quartet, methoxy singlet, and α-methylene triplet in accordance with 4-methoxy-1,1-diphenyl-1-butene (XI), n^{26}D 1.5802.

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.82; H, 7.68.

In another run, 2.6 g (11.6 mmoles) of diphenylcyclopropylcarbinol was warmed in 5 ml of methanol and treated with 5 drops of concentrated sulfuric acid. The mixture separated into two phases and was allowed to stand at room temperature for 10 min with occasional shaking. After the addition of sodium bicarbonate solution, the products were extracted twice with ether. The combined organic layers were washed with water and dried over sodium sulfate. The solvent was evaporated and the residue (2.7 g) was distilled at 0.2 mm and yielded 2.15 g (78%) of a viscous oil, bp 120°, which was shown by vpc (silicone column, 200°) and nmr to consist of diphenylcyclopropylcarbinyl methyl ether (89.5%), diphenylcyclopropylcarbinol (7%), and 4-methoxy-1,1-diphenyl-1-butene (3.5%).

One gram of the distillate was dissolved in methanol containing 3.6 ml of concentrated sulfuric acid per 100 ml of solvent. After 18 hr at room temperature, water was added and the products were extracted twice with ether. The organic layer was washed with a sodium bicarbonate solution and dried over sodium sulfate. The solvent was evaporated and the colorless residue (1.0 g) was shown by vpc analysis and nmr spectroscopy to be pure 4-methoxy-1,1-diphenyl-1-butene (XI).

The ether was also prepared by the Williamson method.[16] Potassium sand (8.2 g, 0.21 g-atom) was prepared in the usual manner in 250 ml of benzene under nitrogen using a high-speed stirrer; then 44.8 g (0.2 mole) of diphenylcyclopropylcarbinol dissolved in 75 ml of benzene was added dropwise, and stirring was continued until all the potassium dissolved. The mixture was cooled to room temperature, 100 g (0.7 mole) of methyl iodide added, and the whole stirred and heated under reflux for 24 hr. The potassium iodide was removed by filtration and washed with ether. The filtrate was evaporated and the crude ether (45.1 g, 95%), which contained up to 10% each of diphenylcyclopropylmethane and starting material, was distilled at 0.5 mm, whereby three fractions were obtained: (a) 5.9 g, bp 95–122°; (b) 32.5 g, bp 122–126°; (c) 4.4 g, bp >126°, lit[16] bp 140° (1.5 mm). Vpc analysis (silicone column, 180°) and nmr spectroscopy showed that fraction b consisted of diphenylcyclopropylcarbinyl methyl ether (87.5%), diphenylcyclopropylmethane (7.5%), and diphenylcyclopropylcarbinol (5%). Fraction a contained more hydrocarbon but no carbinol, while fraction c contained no hydrocarbon but more carbinol. The over-all yield was 68%.

Sodium–potassium alloy[30] was prepared by melting 8 g of potassium and 1.6 g of sodium together under *p*-xylene and shaking gently after the addition of a few drops of *t*-butyl alcohol. The liquid metal was cooled to room temperature and washed several times with anhydrous ether and stored under ether. The composition was such that 5.5 ml corresponded to 0.1 g-atom of potassium.

Diphenylcyclopropylcarbinylpotassium (XIV). A. Hydrolysis in Diethyl Ether. In a 100-ml, three-necked flask with nitrogen inlet, dropping funnel, and high-speed stirrer was placed a mixture of 50 ml of anhydrous ether and 2.75 ml (0.05 g-atom of potassium) of sodium–potassium alloy in a nitrogen atmosphere. A solution of 4.0 g (16.8 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) in 5 ml of anhydrous ether was then added over about 5 min. Within a few minutes, a deep-red precipitate was formed and the mixture became warm so that occasional cooling with ice–water was necessary. After 4 hr of stirring at room temperature, water was added dropwise with ice cooling, whereby the color completely disappeared. The aqueous layer was extracted twice with ether, the combined organic layers were washed with sodium chloride solution and dried over sodium sulfate, and the solvent was removed. The residue (3.5 g, quantitative) was shown by vpc analysis and nmr spectroscopy to be pure diphenylcyclopropylmethane,[6] bp 99–100° (0.2 mm). The nmr spectrum (ppm) showed a phenyl peak (7.26), benzhydryl doublet (3.2), cyclopropyl methine resonances (0.9–1.6), and cyclopropyl methylene resonances (0.0–0.7) in a ratio of 10:1:1:4. Not a trace of olefinic products could be detected.

B. Carbonation in Diethyl Ether. The organometallic compound (16.8 mmoles) was prepared as described in the previous run, and after 4 hr of stirring at room temperature, the dark-red mixture was cooled in a Dry Ice–acetone and treated with an excess of solid carbon dioxide. After the color disappeared, the mixture was allowed to warm up to about 0°, water was added dropwise, and the aqueous layer was extracted with ether. The combined ether layers were washed with water and dried over sodium sulfate. Evaporation of the solvent afforded 0.9 g (25%) of diphenylcyclopropylmethane containing a small amount of diphenylcyclopropylcarbinol, an impurity of the starting material.

The aqueous layer was acidified with 6 *N* hydrochloric acid, whereby a colorless oil separated which soon crystallized. The white crystals were removed by suction filtration, washed with water, and dried over Drierite. The yield of nearly pure diphenylcyclopropylacetic acid (XV) was 3.05 g (72%), mp 137–139.5°. The analytical sample was recrystallized once from carbon tetrachloride and twice from ethanol and had mp 142–143°.

