Small-Ring Compounds. XLV. Influence of Vinyl and Phenyl Substituents on the Interconversion of Allylcarbinyl-Type Grignard Reagents[1]

Merlin E. H. Howden, Adalbert Maercker, James Burdon, and John D. Roberts

Contribution No. 3280 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California.

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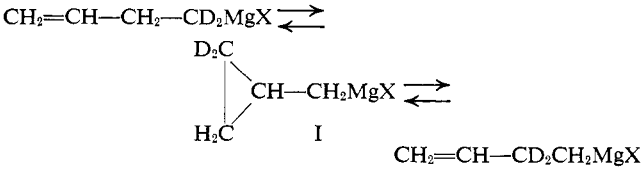
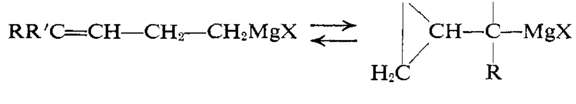
Abstract: Equilibration of the α and β positions in γ,γ-diphenylallylcarbinylmagnesium bromide was complete after 5 hr at room temperature. Less than 0.3% of the isomeric cyclopropylcarbinyl derivative, however, is in equilibrium with the ring-opened species. While reactions of the Grignard reagents normally expected to have anionic-type mechanisms were found to lead to allylcarbinyl products only, substantial amounts of cyclic products were formed with molecular oxygen.

Allylcarbinyl Grignard reagents undergo a remarkable rearrangement in which the α and β carbons exchange positions.[2] The mechanism of the interconversion is not known, although the plausible intermediate is the cyclopropylcarbinyl Grignard reagent I, which by opening the ring in two ways can lead to equilibration of the α and β positions. Strong support for this mechanism recently was obtained by the successful preparation of the assumed cyclopropylcarbinylmagnesium bromide (I, X = Br).[3] While the Grignard reagent prepared in the ordinary way from cyclopropylcarbinyl halides possesses the allylcarbinyl structure to the extent of more than 99%,[2-4] the cyclopropylcarbinylmagnesium halide can be trapped by hydrolysis *in situ* or by working at low temperatures,[3] where the equilibrium is established rather slowly. Thus the rearrangement of the cyclopropylcarbinylmagnesium bromide to allylcarbinylmagnesium bromide at −24° has a half-time of about 2 hr.[3] Similarly cyclopropylcarbinyllithium[5] can be successfully prepared only at low temperatures, preferably in the presence of nonpolar solvents which tend to retard the establishment of the equilibrium.

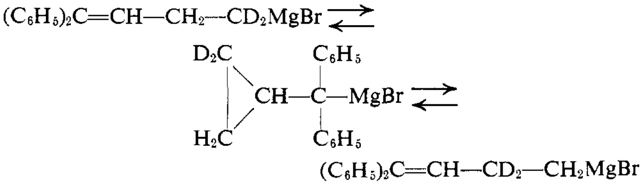


In the present work a study was made of the reactions of 4-substituted allylcarbinyl Grignard reagents. It was anticipated that phenyl or vinyl substitution at these positions might facilitate the rearrangement by stabilization of the partial negative charge in the cyclic Grignard reagent and that this might also be manifested by formation of cyclopropylcarbinyl products.



Results and Discussion

γ,γ-Diphenylallylcarbinyl Grignard Reagents. The interconversion of the α and β positions in unsubstituted allylcarbinyl Grignard reagents occurs rather slowly, the half-life for equilibration being 30 hr at +27° and 40 min at +55°, corresponding to an activation energy of about 26 kcal/mole.[2] This interconversion is much faster in the case of γ,γ-diphenylallylcarbinylmagnesium bromide. The nmr spectrum of the Grignard reagent prepared from 4,4-diphenyl-1-bromo-3-butene-1,1-d_2 is shown in Figure 1. It was taken 5 hr after the start of preparation at 20° and did not change with time. The sizable α-methylene singlet at high field indicates that equilibration of the α and β positions in the Grignard reagent was already complete by the time the first spectrum was taken.



The results are accommodated by intermediacy of the cyclopropylcarbinyl Grignard reagent. If the rate-determining step in this mechanism is the ring closure, then the equilibration of the α and β positions would be expected to be faster than with the unsubstituted compound because of the conjugative effect of the two phenyl groups with the partially ionic carbon–magnesium bond, which will tend to favor not only the cyclic isomer but also the corresponding transition state.

It was therefore of interest to determine whether the presence of the diphenylcyclopropylcarbinyl form of the Grignard reagent could be gleaned from its nmr spectrum. The best criterion for the latter is likely to be the cyclopropane–methylene peaks which generally occur at higher fields than methyl resonances. Figure 1 shows that there is indeed a broad peak upfield from the methyl resonance of the ether, having the expected chemical shift and which might be due to some cyclo-

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

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

(3) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965).

(4) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

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

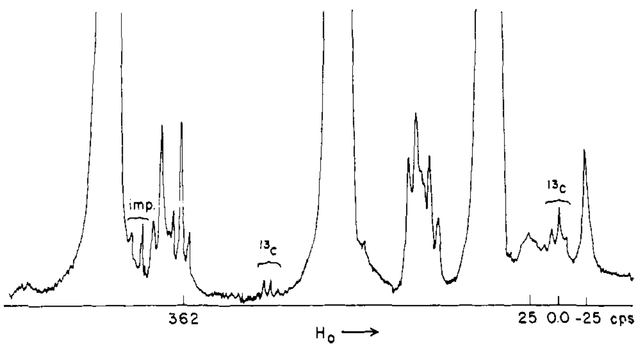


Figure 1. Proton nmr spectrum of the Grignard reagent from 4,4-diphenyl-1-bromo-3-butene-1,1-d_2 in ether.

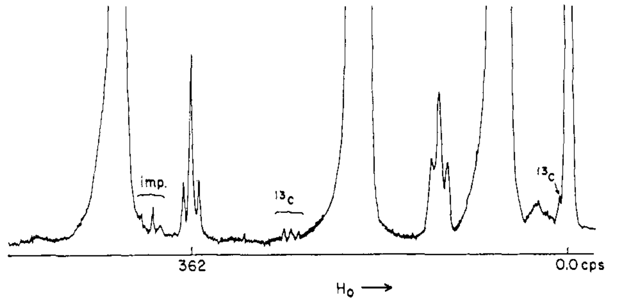
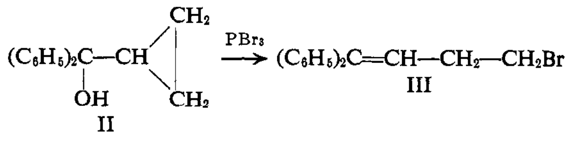


Figure 2. Proton nmr spectrum of the product of reaction of the nmr sample corresponding to Figure 1 with methanol.

propyl species. However, the spectrum is complicated by extraneous vinyl triplet and midfield methylene absorptions which are properly attributed to deuterated 1,1-diphenyl-1-butene. This conclusion is supported by the nmr spectrum of the product obtained when the nmr sample of the Grignard reagent used in Figure 1 was treated with methanol (Figure 2). Substantial simplification of the spectrum resulted because of formation of more 1,1-diphenyl-1-butene consisting of $(C_6H_5)_2C{=}CH{-}CH_2{-}CD_2H$ and $(C_6H_5)_2C{=}CH{-}CD_2{-}CH_3$. Again a small peak just to the low-field side of the tetramethylsilane resonance is present which might be attributed to the cyclopropane methylene hydrogens of diphenylcyclopropylmethane. Area measurements indicate that the relative proportion of the latter is about 7%, in fair agreement with the amount isolated in preparative reactions using the unlabeled γ,γ-diphenylallylcarbinylmagnesium bromide. The nmr spectrum of the unlabeled Grignard reagent was taken in hexadeuteriodiethyl ether, $(CD_3CH_2)_2O$, in order to keep the cyclopropyl region as free as possible from ^{13}C satellites of the ether methyl group. Again a small amount (*ca.* 3%) of cyclopropane methylene protons could be detected. These absorptions seemed to indicate the presence of at least some diphenylcyclopropylcarbinyl Grignard reagent and prompted a more extensive study to see if addition products could be isolated corresponding to the cyclopropane structure.

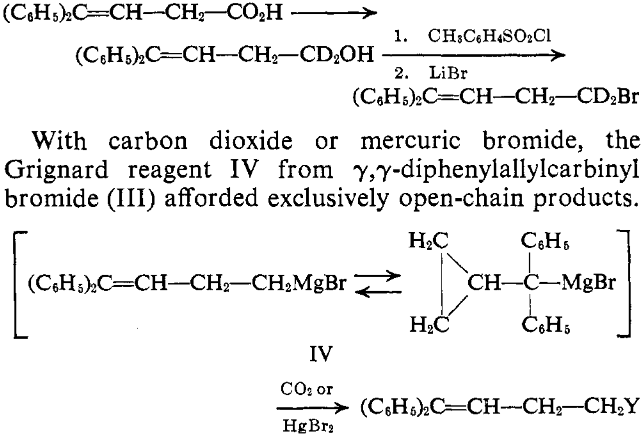
In connection with this work, we had occasion to attempt to prepare diphenylcyclopropylcarbinyl bromide and obtained results quite contradictory to those of Lipp.[6] We observed that treatment of diphenylcyclopropylcarbinol (II) with phosphorus tribromide gives exclusively γ,γ-diphenylallylcarbinyl bromide (III), whose structure was firmly established; no diphenylcyclopropylcarbinyl bromide was detected.



This turns out to be an easy synthesis of the bromide III, although, of course, unsuitable for the α,α-deuterium-labeled halide, which was obtained by the following sequence of reactions.

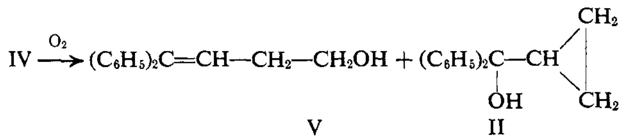
$$(C_6H_5)_2C{=}CH{-}CH_2{-}CO_2H \xrightarrow{LiAlD_4} (C_6H_5)_2C{=}CH{-}CH_2{-}CD_2OH \xrightarrow[2.\ LiBr]{1.\ CH_3C_6H_4SO_2Cl} (C_6H_5)_2C{=}CH{-}CH_2{-}CD_2Br$$

With carbon dioxide or mercuric bromide, the Grignard reagent IV from γ,γ-diphenylallylcarbinyl bromide (III) afforded exclusively open-chain products.



