3000 cm.$^{-1}$. The n.m.r. spectrum displayed a sharp singlet at δ 2.47, doublet at δ 2.96, vinyl multiplet between δ 4.8 and 5.8, and aromatic multiplet between δ 7.1 and 7.55.

The foregoing procedure was executed several times with resulting yields of the carbinol in the range 65–75%. A considerable amount of higher boiling residue was always observed. Fractional redistillation of such residues gave a forerun of allyldiphenylcarbinol and a colorless fraction, b.p. 155–160° (0.5 mm.). This latter fraction has been identified as 1,1-diphenyl-6-hepten-1-ol.[15]

1,1-Diphenyl-1,3-butadiene (II).—Since this diene undergoes resinification easily, the dehydration of the carbinol and the purification of the diene should be done over as short a period as is feasible. Once the diene has crystallized, it should be stored under nitrogen in a refrigerator. Discoloration and liquefaction indicate the onset of decomposition.

A solution of 22.4 g. (0.10 mole) of allyldiphenylcarbinol in 100 ml. of benzene was heated for 2 hr. under reflux in the presence of *ca.* 50 mg. of *p*-toluenesulfonic acid and 25 mg. of hydroquinone. During this time the theoretical quantity of water, 1.8 ml., was collected in the attached Dean-Stark trap. The benzene solution was washed with 5% sodium carbonate solution and then with water. The organic layer was dried over anhydrous calcium sulfate, and the solvent was thereupon removed with a rotary film evaporator. Distillation of the crude product at reduced pressure through a 25-cm. Vigreux column gave 15.9 g. (77%) of the colorless, piquant-smelling diene, b.p. 93–94° (0.3 mm.). Upon standing this product crystallized to a colorless solid. Recrystallization from ethanol or, at −30°, from *n*-heptane, produced colorless prisms, m.p. 38–39°.[16]

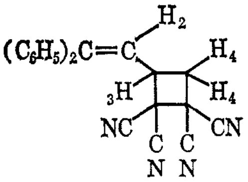
Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.16; H, 6.70.

Characteristic infrared absorptions were displayed at 1625, 1610, 1595 (C=C conjugated with phenyl), 905, 995 ($CH{=}CH_2$), 695, 760 (monosubstituted benzene), 775, 730, 640 cm.$^{-1}$. The ultraviolet spectrum in cyclohexane displayed a peak at 297 mμ (log ϵ 4.26) and a shoulder at 236 mμ (log ϵ 3.71). The n.m.r. spectrum exhibited only a phenyl doublet (δ 7.22 and 7.24, 10 protons) and vinyl proton resonances (multiplets at δ 4.98–5.60, 2 protons, and δ 6.14–6.8, 2 protons).

Adduction of 1,1-Diphenyl-1,3-butadiene with Tetracyanoethylene. Lower Melting Isomer (III, B).—A solution of 4.37 g. (0.0212 mole) of freshly purified 1,1-diphenyl-1,3-butadiene and 2.72 g. (0.0212 mole) of tetracyanoethylene in 50 ml. of dry benzene was heated at reflux for 5 hr. The initial dark green solution changed to dark amber during this time. The majority of the benzene was distilled off and 50 ml. of heptane was added to the semisolid residue. The resulting cream-colored solid was filtered and washed with heptane to yield 6.51 g. (92%) of crude product, melting at 150–153°, resolidifying, and finally remelting to a dark red liquid between 178 and 186°. Recrystallization from benzene gave 4.71 g. (66%) of almost colorless prisms, m.p. 153–155°, red melt, with no solidification upon further heating. Repeated recrystallization produced a colorless solid of the same melting point. However, the benzene solution invariably turned intensely yellow upon heating. This strongly suggests a dissociation of the adduct, leading to free tetracyanoethylene, which then forms a complex with the solvent.

Anal. Calcd. for $C_{22}H_{14}N_4$: C, 79.02; H, 4.22; N, 16.76; mol. wt., 334.3. Found: C, 78.76; H, 4.15; N, 16.92; mol. wt., 390 (Rast, orange melt formed in camphor).

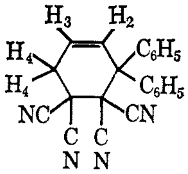
The infrared spectrum displayed important bands at 1630 (C=C), 1610, 1580 (C=C conjugated with phenyl), 1235, 1075, 1030, 945, 925, 880, 765, 725, and 690 cm.$^{-1}$. The ultraviolet spectrum in cyclohexane showed a peak at 268 mμ (ϵ 13,100) and a shoulder at 233 mμ. In acetone-d_6, the n.m.r. spectrum consisted of a complex phenyl multiplet between δ 7.2 and 7.7 (10 protons), a vinyl doublet (H-2) at δ 6.5 (1 proton, $J_{2,3}$ = 9 c.p.s.), a saturated CH triplet (H-3) centered at δ 4.2 (1 proton, $J_{3,2}$ = 9 c.p.s., $J_{3,4}$ = 9 c.p.s.; possible peak at 4.52 obscured by solvent), and a saturated CH doublet (H-4) at δ 3.44 (2 protons, $J_{4,3}$ = 9 c.p.s.).



Higher Melting Isomer (IV, C).—Concentration of the mother liquors from which the lower melting adduct (m.p. 153–155°) was obtained yielded 0.45 g. (6%) of colorless rosettes, melting at 196–200° (slight softening at 160°). Recrystallization from benzene (colorless solution, *vide supra*) gave a colorless product, m.p. 199–200° (solid beginning to turn yellow at 186° and red at 198°).