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.10; H, 6.35.

The nmr spectrum of the acid showed only carboxyl, phenyl, and cyclopropyl protons (ratio 1:10:5); no vinyl protons could be detected.

C. Carbonation in Tetrahydrofuran. Diphenylcyclopropylcarbinylpotassium was prepared in the usual manner at 0° from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in 35 ml of tetrahydrofuran and carbonated with solid carbon dioxide as described in the previous experiment. The neutral material (0.74 g, 35%) consisted of diphenylcyclopropylmethane (65%) and diphenylcyclopropylcarbinol (35%) according to vpc analysis and nmr spectroscopy. The yield of pure diphenylcyclopropylacetic acid was 1.65 g (65%), mp 139.5–141°.

D. Nmr spectra of diphenylcyclopropylcarbinylpotassium were taken of material prepared under argon from 4.76 g (20 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 2.2 ml of sodium–potassium alloy in a total of 20 ml of tetrahydrofuran using the high-speed stirring apparatus described previously. After 0.5 hr at 0°, 130 g (0.65 g-atom) of mercury metal was added carefully to remove the excess of sodium in the solution, and stirring was continued for 2 hr. Finally, about 1 ml of the deep-red solution was transferred under argon to an nmr tube which was then sealed under argon. The nmr spectra indicated the final product to be a mixture of 75% of diphenylcyclopropylcarbinylpotassium and 25% of diphenylcyclopropylmethane (plus some diphenylcyclopropylcarbinol from the starting material). This ratio was unchanged after 20 days in a refrigerator.

Phenylmethylcyclopropylcarbinol (XVI). To the ice-cooled Grignard reagent prepared from 10.0 g (0.41 g-atom) of magnesium turnings and 58.0 g (0.41 mole) of methyl iodide in 150 ml of diethyl ether was added dropwise a solution of 45.3 g (0.31 mole) of cyclopropyl phenyl ketone in 50 ml of ether. The mixture was stirred at room temperature overnight and then hydrolyzed by adding ice and water. Hydrochloric acid (6 *N*) was added dropwise until most of the precipitate dissolved, but, in order to avoid rearrangement of the product by the acid, the rest of the precipitate was dissolved by adding ammonium chloride solution. The aqueous layer was extracted twice with ether, and the combined organic layers were washed with sodium chloride solution and dried over sodium sulfate. The solvent was evaporated and the residue (51 g) was distilled at 0.3 mm yielding 42.1 g (84%) of pure phenylmethylcyclopropylcarbinol, bp 78–81° (0.3 mm), n^{27}D 1.5324, lit[31] n^{20}D 1.5370.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.30; H, 8.74.

Only a trace of 1-phenyl-1-cyclopropylethylene was detectable by vpc analysis (TCEP column, 150°). The nmr spectrum showed phenyl peaks, hydroxyl singlet, methyl singlet, cyclopropyl methine, and cyclopropyl methylene hydrogens.

Phenylmethylcyclopropylcarbinyl Methyl Ether (XVIII). A solution of 6 g (37 mmoles) of phenylmethylcyclopropylcarbinol (XVI) in a mixture of 10 ml of methanol and 0.36 ml of concentrated sulfuric acid was allowed to stand at room temperature for 5 hr, then diluted with water. The products of the reaction were dissolved in ether, and the combined ether extracts were washed

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with a sodium bicarbonate solution and with water. The solution was dried over sodium sulfate and evaporated to yield 6.2 g of residue consisting mainly of 1-phenyl-1-cyclopropylethylene (40%), phenylmethylcyclopropylcarbinyl methyl ether (40%), and 4-methoxy-1-phenyl-1-methyl-1-butene (20%) as shown by vpc analysis (TCEP column, 150°). The compounds were characterized by their nmr spectra. The percentages given are approximate since a test mixture of the three compounds for quantitative vpc analysis was not prepared.

The ether (XVIII) was also prepared by the Williamson method as follows. Potassium sand (3.3 g, 84.5 mg-atoms) was prepared in the usual manner in benzene (100 ml) under nitrogen using a high-speed stirrer. A solution of 13.7 g (84.5 mmoles) of phenylmethylcyclopropylcarbinol (XVI) in 25 ml of benzene was added dropwise, and stirring was continued until all the potassium dissolved. The mixture was allowed to cool to room temperature, then 25.0 g (176 mmoles) of methyl iodide was added, and the whole was refluxed for 24 hr with continued stirring. The potassium iodide was removed by filtration and washed with ether. The organic solvents were evaporated and the crude product (14.5 g) was distilled at 17 mm giving two fractions: (a) 1.8 g, bp 85–100°; (b) 11.8 g, bp 100–108°. Vpc analysis (TCEP column, 150°) showed that while the crude product consisted of phenylmethylcyclopropylcarbinyl methyl ether (90%) and phenylmethylcyclopropylmethane (10%), fraction a contained 75% of the hydrocarbon and only 25% of the ether, and fraction b was nearly pure phenylmethylcyclopropylcarbinyl methyl ether, n^{27}D 1.5131.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.80; H, 9.02.

The nmr spectrum was similar to that of the corresponding carbinol, the hydroxyl singlet resonance being replaced by a methoxy singlet resonance.