Y = CO_2H, HgBr

However, the reaction with oxygen gave a 66.5% yield of γ,γ-diphenylallylcarbinol (V) and diphenylcyclopropylcarbinol (II) in a ratio of 2.5:1.



The high proportion of rearrangement observed with oxygen was unexpected and may be due to mechanistic factors operative in the oxygenation reactions of Grignard reagents, in general, which have not yet been elucidated. Hock, *et al.*,[7] have emphasized the possible role of free radicals in these reactions.

That only open-chain products were obtained with carbon dioxide or mercuric bromide does not necessarily mean that no appreciable amount of the diphenylcyclopropylcarbinyl form is present in the Grignard solution. The open-chain carboxylic acid might conceivably be formed directly from cyclopropylcarbinyl Grignard reagent and carbon dioxide. Or, alternatively, carbon dioxide might react much more rapidly with the γ,γ-diphenylallylcarbinyl than with the cyclopropylcarbinyl form, and, if the rate of rearrangement is faster than the reaction with carbon dioxide, only open-chain acid would be formed. It is interesting to note in this connection that carbon dioxide affords exclusively the α-methylallyl product in the reaction with the γ-methylallyl Grignard reagents.[8]

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(6) P. Lipp, J. Buchkremer, and H. Seeles, *Ann.*, **499**, 1 (1932).

(7) H. Hock, H. Kropf, and F. Ernst, *Angew. Chem.*, **71**, 541 (1959).

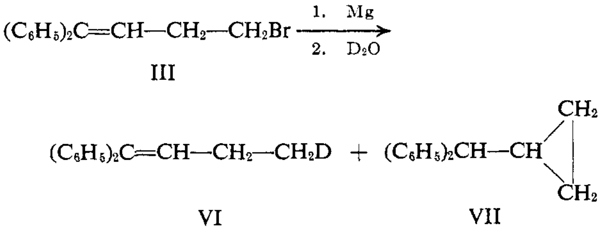
(8) (a) J. F. Lane, J. D. Roberts, and W. G. Young, *J. Am. Chem. Soc.*, **66**, 543 (1944); (b) J. E. Nordlander, W. G. Young, and J. D. Roberts, *ibid.*, **83**, 494 (1961).

Table I. Hydrocarbons from the Grignard Reagent Derived from γ,γ-Diphenylallylcarbinyl Bromide

	% yield of hydrocarbons[a]	Mole fraction of diphenylcyclopropylmethane[b]	Over-all yield of diphenylcyclopropylmethane, %
Carbon dioxide	14.3, 10.1	0.22, 0.29	3.1, 2.9
Carbon dioxide (absence of oxygen)	22.0	0.26 ± 0.01[c]	5.7
Mercuric bromide	17.9	0.26	4.6
Oxygen	18.9	0.23	4.3
Ammonium chloride solution	90.5	0.04	3.6
Methanol	86.6	0.05	4.3
Hydrogen chloride (gas)	89.5	0.09	8.1
Phenylacetylene	90.5	0.10	9.1
Cobaltous chloride (catalytic amount)	35.1	0.35	12.3

[a] After distillation, based on bromide. [b] Diphenylcyclopropylmethane relative to diphenylcyclopropylmethane plus 1,1-diphenyl-1-butene as measured by vpc. [c] Standard deviation.

Substantial amounts of 1,1-diphenyl-1-butene and diphenylcyclopropylmethane, with the former predominating, were isolated from reactions of the Grignard reagent with oxygen, carbon dioxide, and mercuric bromide. In the reaction with carbon dioxide, the hydrocarbon mixture appeared to be present even when oxygen was rigorously excluded. Diphenylcyclopropylmethane was also present in the products of active hydrogen compounds with the Grignard reagent. The results of these experiments are summarized in Table I. It should be emphasized that the results in Table I were obtained under widely different conditions for preparation and reaction of the Grignard reagent (see Experimental Section), and any conclusion from the data must be tempered by this fact. Nonetheless, in most of the reactions the actual yield of diphenylcyclopropylmethane lies between 3 and 5%. This indicated to us that the diphenylcyclopropylmethane is most likely to be formed during reaction of the bromide with magnesium, while the reaction of the active hydrogen compounds with the Grignard reagent later on afforded exclusively 1,1-diphenyl-1-butene.

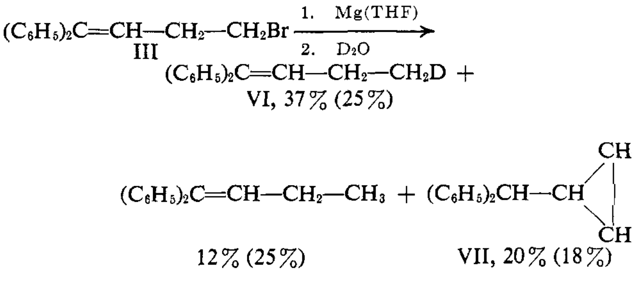


Evidence for this hypothesis was obtained by hydrolysis of the Grignard reagent with deuterium oxide which gave a 97:3 mixture of 1,1-diphenyl-1-butene-4-*d* (VI) and *deuterium-free* diphenylcyclopropylmethane (VII), indicating that diphenylcyclopropylcarbinyl Grignard reagent had not been present in significant quantities (<0.3%). The cyclopropane methylene absorption in the nmr spectrum of the Grignard reagent mentioned earlier seems *wholly* to be attributed to diphenylcyclopropylmethane formed in the preparation of the Grignard reagent rather than to the cyclic isomer.

The reason for the formation of relatively large amounts of cyclic hydrocarbon in acidolysis of the Grignard reagent with hydrogen chloride and phenylacetylene (see Table I) is not known. It should be pointed out, however, that simply preparing the Grignard reagent in air instead of an inert atmosphere, the diphenylcyclopropylmethane percentage was sometimes found to rise to about 8% even on hydrolysis with water. On the other hand, the 3% figure was unchanged when the Grignard reagent was allowed to stand, under helium, for 70 hr at room temperature before being treated with water.

That any agents which induce free-radical reactions increase the amount of cyclopropyl product is clearly demonstrated by the results with cobaltous chloride (Table I). Grignard formation itself seems to be a radical process on the magnesium surface.[9] The radicals appear to break free occasionally and abstract a hydrogen from the solvent and thereby produce 1,1-diphenyl-1-butene and diphenylcyclopropylmethane in a ratio of about 3:1 (*cf.* the first four reactions in Table I). The presence of 1,1-diphenyl-1-butene in the Grignard solution is clear from the nmr spectrum (Figure 1).

Interestingly, preparation of the Grignard reagent in tetrahydrofuran instead of diethyl ether gave up to 20% of diphenylcyclopropylmethane. Hydrolysis with deuterium oxide, however, again demonstrated without doubt that the Grignard reagent itself was not involved in this side reaction. In the following reaction two yields are given for each product: one from heating under reflux for 1.5 hr before hydrolysis; the other (in parentheses) from heating under reflux for 6 hr before hydrolysis.



The Grignard reagent is cleaved by the solvent on long heating, but this reaction is not involved in the formation of diphenylcyclopropylmethane because increasing the reflux time does not increase the yield of the cyclic hydrocarbon. Essentially the same result was obtained on carbonation of the Grignard reagent after 1.5 hr of reflux.

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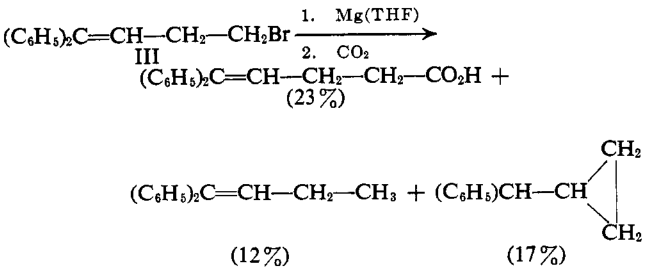
(9) (a) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p 61; (b) C. Rüchardt and H. Trautwein, *Chem. Ber.*, **95**, 1197 (1962); (c) H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3288 (1964).

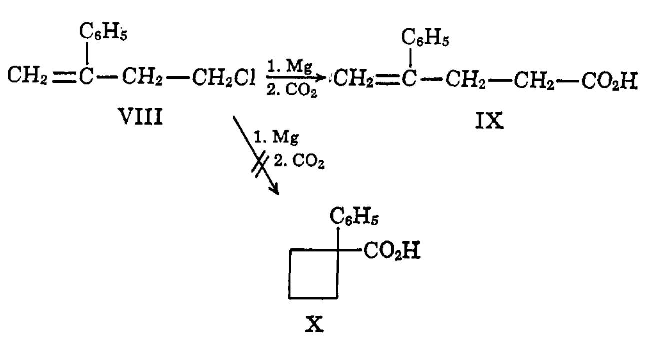


The hydrocarbon fraction of these reactions usually contained up to 10% of a third compound which, from its nmr spectrum, appeared to be 1,1-diphenyl-1,3-butadiene. This substance might reasonably be formed by disproportionation of γ,γ-diphenylallylcarbinyl free radicals.[10]

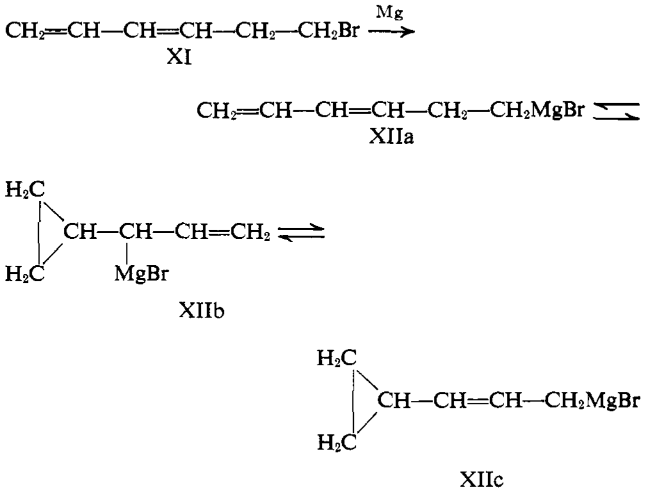
$$2(C_6H_5)_2C{=}CH{-}CH_2{-}\dot{C}H_2 \longrightarrow (C_6H_5)_2C{=}CH{-}CH_2{-}CH_3 + (C_6H_5)_2C{=}CH{-}CH{=}CH_2$$

The substantially higher yields of hydrocarbons in the formation of γ,γ-diphenylallylcarbinylmagnesium bromide in tetrahydrofuran compared with diethyl ether is in contrast to the results of Walborsky[9c] who reports that, during the formation of 1-methyl-2,2-diphenylcyclopropylmagnesium bromide, diethyl ether is cleaved to a greater extent than tetrahydrofuran. The difference could be due to the possibility that, in our case, ring closure of the initially formed γ,γ-diphenylallylcarbinyl radicals, probably on the magnesium surface, is rate determining for loss of radicals from magnesium and might be faster in tetrahydrofuran than in ether. The greater proportion of diphenylcyclopropylmethane in the hydrocarbon product in tetrahydrofuran could well be due to a greater reactivity of the diphenylcyclopropylmethyl radical toward this solvent than toward ether because of steric hindrance.

No cyclobutane derivatives have so far been found in radical or anionic cyclopropylcarbinyl–allylcarbinyl rearrangements, and actually the formation of a nonclassical bicyclobutonium radical or anion is not very likely.[11] We have now found that carbonation of the Grignard reagent from β-phenylallylcarbinyl chloride (VIII) gives a 61% yield of β-phenylallylacetic acid (IX) and no 1-phenylcyclobutanecarboxylic acid (X). Thus, even when tempted with a well-placed phenyl group, the allylcarbinyl Grignard reagent cannot be induced to give significant amounts of cyclobutyl products. This result, of course, does not rule out the possibility that some 1-phenylcyclobutyl Grignard reagent is present in equilibrium with the open-chain Grignard reagent prior to reaction with carbon dioxide.



γ-Vinylallylcarbinyl Grignard Reagents. Another system investigated was the Grignard reagent from 1-bromo-3,5-hexadiene (XI), a 4-vinyl-substituted allylcarbinyl halide. Here there is a possibility of an equilibrium with two cyclopropane derivatives (XIIb and XIIc) which, like other allylic Grignard reagents,[8b] would probably exist as a rapid equilibrating mixture of the α- and γ-cyclopropylallyl forms with the latter predominating. The products isolated from reactions of the Grignard reagent XII with carbon dioxide, allyl bromide, ethanol, and oxygen are shown in Figure 3.



Like the Grignard reagents from allylcarbinyl and γ,γ-diphenylallylcarbinyl halides, carbonation afforded open-chain acid as the only carboxylic acid product, while the highest amount of cyclic products was obtained with oxygen. The percentages given apply to the relative proportions of compounds in the separated product mixture and sometimes are very approximate because of difficulties in achieving satisfactory vpc resolution. In the mixture of *cis*- and *trans*-propenylcyclopropane obtained in the reaction with ethanol, one isomer predominated by a factor of 1.8, while in the mixture of *cis*- and *trans*-γ-cyclopropylallyl alcohol, obtained with oxygen, one stereoisomer predominated by a factor of 3. The cyclopropylallyl coupling products with allyl bromide were found in comparable amounts, as has also been found by Young, *et al.*,[12] for the reaction of the crotyl Grignard reagent with allyl bromide (1:1 ratio of secondary to primary isomers). It seems possible that these reactions may involve free-radical mechanisms.

The hydrocarbon fraction obtained in the carbonation reaction consisted mainly of what appeared to be 1,6-dicyclopropyl-1,5-hexadiene (XIII) and 1,4-dicyclopropyl-1,5-hexadiene (XIV) in the ratio 62:35, together with some allylcyclopropane and 3,5-hexadiene. The cyclopropylallyl coupling products XIII and XIV, the only high-boiling materials observed in this fraction,

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[10] The behavior of this radical produced independently is being investigated further.

[11] M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, **2**, 403 (1963).

[12] W. G. Young, J. D. Roberts, and H. Wax, *J. Am. Chem. Soc.*, **67**, 841 (1945).

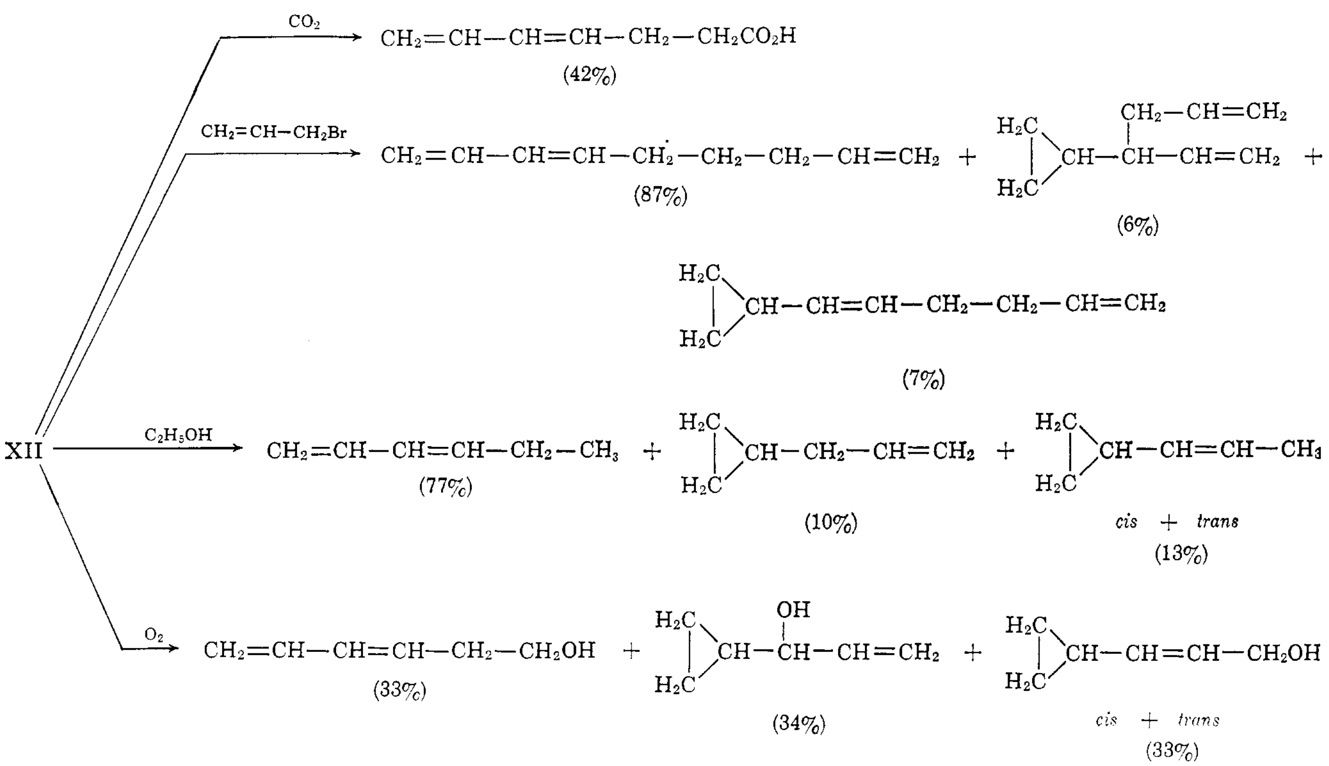


Figure 3.

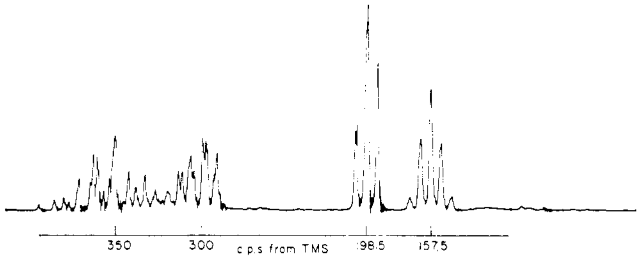
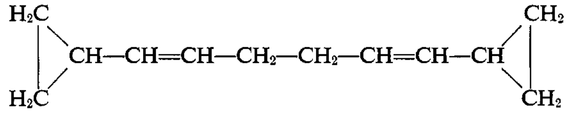
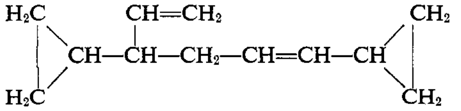


Figure 4. Nmr spectrum at 60 Mcps of 1-bromo-3,5-hexadiene as a 50% solution in CCl_4.

probably were formed during reaction of the bromide with magnesium *via* γ-vinylallylcarbinyl free radicals. These might be expected to rearrange to cyclopropylallyl

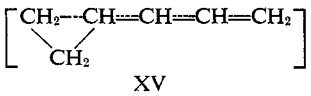


XIII



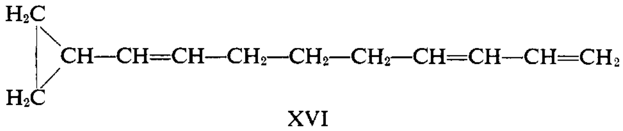
XIV

radicals, since the enthalpy difference between them is calculated by a thermodynamic cycle procedure[11] to be −16 kcal/mole. Coupling of the resultant stabilized cyclopropylallyl radicals (or of resonance-stabilized nonclassical radicals of the type XV) could then give XIII and XIV.



XV

Support for this hypothesis was obtained by the reaction of 1-bromo-3,5-hexadiene (XI) with magnesium metal and cobaltous chloride, a reaction which is known to generate alkyl free radicals from the halide.[13] A 41% yield (based on bromide) of a hydrocarbon fraction was obtained, which consisted mainly of XIII and XIV, and a compound characterized by its spectra as 1-cyclopropylnona-1,6,8-triene (XVI), in the ratio 40:29:7.5, as well as other lower boiling unidentified compounds. Except for XVI the products are essentially the same as in the hydrocarbon fraction discussed



XVI

earlier, providing a measure of support for the postulation of free radicals as precursors of the coupling products XIII and XIV. The hydrocarbon XVI, composed of coupled γ-cyclopropylallyl and γ-vinylallylcarbinyl fragments, may arise because of local concentration of γ-vinylallylcarbinyl free radicals generated in the solution, not all of which have time to rearrange before coupling.

Although the present results do not allow one to make final conclusions concerning the mechanism of those rearrangements, it is at least apparent that vinyl and phenyl groups markedly enhance the ease of ring closure of allylcarbinyl free radicals and anions.

Experimental Section

All boiling points and most of the melting points are uncorrected. Corrected melting points were taken with a Reichert Kofler Block apparatus. Microanalyses were performed by Dr.

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[13] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 588.