Phenylmethylcyclopropylcarbinylpotassium (XXI). A. Carbonation. The potassium organic compound was prepared in the usual manner from 3.52 g (20 mmoles) of phenylmethylcyclopropylcarbinyl methyl ether (XVIII) and 2.75 ml (0.05 g-atom of potassium) of sodium–potassium alloy in a total of 55 ml of anhydrous ether using the high-speed stirring apparatus previously described. Within a few minutes the color turned to deep red. After 0.5 hr of stirring in an ice bath, the mixture was cooled in a Dry Ice–acetone bath and carbonated as usual. From the ether layer, 0.78 g of neutral material was obtained consisting of phenylmethylcyclopropylmethane (total yield 18%) and phenylmethylcyclopropylcarbinol (XVI) in the ratio 2:1 as shown by vpc analysis (TCEP column, 150°) and nmr spectroscopy.

The aqueous layer was acidified with concentrated hydrochloric acid and extracted twice with ether. The combined ether layers were washed with water and dried over sodium sulfate. Evaporation of the solvent yielded 2.83 g (73.5%) of white crystals, mp 47–51°, which by nmr spectroscopy consisted of nearly pure phenylmethylcyclopropylacetic acid (XXII). The nmr spectrum showed carboxyl singlet, phenyl peaks, methyl singlet, cyclopropyl methine, and cyclopropyl methylene resonances in the proper intensities. One recrystallization from aqueous ethanol and two from carbon tetrachloride–heptane afforded an analytical sample of mp 71.5–73°.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.65; H, 7.34.

B. Hydrolysis. The organometallic compound (20 mmoles) was prepared in the usual manner and stirred for 2 hr at room temperature. The deep-red mixture was then cooled in an ice bath and hydrolyzed by the dropwise addition of water whereby the the color completely disappeared. The same isolation procedure used in previous runs afforded 3.0 g of a crude material, the main component of which was phenylmethylcyclopropylmethane (more than 50%). Five by-products, two of about 20% each and three of less than 5% each, were detected by vpc analysis (TCEP column 100°). These substances, which could not be separated by distillation, were not further investigated except that the mixture displayed strong vinyl resonances in the nmr spectrum.

Phenylcyclopropylcarbinyl Methyl Ether (XIII). A solution of 6 g (0.04 mole) of phenylcyclopropylcarbinol (XII) in 10 ml of methanol containing 0.36 ml of concentrated sulfuric acid was allowed to stand at room temperature for 24 hr. The mixture was diluted with water and extracted with ether. The combined ether extracts were washed with a sodium bicarbonate solution and water and dried over sodium sulfate. After removal of the ether, the residue (6.3 g.) was distilled under reduced pressure and yielded 5.6 g (86.5%) of phenylcyclopropylcarbinyl methyl ether, bp 105° (18 mm), n^{25}D 1.5098.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.60; H, 8.66.

The nmr spectrum showed phenyl peaks, benzyl doublet, methoxy singlet, cyclopropyl methine, and cyclopropyl methylene resonances.

Phenylcyclopropylcarbinylpotassium (XXIII). The potassium organic compound was prepared in the usual manner under nitrogen using high-speed stirring from 3.24 g (20 mmoles) of phenylcyclopropylcarbinyl methyl ether (XIII) and 2.75 ml (0.05 g-atom of potassium) of sodium–potassium alloy in 50 ml of anhydrous ether. The deep-red mixture was stirred in an ice bath for 1 hr and then carbonated, and the products were isolated as before. The neutral material (0.34 g.) was shown by vpc and nmr to consist mainly of benzylcyclopropane. Some phenylcyclopropylcarbinol (XII) but no trace of phenylmethylcyclopropylcarbinol (XVI) could be detected by vpc analysis. The crude phenylcyclopropylacetic acid (XXIV), 2.96 g (84%), had mp 76–79° and was quite pure as judged from its nmr spectrum, there being the expected carboxyl singlet, phenyl peaks, benzyl doublet, cyclopropyl methine, and cyclopropyl methylene resonances in the proper areas (1:5:1:1:4). Several crystallizations from aqueous ethanol and from carbon tetrachloride gave the analytical sample, mp 92–93°.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.84; H, 6.86.

Dicyclopropylphenylcarbinol. To a well-stirred Grignard reagent prepared from 14.6 g (0.6 g-atom) of magnesium and 94.2 g (0.6 mole) of bromobenzene in 175 ml of anhydrous ether was added dropwise a solution of 58.0 g (0.5 mole) of dicyclopropyl ketone (XXVII) in 50 ml of ether under an argon atmosphere. The mixture, in which a white precipitate formed, was stirred for 2 hr and then allowed to stand overnight. After hydrolysis with ice and an ammonium chloride solution, the layers were separated and the aqueous layer was extracted with ether. The combined organic layers were washed with sodium chloride solution and dried over sodium sulfate. The ether was removed by evaporation, and the crude residual product (95.7 g) was distilled under reduced pressure. A middle fraction of 67.2 g (72%) was pure dicyclopropylphenylcarbinol, bp 97–98° (0.2 mm), n^{26}D 1.5435, according to vpc analysis and its nmr spectrum.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.09; H, 8.50.

The nmr spectrum showed the expected phenyl peaks, hydroxyl singlet, cyclopropyl methine, and cyclopropyl methylene resonances.