A. Elek, Elek Microanalytical Laboratories, Los Angeles. Infrared spectra were run either on a double-beam Perkin-Elmer Model 21 infrared spectrophotometer or on a Beckman infrared spectrometer, Model IR-7. The vapor-phase chromatograms were obtained with a Perkin-Elmer vapor fractometer, Model 154-C, except where noted otherwise. The nuclear magnetic resonance spectra were recorded at 60 Mcps with the Varian Associates HR-50 or A-60 spectrometers.

Preparation of 4,4-Diphenyl-1-bromo-3-butene-1,1-d_2. β-Carbomethoxy-γ,γ-diphenylvinylacetic acid was prepared by Stobbe condensation of 29.2 g (0.16 mole) of benzophenone and 35.2 g (0.24 mole) of dimethyl succinate with potassium *t*-butoxide following the procedure of Johnson and Daub.[14] The only modifications were the addition of some benzene (15 ml) to the reaction mixture to prevent crystallization of the *t*-butyl alcohol in the condenser, and the use of dimethyl instead of diethyl succinate. The wet crystalline product was not purified further but was directly used in the ensuing decarboxylation reaction. A dried sample had mp 128–129°.

γ,γ-Diphenylvinylacetic acid was prepared from approximately 40 g (0.136 mole) of the foregoing β-carbomethoxy-γ,γ-diphenylvinylacetic acid by hydrolysis and decarboxylation in a mixture of 635 ml of glacial acetic acid, 423 ml of 48% aqueous hydrobromic acid, and 212 ml of water at reflux.[15] The product was recrystallized from aqueous ethanol and gave a first crop, 28.6 g, mp 117.5–119°, and a second crop of 4.9 g, mp 117–119° (total 87.7% based on benzophenone), lit[15] mp 117.5–118.5°.

4,4-Diphenyl-3-buten-1-ol-1,1-d_2. A solution of 14 g (58.9 mmoles) of γ,γ-diphenylvinylacetic acid in 80 ml of ether was added dropwise to a solution of 2.02 g (48.1 mmoles) of lithium aluminum deuteride in 75 ml of ether over 0.5 hr. The mixture was heated under reflux for 4 hr, then stirred for 40 hr at room temperature. A solution of 5 g of ammonium sulfate in 50 ml of water was added, and the resulting precipitate was removed by filtration through Celite. The ether layer of the filtrate was separated and the aqueous layer was extracted with two 30-ml portions of ether. The combined ether extracts were washed with water, dried over sodium sulfate, and evaporated. The residue was distilled through a Claisen head and gave 9.82 g (74%) of 4,4-diphenyl-3-buten-1-ol-1,1-d_2, bp 164–165° (2 mm), $n^{24}\text{D}$ 1.6069. The nmr spectrum of a carbon tetrachloride solution showed a phenyl singlet, vinyl triplet, hydroxyl singlet, and β-methylene doublet in agreement with the required structure. No α-methylene resonance was observed.

4,4-Diphenyl-3-buten-1-yl-1,1-d_2 *p*-Toluenesulfonate. Ten grams (52.5 mmoles) of *p*-toluenesulfonyl chloride was added to an ice-cooled, stirred solution of 9.5 g (42 mmoles) of 4,4-diphenyl-3-buten-1-ol-1,1-d_2 in 14 g (0.177 mole) of pyridine over 15 min. After a further 15 min, the mixture was stirred for 6 hr at room temperature, then poured into water, and extracted with four 100-ml portions of ether. The combined ether layers were washed with water, dried over calcium sulfate, and evaporated. The residue amounted to 12.9 g (80.5%) of 4,4-diphenyl-3-buten-1-yl-1,1-d_2 *p*-toluenesulfonate, mp 82–84°.

4,4-Diphenyl-1-bromo-3-butene-1,1-d_2. A solution of 12.9 g (33.9 mmoles) of 4,4-diphenyl-3-buten-1-yl-1,1-d_2 *p*-toluenesulfonate and 15 g (0.173 mole) of lithium bromide in 150 ml of acetone was heated under reflux for 3 hr. Most of the acetone was distilled off, and the residue was treated with 50 ml of water and extracted with four 75-ml portions of pentane. The pentane extracts were washed with water, dried over sodium sulfate, and evaporated. The residue was chromatographed on 100 g of alumina. Elution with pentane gave an eluate which was distilled through a Claisen head and yielded 8.71 g (89%) of 4,4-diphenyl-1-bromo-3-butene-1,1-d_2, bp 157–160° (2 mm), $n^{23}\text{D}$ 1.6157. The nmr spectrum of the product in carbon tetrachloride showed a phenyl singlet, vinyl triplet, β-methylene doublet, and only very small peaks due to an impurity. No α-methylene peaks were detected.

Grignard Reagent from 4,4-Diphenyl-1-bromo-3-butene-1,1-d_2. The Grignard reagent was maintained in an atmosphere of prepurified nitrogen throughout its preparation and transfer to an nmr tube. High-purity resublimed magnesium (0.15 g, 6.16 mg-atoms) in 5 ml of ether was activated by addition of several drops of 1,2-dibromoethane. A solution of 0.65 g (2.25 mmoles) of 4,4-diphenyl-1-bromo-3-butene-1,1-d_2 in 7 ml of ether was added dropwise with magnetic stirring at 20° over 1.75 hr. The mixture was stirred for an additional 3 hr at 20°, then filtered through a fritted-glass disk, and most of the ether was evaporated at 20° by passage of a current of nitrogen over the surface of the solution. The residual Grignard solution was poured into nmr tubes attached to the evaporation flask, and these were sealed under nitrogen. The nmr spectrum (Figure 1) of the Grignard reagent was taken 5 hr after the start of its preparation and was found to be invariant with time, so that equilibration of the α and β positions was complete in less than 5 hr at 20°. The spectrum also indicated the presence of substantial amounts of 1,1-diphenyl-1-butene with deuterium in the 3- and 4-positions, which gave rise to midfield methylene peaks, and a vinyl singlet superimposed on a vinyl triplet. A broad peak was also evident between the methyl resonance of the ether and its upfield ^{13}C-satellite which was reasonably attributed to cyclopropyl hydrogens. When 2.2 mmoles of methanol was added to the nmr sample, a dense white precipitate was formed, most of which on centrifugation went to the top of the tube. The nmr spectrum (Figure 2) of the liquid product was drastically simplified relative to that of the Grignard reagent. A superimposed vinyl triplet and singlet due to the α- and β-deuterated forms of 1,1-diphenyl-1-butene, respectively, a methylene triplet for the α-deuterated hydrocarbon, and a small broad peak in the cyclopropyl region were observed. The ratio of the intensity of the cyclopropyl peaks to the vinyl peaks was 1:6.96. Thus, the relative proportion of deuterated diphenylcyclopropylmethane is calculated to be 7%.

γ,γ-Diphenylallylcarbinyl Chloride and Bromide. γ,γ-Diphenylallylcarbinyl *p*-Toluenesulfonate. To a solution of 48.4 g (0.2 mole) of 1,1-diphenylbutane-1,4-diol, prepared by the method of Vozza,[16] in 70 ml of pyridine at 0° was added 50 g (0.26 mole) of *p*-toluenesulfonyl chloride over 0.5 hr. The mixture was stirred at room temperature for 5 hr, then poured into 250 ml of 2 *N* hydrochloric acid and extracted with 400 ml of ether in four portions. The ether extracts were washed repeatedly with 2 *N* hydrochloric acid, then with 2 *N* sodium bicarbonate solution and water. The solution was dried over sodium sulfate and evaporated. Crystallization of the residue from dichloromethane–pentane yielded needles, 26.8 g, mp 80–83.5°; second crop, 3.1 g, mp 82–83.5° (total 39.6%). Two crystallizations from methanol afforded an analytical sample, mp 84.5–85.5°.

Anal. Calcd for $C_{23}H_{22}O_3S$: C, 72.97; H, 5.86; S, 8.47. Found: C, 72.83; H, 5.77; S, 8.46.

The compound decolorized bromine and potassium permanganate and was further identified by bands at 1370, 1190, and 1178 cm^{-1} in the infrared spectrum due to the sulfonate group, and the lack of O–H absorption. Infrared examination of the mother liquor indicated the presence of considerable amounts of 2,2-diphenyltetrahydrofuran.

γ,γ-Diphenylallylcarbinyl Chloride from γ,γ-Diphenylallylcarbinyl *p*-Toluenesulfonate. A solution of 9.7 g (0.026 mole) of γ,γ-diphenylallylcarbinyl *p*-toluenesulfonate and 7 g (0.165 mole) of anhydrous lithium chloride in 100 ml of absolute ethanol was heated under reflux for 15 hr. Most of the ethanol was then evaporated and the residue was poured into water and extracted three times with 50 ml of ether. The ether extracts were dried over sodium sulfate and evaporated. The residue was distilled through a Claisen head and gave 6.05 g (97.1%) of the chloride, bp 150° (1 mm), $n^{24}\text{D}$ 1.5982. The chloride was unsaturated and the nmr spectrum of a carbon tetrachloride solution showed phenyl peaks, a vinyl triplet, α-methylene triplet, and β-methylene quartet.

Anal. Calcd for $C_{16}H_{15}Cl$: C, 79.20; H, 6.23; Cl, 14.61. Found: C, 79.31; H, 6.25; Cl, 14.49.

γ,γ-Diphenylallylcarbinyl Bromide (III) from γ,γ-Diphenylallylcarbinyl *p*-Toluenesulfonate. A solution of 15 g (0.04 mole) of the tosylate and 14 g (0.161 mole) of anhydrous lithium bromide in 200 ml of acetone was heated under reflux for 15 hr. The products were isolated as for γ,γ-diphenylallylcarbinyl chloride and gave 11.75 g of an oil which was chromatographed on 350 g of Merck alumina. Elution with pentane yielded an eluate which was distilled through a Claisen head to yield 10.24 g (90.1%) of γ,γ-diphenylallylcarbinyl bromide, bp 165–170° (2 mm), $n^{25}\text{D}$ 1.6150. The product was unsaturated and its infrared spectrum was very similar to that of γ,γ-diphenylallylcarbinyl chloride.

Anal. Calcd for $C_{16}H_{15}Br$: C, 66.91; H, 5.26; Br, 27.83. Found: C, 66.92; H, 5.20; Br, 27.82.

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(14) W. S. Johnson and G. H. Daub, *Org. Reactions*, **6**, 42 (1951).

(15) W. S. Johnson, J. W. Petersen, and W. P. Schneider, *J. Am. Chem. Soc.*, **69**, 74 (1947).

(16) J. F. Vozza, *J. Org. Chem.*, **24**, 720 (1959).

γ,γ-Diphenylallylcarbinyl Chloride from Diphenylcyclopropylcarbinol (II). A solution of 5 g (0.022 mole) of diphenylcyclopropylcarbinol, prepared from ethyl cyclopropanecarboxylate and phenylmagnesium bromide, and 2.1 g (0.027 mole) of acetyl chloride in 15 ml of benzene was heated under reflux for 6 hr. The excess acetyl chloride and solvent were then evaporated and the residue was distilled through a Claisen head and gave 4.94 g (91%) of a liquid, bp 162° (2.5 mm), identical in its infrared spectrum with that of the γ,γ-diphenylallylcarbinyl chloride described earlier.

γ,γ-Diphenylallylcarbinyl Bromide (III) from Diphenylcyclopropylcarbinol (II). A solution of 10 g (0.045 mole) of diphenylcyclopropylcarbinol in 20 ml of dichloromethane was added to 6 g (0.022 mole) of phosphorus tribromide over 0.5 hr with ice cooling. The mixture was stirred for 1 hr at room temperature; then the excess phosphorus tribromide was decomposed by addition of ice. The dichloromethane layer was separated, washed with water, dried over sodium sulfate, and evaporated. The residue was distilled through a Claisen head and yielded 12.0 g (93.8%) of bromide III, bp 169° (2 mm), $n^{24}\text{D}$ 1.6167, identical in infrared spectrum and nmr spectrum with γ,γ-diphenylallylcarbinyl bromide prepared from the corresponding tosylate. No trace of cyclopropyl absorption was detected, indicating that diphenylcyclopropylcarbinyl bromide[6] was not an isolable product of the reaction.

Preparation of Ethanol-2-d_3. Tetradeuterioacetic acid (17.7 g) was added dropwise with stirring to an ice-cooled solution of sodium borohydride (10.0 g) in diglyme (200 ml) over a period of about 20 min. This was followed by the addition, over 1 hr at 0°, of 70 g of boron trifluoride mono(di-*n*-butyl etherate), bp 86–88° (60 mm), prepared by bubbling boron trifluoride into di-*n*-butyl ether below 60°. The reaction mixture was then stirred at room temperature for 19 hr; then 20 ml of 11 *N* hydrochloric acid was added carefully, followed by 250 ml of water. After an hour, the layers were separated, the organic layer was extracted twice with water, and the combined aqueous layers were distilled through a 9-in. column packed with glass helices to give the deuterio alcohol as a 71% molar solution in water (15.4 g, 81% yield). The solution was analyzed by nmr (comparison of the intensities of the OH and CH_2 peaks).

Preparation of Hexadeuteriodiethyl Ether. A total of 30.8 g of the aqueous deuterioethanol solution prepared as described above was passed over dehydrated alum at 226° in a stream of nitrogen.[17] The product was collected in traps cooled to −78° and was distilled through a 9-in. column to give the crude ether (11.8 g), bp 25–40°. The residue was repyrolyzed to give a further amount of crude ether (2.1 g). The ether was dried over magnesium sulfate, distilled, refluxed with lithium aluminum hydride, redistilled, and stored over sodium. The nmr spectrum of the pure ether (6.8 g) showed that the minor peaks due to the CD_2H group were no larger than in the original perdeuterioacetic acid.

Preparation of γ,γ-Diphenylallylcarbinylmagnesium Bromide (IV) in Hexadeuteriodiethyl Ether. An nmr tube was half-filled with the deuterated ether, and a few small turnings of high-purity resublimed magnesium were added. The turnings were punctured several times with a tantalum rod (this enables the Grignard reaction to start more easily), and the tube was heated until the ether refluxed gently for a few minutes. Two drops of γ,γ-diphenylallylcarbinyl bromide was then added and the reaction began immediately. When the bromide had reacted, another drop was added; this was continued until the magnesium had almost all dissolved, when more magnesium was added followed by more bromide. The reaction was terminated when about a 20% solution had been made. The Grignard reagent was then centrifuged and the clear supernatant liquid was decanted, under nitrogen, into another nmr tube. The nmr spectrum showed a triplet at 0.5 ppm upfield from TMS due to the α-methylene group of the Grignard reagent, and there were several small peaks in the cyclopropyl region corresponding to about 3% of cyclopropane species in the solution.

Synthesis of Diphenylcyclopropylmethane (VII). Diethyl benzhydrylmalonate was prepared by the procedure of Gupte and Sunthankar.[18] The product from the reaction of 43.2 g (0.2 mole) of diethyl ethoxymethylenemalonate with phenylmagnesium bromide, prepared from 72 g (0.45 mole) of bromobenzene, was distilled through a Claisen head and gave a forerun, 7.45 g, bp 100–180° (3 mm), and a main fraction, 53.1 g, bp 180–240° (3 mm). The main fraction crystallized from hexane as needles, 45.1 g (69%), mp 50.5–52.5°, lit[18] mp 53°.

2-Benzhydrylpropane-1,3-diol. To a solution of 1.5 g (39.5 mmoles) of lithium aluminum hydride in 50 ml of ether was added a solution of 10 g (30.7 mmoles) of diethyl benzhydrylmalonate in 30 ml of ether at such a rate as to keep the ether refluxing (0.5 hr). The mixture was heated under reflux for a total of 6 hr and allowed to stand for 15 hr. Excess hydride was decomposed with 5 ml of *t*-butyl alcohol; then 15 ml of water and 150 ml of 6 *N* sulfuric acid were added. The ether layer was washed with a sodium bicarbonate solution and water, dried over sodium sulfate, and on evaporation of the solvent yielded 8 g. of crystals which were recrystallized from benzene–ligroin. There was obtained 6.42 g (86.5%) of 2-benzhydrylpropane-1,3-diol as needles, mp 79–81°. The infrared spectrum in carbon tetrachloride showed strong hydroxyl bands at 3600, 3340, and 1030 cm^{-1}. An analytical sample was recrystallized twice from benzene–ligroin and had mp 81–82°.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.46; H, 7.55.

2-Benzhydryl-1,3-dibromopropane. A mixture of 10.32 g (61.2 mmoles) of 48% aqueous hydrobromic acid and 1.68 ml of concentrated sulfuric acid was added dropwise to 6 g (24.8 mmoles) of the diol over 10 min with stirring. Concentrated sulfuric acid (2.7 ml) was then added over 15 min. The mixture was heated at 120° for 6 hr, a brown upper layer being formed after 10 min of heating, then poured into water, and extracted with three 50-ml portions of ether. The ether extracts were washed with a sodium bicarbonate solution and water, dried over sodium sulfate, and when evaporated yielded 8.2 g of crude product, which was chromatographed on 210 g of Merck alumina. Elution with pentane and 1:1 benzene–pentane gave an eluate which after distillation at 1.5 mm (bath temperature 160°) yielded 0.77 g of an oil which subsequently crystallized. The product was recrystallized from pentane forming flat needles, mp 78.5–80°. The compound was saturated and gave a positive Beilstein halogen test. Its infrared spectrum (carbon tetrachloride solution) showed no hydroxyl bands but had sharp peaks at 1430 and 1260 cm^{-1}. Two further crystallizations from pentane afforded an analytical sample, mp 80–81°.

Anal. Calcd for $C_{16}H_{16}Br_2$: C, 52.22; H, 4.38; Br, 43.42. Found: C, 52.12; H, 4.50; Br, 43.25.

Further elution with ether afforded a liquid eluate which was distilled at 1.5 mm with a bath at 190° and yielded 3.79 g of a viscous oil which did not crystallize. The infrared spectrum was similar to that of the first eluate except for the presence of weak hydroxyl bands at 3620 and 3400 cm^{-1}.

Diphenylcyclopropylmethane (VII) from 2-Benzhydryl-1,3-dibromopropane. To a solution of 2.32 g (6.3 mmoles) of 2-benzhydryl-1,3-dibromopropane in 3 ml of 95% ethanol and 0.3 ml of water was added 1.7 g (26 mg-atoms) of zinc dust, and the mixture was heated under reflux for 5 hr. The zinc was removed by filtration and washed with ethanol. The filtrate was poured into water and extracted with three 50-ml portions of ether. The ether extracts were washed with water, dried over sodium sulfate, and evaporated. The residue after distillation at a bath temperature of 160° (1.5 mm) afforded 1.34 g of saturated product, giving a negative Beilstein test. The product was chromatographed on 40 g of alumina. Elution with pentane gave an eluate which was distilled at 1.5 mm with a bath at 140° and yielded 0.585 g (44.7%) of diphenylcyclopropylmethane, $n^{22.5}\text{D}$ 1.5747. The product was shown to be better than 99% pure by vpc. Its infrared spectrum (carbon tetrachloride solution) showed a cyclopropyl band at 1019 cm^{-1} and a band at 727 cm^{-1}. The nmr spectrum showed phenyl peaks, a benzhydryl doublet, a cyclopropyl methine multiplet, and complex upfield cyclopropyl methylene peaks.

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.06; H, 7.74.

Reactions of γ,γ-Diphenylallylcarbinylmagnesium Bromide (IV). (a) Carbon Dioxide. The Grignard reagent was prepared from 7.02 g (27.8 mmoles) of γ,γ-diphenylallylcarbinyl bromide and 0.75 g (30.9 mg-atoms) of magnesium in 30 ml of ether, and heated under reflux for 1 hr. Then an excess of solid carbon dioxide was added. The mixture was acidified with 2 *N* sulfuric acid; the ether layer was separated, washed with water, and extracted several times with a 10% sodium carbonate solution. The sodium carbonate extracts were acidified with 5 *N* hydrochloric acid and then extracted with four 30-ml portions of ether. The ether extracts were washed twice with water, dried over sodium sulfate, and evaporated. The crystalline residue after crystallization from hexane yielded 4.25 g (69%) of γ,γ-diphenylallylacetic acid, mp 81.5–83°. The infrared spectrum in chloroform showed bands at 3480 (weak), 2300–2700 (broad), and 1710 cm^{-1} (strong), typical of a carboxyl

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[17] S. K. K. Jatkar and H. E. Watson, *J. Indian Inst. Sci.*, **9A**, 71 (1926); *J. Soc. Chem. Ind.*, **45**, 168 (1926).

[18] S. D. Gupte and S. V. Sunthankar, *J. Org. Chem.*, **24**, 1334 (1959).

group. The nmr spectrum showed a carboxyl singlet, phenyl peaks, a vinyl triplet, and a broad peak due to overlapping α- and β-methylene resonances. An analytical sample had mp 83–83.5°.

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.77; H, 6.16.