Dicyclopropylphenylcarbinyl Methyl Ether (XXVI). Potassium sand (10.0 g, 0.255 g-atom) was prepared in 250 ml of benzene under argon using a high-speed stirrer. A solution of 47.0 g (0.25 mole) of dicyclopropylphenylcarbinol in 50 ml of benzene was added dropwise and stirring was continued until the evolution of hydrogen had ceased. The mixture was allowed to cool to room temperature, 71 g (0.5 mole) of methyl iodide was added, and the mixture was heated under reflux for 24 hr. The mixture was cooled and the precipitate of potassium iodide was removed by suction filtration and washed several times with ether. The solvents were removed from the combined organic material by evaporation, and the residue (49.5 g) was distilled under reduced pressure. The dicyclopropylphenylcarbinyl methyl ether, 38.6 g (76.5%), so obtained seemed very pure as judged by vpc analysis and its nmr spectrum, bp 142–145° (20 mm), n^{26}D 1.5268.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.96; H, 8.97.

The nmr spectrum showed phenyl peaks (two groups), methoxy singlet and cyclopropyl resonances (the methine and methylene hydrogens were indistinguishable).

Dicyclopropylphenylcarbinylpotassium (XXV). A. Hydrolysis. The potassium organic compound was prepared in the usual manner under argon from 4.05 g (20 mmoles) of dicyclopropylphenylcarbinyl methyl ether (XXVII) and 2.75 ml (0.05 g-atom of potassium) of sodium–potassium alloy in 55 ml of anhydrous ether and stirred for 0.5 hr in an ice bath. The deep-red mixture was hydrolyzed by the dropwise addition of water, whereby the color completely disappeared. The isolation procedure used for previous experiments afforded 3.4 g of a crude product consisting of dicyclopropylphenylmethane (95%) and dicyclopropylphenylcarbinyl methyl ether (5%). Distillation under reduced pressure yielded 2.6 g (75.5%) of pure dicyclopropylphenylmethane (XXVIII), bp 120–121° (20 mm), n^{27}D 1.5210.

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.40; H, 9.52.

The nmr spectrum showed phenyl peaks, distorted benzyl triplet overlapping with cyclopropyl methine resonances, and cyclopropyl methylene resonances.

B. Carbonation. Another batch of the organometallic compound (20 mmoles) prepared as described above was cooled with a Dry Ice–acetone bath and treated with carbon dioxide. The isolation procedure used for previous carbonations afforded 0.7 g (20%) of neutral material consisting of dicyclopropylphenylcarbinyl methyl ether (XXVI), dicyclopropylphenylmethane (XXVIII), and dicyclopropylphenylcarbinol in about equal concentrations as shown by vpc and nmr spectroscopy.

The aqueous layer was acidified whereby dicyclopropylphenylacetic acid (XXIX) separated as a colorless oil which soon crystallized. The yield was 3.47 g (80%), 118–123°. Two crystallizations from carbon tetrachloride afforded the analytical sample, mp 123.5–125°.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.74; H, 7.39.

The nmr spectrum showed the expected carboxyl singlet, phenyl peaks, cyclopropyl methine, and cyclopropyl methylene resonances. No vinyl protons were detected.

γ,γ-Diphenylallylcarbinylmercuric Bromide with Sodium–Potassium Alloy. A solution of 1.01 g (2.07 mmoles) of γ,γ-diphenylallylcarbinylmercuric bromide[5] (XXXI) in 15 ml of tetrahydrofuran was added dropwise to 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy suspended in 20 ml of tetrahydrofuran stirred with a high-speed stirrer under argon and cooled in an ice bath. The mixture immediately became black; the color, however, soon turned to brown-red. After 0.5 hr, the mixture was carbonated as usual, whereby the color disappeared. The isolation procedure used for previous carbonations afforded 59 mg (14%) of neutral material which according to vpc analysis (Ucon-Polar column, 200°) consisted of diphenylcyclopropylmethane (85%), diphenylcyclopropylcarbinol (7%), 1,1-diphenyl-1-butene (1%), and 1-phenyl-3,4-dihydronaphthalene (3%). Elemental mercury was recovered amounting to 0.31 g (75%).

Acidification of the aqueous layer with hydrochloric acid afforded 0.44 g of crude diphenylcyclopropylacetic acid, mp 131–136°. One crystallization from carbon tetrachloride raised the mp to 138–139.5° which was undepressed on admixture with an authentic sample. The nmr spectrum of the mother liquor from the crystallization showed that it contained no γ,γ-diphenylallylacetic acid. Judging from the nmr spectra the yield was about 80%.

Dicyclopropylphenylcarbinylpotassium with Magnesium Bromide. The organometallic compound was prepared in the usual manner starting with 4.05 g (20 mmoles) of dicyclopropylphenylcarbinyl methyl ether (XXVI) in 5 ml of anhydrous ether and 2.2 ml (40 mg-atoms of potassium) of sodium–potassium alloy in 50 ml of ether under argon using the high-speed stirring apparatus. The reaction time was 0.5 hr at 0°.

In a second 100-ml, three-necked flask equipped with magnetic stirrer, dropping funnel, and reflux condenser, there was prepared a magnesium bromide solution in ether from the reaction of 7.5 g (40 mmoles) of 1,2-dibromoethane with 1.22 g (50 mg-atoms) of magnesium turnings in 20 ml of ether, again under argon. The magnesium bromide solution was filtered under argon through a glass-wool plug directly into the dropping funnel of the high-speed stirring apparatus.