Hydrogenation of a sample with hydrogen and platinum oxide as the catalyst afforded 5,5-diphenylpentanoic acid in 90% yield, mp 90–92.5° cor, lit[19] 89–90°. The nmr spectrum of a chloroform solution showed a carboxyl singlet, phenyl singlet, benzhydryl triplet, and broad multiplet due to overlapping methylene peaks.

The ether layer remaining after extraction of the carboxylic acid was washed with water, dried over sodium sulfate, and evaporated. The residue was distilled at 2 mm with a bath at 150° and gave 0.83 g (14.3%) of distillate and 0.58 g of residue. Analysis of the distillate by vpc at 250° (Apiezon L grease on firebrick) indicated the presence of diphenylcyclopropylmethane (21.5%), 1,1-diphenyl-1-butene (78.5%), and an unidentified component of longer retention time (23% of total).

In another preparation, the Grignard reagent from 25.4 g (88.5 mmoles) of γ,γ-diphenylallylcarbinyl bromide and 3 g (0.123 g-atom) of magnesium in 100 ml of ether was carbonated, and 17.1 g (76.8%) of γ,γ-diphenylallylacetic acid was isolated in the same way. The neutral fraction gave 1.85 g (10.1%) of distillate and 2 g of residue (tar). Vpc analysis showed diphenylcyclopropylmethane (28.5%), 1,1-diphenyl-1-butene (71.5%), and a small amount of the longer retention time component. The highest yield of γ,γ-diphenylallylacetic acid isolated from this reaction was 81.8%. The same acid was obtained by starting with γ,γ-diphenylallylcarbinyl chloride. The yield and composition of the neutral fraction was essentially unaffected when the powdered solid carbon dioxide was pumped out for 10 min to ensure removal of oxygen.

(b) Mercuric Bromide. The Grignard reagent prepared from 5.76 g (20 mmoles) of γ,γ-diphenylallylcarbinyl bromide and 0.6 g of magnesium in 25 ml of ether was added dropwise to a vigorously stirred suspension of 8.22 g (22.4 mmoles) of mercuric bromide in 15 ml of ether over 15 min. The mixture was heated under reflux for 2 hr and then stirred at room temperature for 24 hr. Water and 5% acetic acid were added; the ether layer was separated, washed with water, and evaporated. The resulting solid was washed with hot 2% acetic acid on a Büchner funnel, then dried, and crystallized from ethanol. There was obtained 2.37 g of γ,γ-diphenylallylcarbinylmercuric bromide as needles, mp 117.5–120°. Two further crystallizations from ethanol and one from acetone gave an analytical sample, mp 123–124°. The mother liquors from the various crystallizations and washings were combined and evaporated and gave 2.24 g of residue, which was chromatographed on 67 g of alumina. Elution with pentane and distillation of the eluate at 2.5 mm with a bath at 140° afforded 0.743 g (17.9%) of distillate containing 1,1-diphenyl-1-butene (74%) and diphenylcyclopropylmethane (26%) according to vpc analysis. Elution with ether afforded 0.524 g of γ,γ-diphenylallylcarbinylmercuric bromide, mp 119.5–120.5° after crystallization from ethanol. Thus, the total yield of the mercurial was 29.5%. The infrared spectrum of a chloroform solution of the product showed aromatic absorption and bands at 1215, 1137, 1070, and 1030 cm^{-1}. The nmr spectrum of the mercurial in pyridine showed a vinyl triplet, β-methylene quartet, and α-methylene triplet.

Anal. Calcd for $C_{16}H_{15}HgBr$: C, 39.41; H, 3.10; Br, 16.39. Found: C, 39.32; H, 3.21; Br, 16.37.

(c) Oxygen. The Grignard reagent was prepared from 10.7 g (37.8 mmoles) of γ,γ-diphenylallylcarbinyl bromide and 1 g (41.2 mg-atoms) of magnesium in 60 ml of ether. The mixture was heated under reflux for 2 hr, then cooled to −20°, and oxygen was passed over the solution for 4 hr at −20° with stirring. A solution of 5 g of ammonium chloride in 17 ml of water was then added. The ether layer was decanted and the residual paste was extracted with two 40-ml portions of ether. The combined ether layers were washed with water, dried over sodium sulfate, and evaporated. Distillation of the resulting oil through a micro-Claisen head gave four fractions (1 mm): (a) 1.46 g, bp 110–147°; (b) 2.23 g, bp 147–158°; (c) 1.80 g, bp 158–164°; (d) 1.66 g, bp 164–165°; and 0.57 g of residue. On standing for several days fraction b partially crystallized. Recrystallization from ligroin yielded 0.24 g of prisms, mp 82–84° undepressed on admixture with authentic diphenylcyclopropylcarbinol (II). The other fractions could not be induced to crystallize. Infrared and nmr spectra of fractions a and d indicated the presence of 1,1-diphenyl-1-butene and γ,γ-diphenylallylcarbinol (V), respectively. Each fraction was chromatographed on alumina (30 g to 1 g of mixture); the over-all chromatographic results corrected for losses prior to, and during, chromatography are given below.

Elution with pentane afforded 1.48 g (18.9%) of a hydrocarbon fraction. Elution with 2–10% ether–benzene gave diphenylcyclopropylcarbinol (II), 1.64 g (19.3%), mp 84–85° on crystallization from ligroin. Elution with ether yielded γ,γ-diphenylallylcarbinol (V), 4.02 g (47.5%). The nmr spectrum of the latter showed a phenyl peak, vinyl triplet, hydroxyl singlet, α-methylene triplet, and β-methylene quartet. Further characterization through reaction with bromine in chloroform gave 1,1-diphenyl-1,2-dibromobutan-4-ol as prisms (from hexane), mp 95–96.5°, lit[16] 96–97°. The hydrocarbon fraction was distilled at 1 mm with a bath at 120°. Analysis by vpc at 250° showed peaks due to diphenylcyclopropylmethane (23%), 1,1-diphenyl-1-butene (77%), and a minor unidentified component of longer retention time. The nmr spectrum of this fraction showed peaks characteristic of both the hydrocarbons.

(d) Ammonium Chloride Solution. The Grignard reagent prepared from 10 g (34.8 mmoles) of γ,γ-diphenylallylcarbinyl bromide and 1 g (41.2 mg-atoms) of magnesium in 50 ml of ether was heated under reflux for 3 hr; then 12 ml of a solution of 7.6 g of ammonium chloride in 23 ml of water was added dropwise with stirring. The ether layer was decanted, the residual paste was extracted twice with ether, and the combined ether layers were washed with ammonium chloride solution and water, dried over sodium sulfate, and evaporated. The product was distilled through a micro-Claisen head and gave 6.56 g (90.5%) of hydrocarbon, bp 117° (1.5 mm), $n^{22}D$ 1.5902, lit[20] for 1,1-diphenyl-1-butene, bp 109° (0.4 mm), $n^{20}D$ 1.5904; and 0.4 g of residue. The product was strongly unsaturated and its nmr spectrum showed a phenyl peak, vinyl triplet, methylene quintet, and methyl triplet. However, vpc analysis at 250° indicated that it consisted of 1,1-diphenyl-1-butene (96%) and diphenylcyclopropylmethane (4%). When the reaction was carried out in air 8% of the cyclopropyl compound was formed.

(e) Methanol. The Grignard reagent prepared from 2.1 g (7.29 mmoles) of the bromide and 0.3 g (12.3 mg-atoms) of magnesium in 10 ml of ether was heated under reflux for 2.5 hr. Anhydrous methanol, 0.24 g (7.43 mmoles), was added; the mixture was stirred for 15 min and then filtered through Celite. The filtrate was evaporated and the residue was distilled at 2 mm with a bath at 150° and afforded 1.31 g (86.6%) of distillate and 0.175 g of residue. Analysis by vpc at 270° indicated that the distillate was composed of 1,1-diphenyl-1-butene (95%) and diphenylcyclopropylmethane (5%).

(f) Hydrogen Chloride. The Grignard reagent prepared from 1.44 g (5 mmoles) of the bromide and 0.2 g (8.2 mg-atoms) of magnesium in 8 ml of ether was heated under reflux for 2 hr. Anhydrous hydrogen chloride gas was passed through a calcium chloride drying tube and over the surface of the Grignard reagent with rapid stirring and ice cooling. A fairly rapid gas flow was maintained for 15 min. When 10 ml of water was added, a rapid reaction involving the excess magnesium took place. The ether layer was separated, washed with 2 *N* sodium bicarbonate solution and water, dried over sodium sulfate, and evaporated. The residue was distilled at 2.5 mm with a bath at 140° and yielded 0.93 g (89.5%) of distillate and 0.18 g of residue. Vpc analysis of the distillate at 240° showed 1,1-diphenyl-1-butene (91%) and diphenylcyclopropylmethane (9%).

(g) Phenylacetylene. The Grignard reagent from 2.88 g (0.01 mole) of γ,γ-diphenylallylcarbinyl bromide and 0.3 g (12.35 mg-atoms) of magnesium in 15 ml of ether was heated under reflux for 2 hr. A solution of 1.2 g (11.75 mmoles) of phenylacetylene in 5 ml of ether was added over 5 min. The mixture was refluxed for 0.75 hr, then stirred for 15 hr. A solution of 3 g of ammonium chloride in 10 ml of water was added, and the ether layer was separated, dried over sodium sulfate, and evaporated. The residue was distilled at 2.5 mm with a bath at 145° and gave 1.88 g (90.5%) of distillate and 0.33 g of residue. Analysis by vpc at 250° indicated that the distillate consisted of 1,1-diphenyl-1-butene (90%) and diphenylcyclopropylmethane (10%).

(h) Cobaltous Chloride. The Grignard reagent from 5 g (17.4 mmoles) of bromide and 0.5 g (20.6 mg-atoms) of magnesium in 25

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(19) F. Salmon-Legagneur and C. Neven, *Compt. Rend.*, **239**, 1811 (1954).

(20) A. W. Schmidt and C. Hartmann, *Ber. Deut. Chem. Ges.*, **74B**, 1325 (1941).

ml of ether was heated under reflux for 2 hr. Anhydrous cobaltous chloride, 0.1 g (0.77 mmole), was added and the mixture was heated under reflux for a total of 16.5 hr and stirred at room temperature for 38 hr. Excess solid carbon dioxide was then added to decompose the remaining Grignard reagent, followed by a solution of 3.8 g of ammonium chloride in 12 ml of water. The same isolation procedure used for previous carbonations afforded 2.2 g of crude acid crystallized from hexane as prisms of γ,γ-diphenylallylacetic acid, 1.72 g (39.2%), mp 80.5–82°. The neutral fraction was distilled at 2 mm with a bath at 150° and gave 1.27 g (35.1%) of distillate and 0.61 g of residue. Analysis by vpc at 250° showed that the distillate consisted of 1,1-diphenyl-1-butene (65%) and diphenylcyclopropylmethane (35%).