The deep-red color of the organopotassium compound disappeared immediately when the magnesium bromide solution was added. The pale yellow mixture was cooled with a Dry Ice–acetone bath and carbonated with solid carbon dioxide as usual. The mixture was placed in an ice bath and water added dropwise. The aqueous layer was acidified with hydrochloric acid and extracted twice with ether. The combined organic layers were washed twice with a sodium hydroxide solution, once with water, and dried over sodium sulfate. Evaporation of the ether left 0.96 g of neutral material which according to vpc analysis (TCEP column, 150°) and nmr spectroscopy consisted of 1-phenyl-1-cyclopropylbutane (10%), 1-phenyl-1-cyclopropyl-1-butene (30%), dicyclopropylphenylmethane (30%), and dicyclopropylphenylcarbinyl methyl ether (30%). Only traces of dicyclopropylphenylcarbinol and an unknown impurity could be detected.

The alkaline aqueous extract was acidified with hydrochloric acid and extracted twice with ether. The combined organic layers were washed with water and dried over sodium sulfate. Evaporation of the solvent gave 3.02 g (70%) of 5-phenyl-5-cyclopropyl-4-pentenoic acid (XXXIV), bp 160–162° (0.2 mm), $n^{27}{}_{D}$ 1.5475.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.82; H, 7.53.

The nmr spectrum showed a carboxyl singlet, phenyl peak, vinyl triplet, cyclopropyl methine, cyclopropyl methylene, and a broad peak due to overlapping α- and β-methylene resonances.

The same acid and hydrocarbons were obtained *via* the Grignard reagent prepared independently from 4-bromo-1-phenyl-1-cyclopropyl-1-butene (XXXVII). The latter was synthesized in poor yield from dicyclopropylphenylcarbinol and phosphorus tribromide, the main product in this reaction being 1,7-dibromo-4-phenyl-3-heptene.

Dicyclopropylphenylcarbinylpotassium with Lithium Bromide. The organometallic compound (20 mmoles) was prepared as described above. A lithium bromide suspension in ether was prepared in a 100-ml, three-necked flask with magnetic stirrer, dropping funnel, and reflux condenser from 7.5 g (40 mmoles) of 1,1-dibromoethane and 0.7 g (0.1 g-atom) of lithium wire in about 40 ml of ether, again under argon. The suspension of lithium bromide was decanted from the unreacted lithium and added directly to the organopotassium compound, whereby the deep-red color immediately disappeared. Isolation of the products as described above afforded 1.45 g of neutral material and 2.55 g (60%) of 5-phenyl-5-cyclopropyl-4-pentenoic acid (XXXIV). Analysis by vpc (TCEP column, 150°) and nmr spectroscopy showed that the neutral material consisted of 1-phenyl-1-cyclopropylbutane (1%), 1-phenyl-1-cyclopropyl-1-butene (50%), dicyclopropylphenylmethane (20%), dicyclopropylphenylcarbinyl methyl ether (25%), and dicyclopropylphenylcarbinol (4%).

One gram of the neutral material was treated under argon with 1.5 ml of sodium–potassium alloy and water in 25 ml of ether. The aqueous layer was extracted twice with ether, and the combined organic layers were washed with sodium chloride solution and dried over sodium sulfate. Evaporation of the solvent yielded 0.91 g of material in which vpc analysis and nmr spectroscopy indicated that the 1-phenyl-1-cyclopropyl-1-butene (XXXV) was completely reduced to 1-phenyl-1-cyclopropylbutane (XXXVI).

Diphenylcyclopropylcarbinylpotassium (XIV) with Kalignost. The potassium organic compound was prepared in the usual manner under argon from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) in 5 ml of tetrahydrofuran and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in 30 ml of tetrahydrofuran. The deep-red color of the solution did not change when a solution of 7.2 g (21 mmoles) of sodium tetraphenylboride "Kalignost"[22] in 30 ml of tetrahydrofuran was added although a white precipitate of potassium tetraphenylboride formed immediately. The mixture was stirred for 1 hr at 0° and carbonated as usual. Water and ether were added and the potassium tetraphenylboride, 7.03 g (98%), was removed by suction filtration. The isolation procedure used for previous carbonations afforded 340 mg of additional potassium tetraphenylboride and 629 mg (30%) of neutral material consisting of diphenylcyclopropylmethane (80%) and diphenylcyclopropylcarbinol (20%) as shown by vpc and nmr.

Acidification of the aqueous alkaline solution gave 1.62 g (65%) of diphenylcyclopropylacetic acid (XV), mp 139.5–141°.

In another run, the mixture was stirred for 63 hr at room temperature after the addition of the Kalignost solution. Besides 7.3 g (quantitative) of potassium tetraphenylboride, 1.11 g (53%) of neutral material was obtained which according to vpc analysis and its nmr spectrum consisted of diphenylcyclopropylmethane (45%), 1,1-diphenyl-1-butene (30%), diphenylcyclopropylcarbinol (15%), and 1,1-diphenylbutane (10%). Only 0.91 g of an unknown acidic fraction was obtained.

Cleavage of Diphenylcyclopropylcarbinyl Methyl Ether with Sodium Metal. A mixture of 2.59 g (10.9 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 4 g (175 mg-atoms) of sodium pieces in 50 ml of anhydrous ether was stirred under argon for 65 hr at room temperature with a high-speed stirrer. The deep-brown reaction mixture was carbonated and the products were isolated as usual, but no acid material could be isolated. The neutral products (2.31 g) consisted of starting material (40%), diphenylcyclopropylmethane (15%), 1,1-diphenyl-1-butene (35%), and 1,1-diphenylbutane (10%) as shown by vpc analysis and nmr spectroscopy.

Diphenylcyclopropylmethane with Sodium Hydride. A mixture of 2.08 g (10 mmoles) of diphenylcyclopropylmethane (VI) and 1 g (23 mmoles) of sodium hydride (55% in mineral oil, freed from mineral oil by washing with pentane) in 10 ml of tetrahydrofuran, containing a few drops of *t*-butyl alcohol as a catalyst, was stirred magnetically for 48 hr at room temperature under argon. No change in color was detected over this period. The mixture was then refluxed for 6 hr whereby the color turned to red. The deep-red reaction product was carbonated as usual whereby the color disappeared. Water was added carefully and the mixture was extracted three times with ether. The products (1.83 g, 88%) consisted of diphenylcyclopropylmethane (65%), 1,1-diphenyl-1-butene (20%), and 1,1-diphenylbutane (13%). The aqueous layer afforded 180 mg of unknown acidic material.

γ,γ-Diphenylallylcarbinyllithium (XLIb). A. Carbonation. Diphenylcyclopropylcarbinylpotassium (XIV) was prepared in the usual manner under argon from 4.76 g (20 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 2.2 ml (40 mg-atoms of potassium) of sodium–potassium alloy in a total of 55 ml of anhydrous ether using the high-speed stirring apparatus. The reaction time was 0.5 hr at 0°.

Lithium bromide (dried to constant weight over phosphorus pentoxide at 110° and 0.1 mm), 4.85 g (56 mmoles), was weighed out under argon in a flask with gas inlet tube which was then connected by Tygon tubing to the high-speed stirring apparatus. The lithium bromide was added directly to the reaction mixture, and over 10 min the deep-red color of the solution turned to brown. The mixture was stirred for 1.5 hr in an ice bath, then carbonated in the usual way. The isolation procedure used for the previous carbonations afforded 1.15 g (25%) of neutral material consisting of diphenylcyclopropylmethane (63%), 1,1-diphenyl-1-butene (28%), and diphenylcyclopropylcarbinol (9%). No starting material or other impurities could be detected by vpc analysis or nmr spectroscopy.

The alkaline aqueous layer was acidified with hydrochloric acid, and 3.63 g (72%) of nearly white crystals, mp 61–76°, was obtained which was shown by nmr spectroscopy to be γ,γ-diphenylallylacetic acid (XLII). After recrystallization from *n*-hexane, the melting point of 78–81° was undepressed by admixture with an authentic sample.[5] Even in the crude acid, no trace of cyclopropyl protons could be detected in the nmr spectrum.

B. Hydrolysis with Deuterium Oxide. The organolithium compound was prepared as described above starting with 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in a total of 35 ml of ether and 3.3 g (38 mmoles) of lithium bromide. The mixture was stirred for 1.5 hr at 0°, then hydrolyzed by the dropwise addition of 5 ml of deuterium oxide. The brown color (probably suspended particles of lithium metal formed by the reaction of lithium bromide with the excess sodium–potassium alloy) completely disappeared. Water was added and the aqueous layer was extracted twice with ether. The combined organic layers were washed with a sodium chloride solution and dried over sodium sulfate. Evaporation of the solvent afforded 2.07 g of a colorless liquid, which according to vpc analysis (Ucon-Polar column, 200°) and its nmr spectrum consisted of deuterium-free diphenylcyclopropylmethane (25%), 1,1-diphenyl-1-butene-4-d_5 (70%), and diphenylcyclopropylcarbinol (5%), the latter being an impurity in the starting material.

C. With Mercury Metal. Diphenylcyclopropylcarbinylpotassium (XIV) was prepared as above from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in 20 ml of ether under argon. After 0.5 hr in an ice bath, 100 g (0.5 g-atom) of mercury metal was added and stirring was continued for 2 hr at 0°. Finally 2.6 g (30 mmoles) of dry lithium bromide was added under argon. Within 10 min, the deep-red color turned through orange to green and finally gray. Then 40 ml of tetrahydrofuran was added, but no further change in color took place. After an additional 1.5 hr at 0°, the mixture was carbonated as usual but no acid was obtained. The crude neutral material (2.71 g) consisted of diphenylcyclopropylmethane (36%), diphenylcyclopropylcarbinol (4%), and bis(γ,γ-diphenylallylcarbinyl)mercury (60%) according to its nmr spectrum. The mixture was heated under reduced pressure; some material distilled but most of the distillate consisted of pyrolysis products. Three fractions were obtained: (a) 605 mg, bp 76–85° (0.05 mm); (b) 287 mg, 200° bath (0.05 mm); (c) 421 mg, 250° bath (0.05 mm). From vpc analysis (Ucon-Polar column, 200°) and nmr spectroscopy, fraction a consisted of diphenylcyclopropylmethane (85%) and 1,1-diphenyl-1-butene (15%). Fraction b contained a little metallic mercury and was composed of 1,1-diphenyl-1-butene (45%), 1,1-diphenyl-1,3-butadiene (39%), diphenylcyclopropylmethane (10%), and diphenylcyclopropylcarbinol (6%), *i.e.*, mainly pyrolysis products. After collection of fraction b and before continuation of the pyrolysis, the nmr spectrum of the residue was taken and confirmed the presence of bis(γ,γ-diphenylallylcarbinyl)mercury (XLIII) through its phenyl peak, vinyl triplet, β-methylene quartet, and α-methylene triplet. Fraction c contained 57 mg of metallic mercury and consisted exclusively of 1,1-diphenyl-1-butene (35%), 1,1-diphenyl-1,3-butadiene (35%), 1-phenyl-3,4-dihydronaphthalene (28%), and 1-phenyl-1,2,3,4-tetrahydronaphthalene (2%). No diphenylcyclopropylmethane was detected in this fraction.