(i) **Deuterium Oxide.** The Grignard reagent from 5.0 g (17.4 mmoles) of bromide and 1.0 g (41.2 mg-atoms) of magnesium in 50 ml of ether was stirred for 3 hr at room temperature before 2.0 ml of deuterium oxide was added. After 15 min of further stirring, saturated ammonium chloride solution was added. The hydrocarbon mixture isolated in the usual manner was distilled at 2 mm with a bath at 150–190° and gave 3.01 g of distillate and 0.44 g of residue. The distillate contained 1,1-diphenyl-1-butene (97%) and diphenylcyclopropylmethane (3 ± 0.5%) only. Separation by preparative scale vpc at 210° on Apiezon gave two fractions. Fraction a was pure 1,1-diphenyl-1-butene-4-*d* (VI), 0.91 g, identified by its nmr spectrum in carbon tetrachloride: phenyl multiplet centered at δ 7.0 ppm, vinyl triplet (J = 8 cps) at δ 5.87 ppm, quadruplet (J = 8 cps) at δ 1.95 ppm (β-methylene group), and triplet (J = 8 cps) at δ 0.85 ppm ($-CH_2D$ group). Fraction b, 0.19 g, was an 80:20 mixture (by vpc) of 1,1-diphenyl-1-butene and diphenylcyclopropylmethane. The nmr spectrum in carbon tetrachloride showed a doublet (J = 9 cps) at δ 3.17 ppm due to the benzhydryl proton of diphenylcyclopropylmethane. Comparison of the intensity of this doublet with the cyclopropyl peaks showed that less than 10% of deuterated compound could have been present.

Preparation of γ,γ-Diphenylallylcarbinylmagnesium Bromide (IV) in Tetrahydrofuran. (a) Hydrolysis with Deuterium Oxide. The Grignard reagent was prepared under argon (magnetic stirrer) from 2.87 g (10 mmoles) of γ,γ-diphenylallylcarbinyl bromide and 0.25 g (10.3 mg-atoms) of magnesium in 20 ml of tetrahydrofuran. After 0.5 hr without external heating, the mixture was heated under reflux for 1.5 hr. After hydrolysis with 5 ml of deuterium oxide, ammonium chloride solution was added and the aqueous mixture was extracted twice with ether. The combined ether layers were washed with water and dried over sodium sulfate. Evaporation of the solvent yielded 2.06 g (99.5%) of a crude product, most of which resinified during distillation. A total of 0.79 g of distillate at bp 75–85° (0.1 mm) was obtained. The crude product according to nmr spectroscopy consisted of 1,1-diphenyl-1-butene-4-*d* (50%, exact amount of deuterium not determined), diphenylcyclopropylmethane (20%), and 1,1-diphenyl-1,3-butadiene (5%) as well as an unknown high-boiling material not detectable by vpc. The distillate according to vpc analysis and nmr spectroscopy was a mixture of 1,1-diphenyl-1-butene-4-*d* (50%), 1,1-diphenyl-1-butene (17%), diphenylcyclopropylmethane (24%, deuterium free), and 1,1-diphenyl-1,3-butadiene (9%), free of other impurities. It is reasonable to assume that one-fourth of the original 50% of 1,1-diphenyl-1-butene in the crude product, also, was deuterium free.

An analogous run after a reflux time of 6 hr gave 2.09 g of crude product consisting of 1,1-diphenyl-1-butene (50%) and diphenylcyclopropylmethane (18%). This time only a trace of 1,1-diphenyl-1,3-butadiene could be detected by vpc analysis. The distillate (0.71 g) consisted of 1,1-diphenyl-1-butene-4-*d* (36.5%), 1,1-diphenyl-1-butene (36.5%), and diphenylcyclopropylmethane (27%, deuterium free).

(b) **Carbonation.** The Grignard reagent prepared in tetrahydrofuran as described above was heated under reflux for 1.5 hr and on carbonation gave 573 mg (23%) of γ,γ-diphenylallylacetic acid, mp 77–81°, and 1.50 g (72%) of crude neutral material, most of which resinified during distillation. The crude product contained diphenylcyclopropylmethane (23%, total yield 17%), 1,1-diphenyl-1-butene (17%, total yield 12%), and 1,1-diphenyl-1,3-butadiene (14%, total yield 10%). The distillate, 374 mg, bp 76–82° (0.05 mm), consisted of diphenylcyclopropylmethane (40%), 1,1-diphenyl-1-butene (32%), and 1,1-diphenyl-1,3-butadiene (13%).

β-Phenylallylcarbinyl Chloride (VIII). 2-Phenylbutane-1,4-diol. A solution of 19.5 g (0.1 mole) of phenylsuccinic acid[21] in 500 ml of ether was added to 12.5 g (0.329 mole) of lithium aluminum hydride in 400 ml of ether with magnetic stirring. The addition took 2 hr, and the mixture was heated under reflux for a further 20 hr. Ice–water (50 ml) was then added cautiously followed by 200 ml of 6 *N* sulfuric acid. The ether layer was separated and combined with two 100-ml ether extracts of the aqueous layer. The ether solution was washed with sodium bicarbonate solution and water, dried over sodium sulfate, and evaporated. The combined aqueous washings were continuously extracted with ether for 15 hr, and the resulting extract was added to the main product. Distillation of the product through a Claisen head afforded 12.2 g (73%) of 2-phenylbutane-1,4-diol as a viscous oil, bp 170° (4 mm), lit[22] 165° (4 mm). After several weeks, the diol crystallized and had mp 63–67° without further purification; lit[23] 70°.

1,4-(2-Phenyl)butyl Bis(*p*-Toluenesulfonate). *p*-Toluenesulfonyl chloride, 4.1 g (22 mmoles), was added portionwise to a solution of 1.66 g (10 mmoles) of 2-phenylbutane-1,4-diol in 6.3 g (80 mmoles) of pyridine over 0.5 hr at 10° with stirring. The mixture was stirred for 3 hr at 15°; then 5 ml of water was added, followed by 12 ml of concentrated hydrochloric acid in 40 ml of water. The mixture was extracted with four 40-ml portions of ether, and the ether layer was washed repeatedly with 2 *N* hydrochloric acid, then with sodium bicarbonate solution, and water. The resulting ether solution was dried over sodium sulfate and when evaporated yielded 4.3 g of oil. The product crystallized from acetone–methanol as needles, 3.14 g, mp 70–73°; second crop, 1.09 g, mp 72–74° (total yield 77%). Its infrared spectrum in carbon tetrachloride showed phenyl absorption and strong tosylate bands at 1370, 1190, and 1178 cm^{-1}. Two further crystallizations from methanol afforded an analytical sample, mp 73–74°.

Anal. Calcd for $C_{24}H_{26}O_6S_2$: C, 60.73; H, 5.52; S, 13.52. Found: C, 60.92; H, 5.56; S, 13.60.

4-Chloro-2-phenylbutyl *p*-Toluenesulfonate. A solution of 2.1 g (49.5 mmoles) of anhydrous lithium chloride in 125 ml of dry acetone was added dropwise to a refluxing solution of 21.2 g (44.7 mmoles) of 1,4-(2-phenyl)butyl bis-*p*-toluenesulfonate in 50 ml of acetone over 0.5 hr. The mixture was refluxed for 17 hr, concentrated on the steam bath to about 40 ml, then poured into 250 ml of water, and extracted with three 50-ml portions of ether. The ether extracts were washed with water, dried over sodium sulfate, and evaporated. The residue crystallized from acetone–methanol as needles of 4-chloro-2-phenylbutyl *p*-toluenesulfonate, 11.5 g (76%), mp 90–92°. Three further crystallizations from methanol afforded an analytical sample, mp 91–92°.

Anal. Calcd for $C_{17}H_{19}O_3SCl$: C, 60.27; H, 5.64; S, 9.46; Cl, 10.47. Found: C, 59.80; H, 5.34; S, 9.92; Cl, 10.29.

β-Phenylallylcarbinyl Chloride (VIII). A solution of 1.1 g (19.6 mmoles) of potassium hydroxide in 20 ml of absolute ethanol was added to a refluxing solution of 6 g (17.7 mmoles) of the above chlorotosylate in 60 ml of anhydrous *t*-butyl alcohol over 1 hr. The mixture was heated under reflux for 1 hr, concentrated to 25 ml under reduced pressure, then poured into 200 ml of water, and extracted with three 75-ml portions of ether. The ether extracts were washed with water, dried over sodium sulfate, and evaporated. Pentane, 20 ml, was added to the resulting oil, and 1.49 g of unreacted chlorotosylate, mp 92–93°, crystallized and was removed by filtration. The filtrate was chromatographed on 90 g of alumina. Elution with pentane afforded a liquid eluate which was distilled at 3 mm with a bath at 100° and gave 1.18 g of distillate. Analysis by vpc at 175° showed that the distillate consisted of 20% of a short retention time component and 80% of β-phenylallylcarbinyl chloride. Thus the yield of the latter based on reacted chlorotosylate was 42%. Redistillation yielded the short retention time component, bp 60–62° (16 mm), which was tentatively identified by its infrared and nmr spectra as 2-phenyl-1,3-butadiene, and pure β-phenylallylcarbinyl chloride, bp 80–82° (7 mm), $n^{25}\text{D}$ 1.5480. The latter was unsaturated and gave a positive Beilstein test. Its infrared spectrum in carbon tetrachloride showed bands at 1633 and 904 cm^{-1} due to the $C{=}CH_2$ group and phenyl absorption, and a weak band at 1575 cm^{-1} due to phenyl conjugated with a double bond. The nmr spectrum showed phenyl peaks, a vinyl doublet with considerable secondary splitting, an α-methylene triplet, and a β-methylene triplet.

Anal. Calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.66; Cl, 21.28. Found: C, 72.03; H, 6.70; Cl, 20.75.

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[21] A. Lapworth and W. Baker, "Organic Synthesis," Coll. Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1941, p 451.

[22] R. H. Manske, *J. Am. Chem. Soc.*, **53**, 1104 (1931).

[23] C. F. H. Allen, C. V. Wilson, and W. L. Ball, *Can. J. Res.* **9**, 432 (1933).