An authentic sample of 1-phenyl-3,4-dihydronaphthalene (XLV) was obtained by the reaction of phenylmagnesium bromide with α-tetralone.[32] Oxidation with sulfur afforded 1-phenylnaphthalene (XLVII); reduction with potassium and water yielded 1-phenyl-1,2,3,4-tetrahydronaphthalene (XLVI).

Di-*n*-butylmercury from *n*-Butyllithium. *n*-Butyllithium was prepared in the usual manner[23] from 6.85 g (50 mmoles) of *n*-butyl bromide, 0.86 g (125 mg-atoms) of lithium wire, and 30 ml of ether. The excess of lithium was removed, and, after addition of 100 g of mercury metal, the mixture was stirred with a high-speed stirrer for 2 hr in an ice bath. The Gilman test[33] for organolithium compounds was then negative. After addition of water, the combined aqueous and mercury phases were extracted three times with ether. The combined organic layers were washed with a sodium chloride solution and dried over sodium sulfate. Evaporation of the solvent yielded 7.11 g (91%) of pure di-*n*-butylmercury having an nmr spectrum identical with an authentic sample. Distillation gave 6.5 g of product of bp 44–45° (0.1 mm).

Diphenylcyclopropylcarbinyllithium (XLIa). A. In Tetrahydrofuran. Diphenylcyclopropylcarbinylpotassium (XIV) was prepared in the usual manner from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in a total of 35 ml of tetrahydrofuran. The mixture was stirred with a high-speed stirrer for 0.5 hr at 0°, and then 3.73 g (43 mmoles) of lithium bromide was added under argon. No change in color was observed after another 1.5 hr at 0°. The mixture was carbonated as usual, then water and hydrochloric acid were added, and the aqueous layer was extracted twice with ether. The combined organic layers were extracted twice with sodium hydroxide solution, washed with sodium chloride solution, and dried over sodium sulfate. Evaporation of the solvent yielded 669 mg (28%) of neutral material which according to vpc analysis (Ucon-Polar column, 200°) and its nmr spectrum consisted of diphenylcyclopropylmethane (55%), diphenylcyclopropylcarbinol (35%), 1,1-diphenyl-1-butene (7%), and diphenylcyclopropylcarbinyl methyl ether (3%).

Acidification of the alkaline extract gave 1.82 g (72%) of diphenylcyclopropylacetic acid (XV), mp 135–139.5°, which on recrystallization from carbon tetrachloride afforded 1.48 g of mp 138–140° (undepressed on admixture with an authentic sample). The nmr spectrum of the mother liquor showed that no other acid was present.

B. In Ether–Tetrahydrofuran (1:1). The organopotassium compound (10 mmoles) was prepared as described in the previous run but in exactly 20 ml of tetrahydrofuran. The excess of sodium–potassium alloy was removed by stirring the mixture for 1.5 hr at 0° with 100 g (0.5 g-atom) of mercury metal. Then 3.0 g (35 mmoles) of lithium bromide was added without removing the mercury, and the mixture was stirred for another 1.5 hr at 0°. The deep-red color did not disappear even after the addition of 20 ml of diethyl ether. After an additional hour at 0° the mixture was carbonated as usual and gave 974 mg (47%) of neutral material consisting of diphenylcyclopropylmethane (80%), 1,1-diphenyl-1-butene (15%), and diphenylcyclopropylcarbinol (5%). The crude acid, 1.33 g (53%), mp 135–140.5°, was recrystallized from carbon tetrachloride and yielded 1.12 g, mp 139.5–141° which was undepressed on admixture with authentic diphenylcyclopropylacetic acid (XV). The nmr spectrum of the mother liquor indicated the presence of the cyclic acid but no γ,γ-diphenylallylacetic acid.

C. In Ether–Tetrahydrofuran (2:1). Diphenylcyclopropylcarbinylpotassium (XIV) was prepared from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in a total of 20 ml of ether. After 0.5 hr at 0°, 3.3 g (38 mmoles) of lithium bromide was added under argon, whereby the deep-red color disappeared within 10 min. The lithium compound was stirred for 1.5 hr at 0° to make sure that the reaction was complete; then 10 ml of tetrahydrofuran was added, whereby the deep-red color reappeared immediately. The mixture was carbonated as usual. The isolation procedure used for previous carbonations afforded 1.086 g

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(32) R. Weiss and K. Woidich, *Monatsh. Chem.* **46**, 453 (1925).

(33) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(51%) of neutral material consisting of diphenylcyclopropylmethane (65%), 1,1-diphenyl-1-butene (20%), and diphenylcyclopropylcarbinol (15%), the latter being an impurity in the starting material. The crude acidic product 1.24 g (49%), mp 121–135°, was recrystallized from carbon tetrachloride and afforded 0.96 g of diphenylcyclopropylacetic acid, mp 136–139°, undepressed on admixture with an authentic sample. The mother liquors (containing 277 mg of acid) were concentrated and found by nmr spectroscopy to contain diphenylcyclopropylacetic acid (75%) and γ,γ-diphenylallylacetic acid (25%). The total yield of diphenylcyclopropylacetic acid was roughly 1.17 g (46%), while the yield of γ,γ-diphenylallylacetic acid was 69 mg (3%).