β-Phenylallylacetic Acid (IX). The Grignard reagent from β-phenylallylcarbinyl chloride was prepared using the entrainment method.[24] A solution of 1.13 g (6 mmoles) of 1,2-dibromoethane in 15 ml of ether was added dropwise to a refluxing solution of 1 g (6 mmoles) of β-phenylallylcarbinyl chloride and 0.4 g (16.5 mg-atoms) of magnesium in 25 ml of ether over 15 hr. Excess solid carbon dioxide was added, followed by 5 ml of concentrated hydrochloric acid in 20 ml of ice–water. The usual isolation procedure yielded a crystalline acid (0.83 g) which, when recrystallized from ligroin, gave large plates of β-phenylallylacetic acid, 0.64 g (60.6%), mp 96–97.5°. The acid was unsaturated and depressed the melting point of authentic 1-phenylcyclobutanecarboxylic acid (mp 105–106.5°) to 72–90°. The infrared spectrum of the acid in chloroform showed phenyl absorption, carboxyl peaks at 3470, 3010, 2650, 1710, and 1290 cm^{-1}, a weak band at 1575 cm^{-1} due to phenyl conjugated with a double bond, and bands at 1633 and 902 cm^{-1} due to $C{=}CH_2$. The nmr spectrum of a chloroform solution showed a carboxyl singlet, phenyl peak, vinyl doublet, and overlapping triplets due to α- and β-methylene groups.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.85; H, 6.87.

3,5-Hexadien-1-ol. A solution of 17.7 g (0.158 mole) of crude 3,5-hexadienoic acid[25] in 70 ml of ether was added to 6.1 g (0.16 mole) of lithium aluminum hydride in 100 ml of ether over 0.5 hr. The mixture was heated under reflux for 3 hr and then stirred at room temperature for 15 hr. Water was added, followed by sufficient 2 *N* sulfuric acid to dissolve the resulitng paste. The ether layer was separated, the aqueous layer was extracted twice with ether, and the combined ether layers were washed with sodium bicarbonate solution and water. The ether solution was dried over sodium sulfate and evaporated under reduced pressure. Distillation of the residue through a Vigreux head at 30 mm yielded the following fractions: (a) 1.23 g, bp 30–79°; (b) 3.25 g, bp 79–82°; (c) 4.84 g, bp 82°; (d) 0.68 g, bp 82°, $n^{22.5}$D 1.4890; (e) 1.18 g, boiling point not determined. The total yield of crude 3,5-hexadien-1-ol was thus 11.2 g (72%). Analysis by vpc at 120° showed that fraction a contained about 25% of 3,5-hexadien-1-ol as well as water and two unidentified components of shorter retention time than the dienol. Fractions b and c consisted predominantly of the dienol plus small amounts of the latter components, while fraction d was essentially pure 3,5-hexadien-1-ol and was used for analysis and spectral characterization. Fraction e contained a trace of higher boiling material.

Anal. Calcd for $C_6H_{10}O$ (fraction d): C, 73.43; H, 10.27. Found: C, 72.96; H, 10.40.

The infrared spectrum of the dienol showed bands (cm^{-1}) at 3620, 3330, and 1043 due to hydroxyl, 3070 and 3000 due to vinyl CH, 1657 and 1608 from conjugated C=C, 1002 and 902 for $-CH{=}CH_2$, and 950 due to $-CH{=}CH-$. Evidence for the conjugated diene system was gained by the ultraviolet spectrum in cyclohexane (c = 0.102 mmole/l.) which showed an intense maximum at 2260 A, log ϵ = 4.3, characteristic of conjugated dienes.[26] The nmr spectrum showed a complex vinyl region, hydroxyl singlet, α-methylene triplet, and β-methylene quintet.

The nmr spectrum of the corresponding bromide (Figure 4) shows a very similar quintet (at 157 cps) for the β-methylene protons. At first sight, these quintet resonances would seem to *exclude* the structures assigned to these compounds. However, as has been pointed out before,[27] in regard to the specific type of structure under consideration here, ABX-type systems with $J_{AX} << J_{BX}$ may give spectra which appear to be of the A_2X type provided that $J_{AB} > J_{BX}$ and $\nu_A - \nu_B$ is small. For the compounds under consideration, this means that the vinyl protons of the $-CH{=}CH{-}CH_2-$ part of the molecule must be rather strongly coupled and have about the same chemical shift.

A rather large number of theoretical spectra were calculated using reasonable parameters for the $-CH{=}CHCH_2CH_2-$ part of the system which was taken to be of the ABXX′YY′ type. It was found possible to reproduce the general line positions quite well with $\nu_A = 360.0$, $\nu_B = 360.0$, $\nu_X = \nu_{X'} = 157.5$, $\nu_Y = \nu_{Y'} = 198.5$, $J_{AB} = 18.0$, $J_{AX} = J_{AX'} = 3.0$, $J_{BX} = J_{BX'} = 11.0$, $J_{AY} = J_{AY'} = J_{BY} = J_{BY'} = 0$, $J_{XX'} = -12.0$, $J_{YY'} = -12.0$, $J_{XY} = J_{X'Y'} = 7.0$, and $J_{XY'} = J_{X'Y} = 7.7$ (all values in cps). The intensities were rather less satisfactory, and the nearly absolute symmetry of the β-methylene quintet was particularly puzzling. It is planned to investigate the spectral problem presented by these compounds in more detail using double resonance or deuterium-labeling techniques.

1-Hexa-3,5-dienyl *p*-Toluenesulfonate. *p*-Toluenesulfonyl chloride, 7 g (36.8 mmoles), was added to a solution of 3.26 g (33.3 mmoles) of 3,5-hexadien-1-ol in 10.5 g (0.133 mole) of pyridine at 5° over 15 min. The mixture was stirred for 3.5 hr at room temperature, then poured into water, and extracted with three 50-ml portions of ether. The ether extracts were washed repeatedly with water, dried over sodium sulfate, and when evaporated under reduced pressure yielded 6.95 g (83%) of the crude tosylate as a colorless liquid which was not purified further.

1-Bromo-3,5-hexadiene (XI). A solution of 18.6 g (74 mmoles) of crude 1-hexa-3,5-dienyl *p*-toluenesulfonate and 30 g (0.345 mole) of anhydrous lithium bromide in 90 ml of dry acetone was heated under reflux for 1.5 hr. Most of the acetone was removed by distillation through a 12-in Vigreux column, and the residue was poured into water and extracted with three 70-ml portions of pentane. The pentane extracts were washed with water and dried over sodium sulfate; the solvent was distilled off through a 12-in. Vigreux column. The residue was fractionated through a Vigreux head at 40 mm and gave the following fractions: (a) 2.51 g, bp 55–68°; (b) 1.57 g, bp 68–72°; (c) 2.13 g, bp 72–75°; (d) 1.03 g, bp 75°, $n^{22.5}$D 1.5170; (e) 1.63 g, boiling point not determined. Vpc analysis at 103° showed that fractions d and e were pure 1-bromo-3,5-hexadiene, while fractions b and c also contained small amounts, and fraction a contained large amounts of two unidentified components of shorter retention time. The infrared spectrum of the pure bromodiene in carbon tetrachloride showed bands (cm^{-1}) at 1607 and 1652 due to conjugated C=C, 1002 and 905 (both strong) due to $-CH{=}CH_2$, and 950 from $-CH{=}CH-$. Evidence for a conjugated diene system was obtained by its ultraviolet spectrum in cyclohexane which displayed an intense maximum at 2265 A, log ϵ 4.41. The nmr spectrum was consistent with the required structure; the β-methylene resonance was a quintet (Figure 3).

Anal. Calcd for C_6H_9Br: C, 44.76; H, 5.63; Br, 49.64. Found: C, 44.80; H, 5.61; Br, 49.54.

Reactions of the Grignard Reagent from 1-Bromo-3,5-hexadiene. (a) Carbon Dioxide. A solution of 2.13 g (13.2 mmoles) of 1-bromo-3,5-hexadiene in 12 ml of ether was stirred with 0.4 g (16.4 mg-atoms) of high-purity resublimed magnesium turnings. After 15 min, most of the magnesium had reacted and the solution was heated under reflux for 24 hr, then poured with stirring onto an excess of solid carbon dioxide. A solution of 1 g of ammonium chloride in 10 ml of water was added, followed by 15 ml of water. The aqueous layer was brought to pH 8 by addition of a few milliliters of dilute ammonium hydroxide. The aqueous layer was separated and combined with an aqueous extract of the ether layer. The combined aqueous layers were acidified with dilute hydrochloric acid and extracted with 350 ml of ether and three 50-ml portions of pentane. The combined pentane–ether extracts were washed with water, dried over sodium sulfate, and evaporated under reduced pressure. Similar treatment of the original ether layer gave a neutral fraction.

Distillation of the acid fraction at 2 mm with a bath at 105° afforded 0.701 g (42.4%) of 4,6-heptadienoic acid, n^{24}D 1.4840. The nmr spectrum showed a carboxyl singlet, a complex vinyl region very similar in detail to that of 1-bromo-3,5-hexadiene, and a large unsymmetrical methylene peak due to overlapping α- and β-methylene resonances. No cyclopropyl absorption was detected. Evidence for a conjugated diene system in the acid was secured by the ultraviolet spectrum, which exhibited a maximum at 2254 A, log ϵ 4.40 (cyclohexane solution). The infrared spectrum was similar to that of the bromodiene except for the presence of carboxyl bands.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 65.88; H, 7.94.

Since the acid gave only a single peak in the vpc at 160° immediately after isolation, the discrepancy in the carbon value is attributed to slight decomposition of the acid prior to analysis.

The neutral fraction was distilled at 13 mm with a bath at 100° and gave 0.355 g (33.1%) of distillate which was examined by vpc at 145°. The two main compounds, 1,6-dicyclopropyl-1,5-hexadiene (XIII, $n^{22.5}$D 1.4897, 62%) and 1,4-dicyclopropyl-1,5-hexadiene (XIV, $n^{22.5}$D 1.4754, 35%), were isolated by preparative vpc

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[25] R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. France*, 108 (1948).

[26] A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," E. Arnold, Ltd., London, 1955, p 82.

[27] J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra," W A. Benjamin, Inc., New York, N. Y., 1961, pp 71–78.

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]

Adalbert Maercker and John D. Roberts

Contribution No. 3279 from the Gates and Crellin Laboratories of Chemistry,
California Institute of Technology, Pasadena, California.

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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

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

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