Diphenylcyclopropylcarbinylpotassium (XIV) with Magnesium Bromide. The organopotassium compound was prepared in the usual manner from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in a total of 55 ml of tetrahydrofuran. After 0.5 hr at 0° a solution of magnesium bromide, prepared separately under argon from 3.75 g (20 mmoles) of 1,2-dibromoethane and 0.6 g (25 mg-atoms) of magnesium in a total of 10 ml of ether, was added dropwise, whereby the red color disappeared. The mixture was carbonated as usual. The isolation procedure used for previous carbonations afforded 752 mg (36%) of neutral material consisting of diphenylcyclopropylmethane (64%), diphenylcyclopropylcarbinol (20%), 1,1-diphenyl-1-butene (14%), and a trace of starting material. A total of 1.60 g (63.5%) of γ,γ-diphenylallylacetic acid, mp 70–81°, was obtained which after one recrystallization from *n*-hexane had mp 79.5–81° (undepressed on admixture with an authentic sample). The crude acid did not contain any diphenylcyclopropylacetic acid as judged by its nmr spectrum.

Similar results were obtained using diethyl ether as solvent.

Diphenylcyclopropylcarbinylpotassium (XIV) with Mercuric Bromide. The potassium organic compound was prepared in the usual manner from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in a total of 35 ml of tetrahydrofuran. After 0.5 hr at 0°, a solution of 9 g (25 mmoles) of mercuric bromide in 20 ml of tetrahydrofuran was added dropwise. Before the addition was half complete the color of the solution had turned from red to black. Stirring was continued for 0.5 hr at 0°; then water was added followed by ether. The black cloudy precipitate was removed by filtration and the aqueous layer extracted twice with ether. The combined organic layers were washed with sodium chloride solution and dried over sodium sulfate. Evaporation of the solvent yielded 2.28 g of crude material consisting mainly of diphenylcyclopropylmethane (60%), but also containing diphenylcyclopropylcarbinol (15%), 1-phenyl-3,4-dihydronaphthalene (15%), 1-phenylnaphthalene (2%), 1,1-diphenyl-1-butene (2%), and probably 1,1-diphenyl-1,3-butadiene (2%). The percentages given are approximate because of difficulties in obtaining satisfactory vpc resolution. The principal products were also identified by their nmr peaks. Reduced pressure distillation gave 1.29 g of distillate, bp 80° (0.1 mm), containing 75% of diphenylcyclopropylmethane and the other products described above in somewhat different proportions.

Diphenylcyclopropylcarbinylpotassium (XIV) with Cobaltous Chloride. The organopotassium compound was prepared in the usual manner from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in 35 ml of tetrahydrofuran. After 0.5 hr at 0°, 63 g (0.32 g-atom) of mercury metal was added in order to remove the excess of sodium–potassium alloy, and stirring was continued for 2 hr at 0°. Finally 0.65 g (5 mmoles) of solid cobaltous chloride, dried at 100°, was added under argon through a Tygon side tube. After 2 hr at 0°, the mixture was carbonated as usual. Water and hydrochloric acid were added and the orange-colored aqueous mixture was extracted three times with ether. The combined organic layers were extracted twice with sodium hydroxide solution and dried over sodium sulfate. Evaporation of the solvent yielded 1.40 g (67%) of neutral material which according to vpc analysis and its nmr spectrum consisted of diphenylcyclopropylmethane (70%), diphenylcyclopropylcarbinol (7%), 1,1-diphenyl-1-butene (14%), and 1-phenyl-3,4-dihydronaphthalene (9%). The aqueous alkaline layer gave 707 mg (28%) of diphenylcyclopropylacetic acid (XV).

A Study of Isologous 1,2-Dithiolane, 1,2-Diselenolane, and 1-Thia-2-selenolane Derivatives[1]

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Abstract: The dipole moments of 1,2-dithiolane-4-carboxylic acid, 1,2-diselenolane-4-carboxylic acid, 1-thia-2-selenacyclopentane-4-carboxylic acid, 2,3-dithiaspiro[4.5]decane, 2,3-diselenaspiro[4.5]decane, and 2-thia-3-selenaspiro[4.5]decane were measured. No significant polarization of the S–Se bond could be detected. The dipole moments of the carboxylic acids were in good agreement with calculated moments assuming free rotation of the carboxyl group. The moment of the methyl ester of 1,2-dithiolane-4-carboxylic acid is similar to that of the free acid. These observations indicate that there is no significant interaction between disulfide and carboxyl groups in the dithiolane system studied.

It has been observed that in noncyclic[3] or cyclic[4] carbamyl compounds substitution of oxygen by sulfur or selenium results in an increase in dipole moment considerably greater than can be attributed to an increase in molecular size. This increase in moment, which is not predictable from the respective electronegativities of oxygen, sulfur, and selenium, may presumably be attributed to the greater tendency of selenium than of sulfur to undergo octet expansion, while no octet expansion is possible for oxygen. Similarly, a relatively high tendency of selenium relative to sulfur to undergo octet expansion can be invoked to account

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