Anal. Calcd. for $C_{22}H_{14}N_4$: C, 79.02; H, 4.22; N, 16.76; mol. wt., 334.3. Found: C, 79.21; H, 4.39; N, 16.78; mol. wt., 320 (Rast, yellow melt in camphor).

The infrared spectrum showed characteristic bands at 1605, 1595, 1265, 1255, 1165, 1135, 1000, 895, 880, 845, 765, 750, 725, 700 and 650 cm.$^{-1}$. The ultraviolet spectrum in cyclohexane consisted of a shoulder at 230 mμ and a weak end absorption in the 240–260-mμ region. In acetone-d_6 the n.m.r. spectrum consisted of an aromatic multiplet between δ 7.3 and 7.5, two vinyl (H-2) triplets centered at δ 6.78 and 6.96 ($J_{2,3}$ = 11 c.p.s., $J_{2,4}$ = 2 c.p.s.), two vinyl triplets (H-3) centered at δ 6.43 and 6.61 ($J_{3,2}$ = 11 c.p.s., $J_{3,4}$ = 4 c.p.s.), and two saturated CH doubets (H-4) centered at δ 3.62 and 3.67 ($J_{4,2}$ = 2 c.p.s., $J_{4,3}$ = 4 c.p.s.). The relative proton count was in the ratio: phenyl:vinyl (H-2 + H-3):alkyl (H-4) 10:2:2.



Isomerization of Isomer Melting at 155° (III → IV).—A 100-mg. sample of the lower melting TCNE adduct in 30 ml. of dry benzene was heated at reflux for 120 hr. Upon initial warming the colorless solution turned distinctly yellow. At the end of the heating period the benzene was evaporated and the residual solid was examined by infrared spectroscopy. Although the bands of the starting isomer still were prominent, new bands characteristic of the higher melting isomer were now evident: 1265, 1000, 895, 845, and 750 cm.$^{-1}$.

Acknowledgment.—The authors wish to express their gratitude to the donors of The Petroleum Research Fund for their support of this research by PRF Grant 723-A, both at the University of Michigan and The Catholic University of America. They also thank Dr. William C. Kaska for his valuable orienting experiments on the synthesis of 1,1-diphenyl-1,3-butadiene.

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[16] Previous reports of the properties of 1,1-diphenyl-1,3-butadiene include its description as (a) a liquid, b.p. 109° (0.3 mm.), $n^{17.5}D$ 1.6412;[10] (b) a solid, m.p. 35–37°;[11] and (c) a solid, m.p. 37–38° (G. Wittig, private communication, 1959).

The Reaction of Δ^2-Cyclohexenone with β-Methylallylmagnesium Chloride and Isobutylmagnesium Chloride. The Effect of Added Cuprous Chloride[1]

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The addition of 1–10 mole % of cuprous chloride has been shown to cause a substantial increase in the pro-

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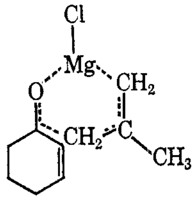
portion of conjugate (or 1,4) addition of alkyl and aryl Grignard reagents to α,β-unsaturated ketones. For example, Kharasch and Tawney[2] have found that the addition of methylmagnesium bromide to isophorone in the absence of cuprous chloride yielded 90.8% of normal addition products, *i.e.*, the tertiary alcohol in 42.6% yield and its dehydration product (diene) in 48.2% yield; no conjugate addition product (saturated ketone) was observed. In the presence of 1 mole % of cuprous chloride, the yield of normal addition product (diene) was reduced to 6.96%, while conjugate addition product occurred in 82.5% yield. Further, House and Thompson[3] have shown that the addition of phenylmagnesium bromide to $\Delta^{8,9}$-octal-1-one in the absence of cuprous chloride results in 43% conjugate addition and 57% normal addition, whereas in the presence of 10 mole % of cuprous chloride, 62% conjugate addition and 38% normal addition was observed. The effect of cuprous chloride on the addition of allylic Grignard reagents to α,β-unsaturated ketones has not been reported; hence, a study of this reaction was of interest.

We have found that exclusively normal (1,2) addition was obtained for the reaction of Δ^2-cyclohexenone with β-methylallylmagnesium chloride under a variety of reaction conditions, *i.e.*, concentration, mole per cent of cuprous chloride added, molar ratio of Grignard reagent and ketone, and temperature, including conditions found to produce a high proportion of conjugate addition.[2,3] The transition state proposed for the observed normal addition may thus be represented as in I in accord with the suggestion of Young and Roberts.[4] The alcohol II resulting from normal (1,2) addition was isolated by preparative gas chromatography and characterized by its infrared absorption spectrum, nmr spectrum, and elemental analysis.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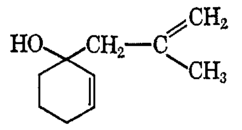
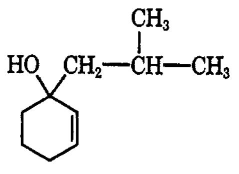
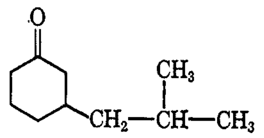
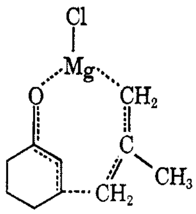

II

To provide further information about this system, the reaction of Δ^2-cyclohexenone with isobutylmagnesium chloride, the saturated counterpart of β-methylallylmagnesium chloride, was studied with and without the addition of cuprous chloride. The effect of cuprous chloride was now in agreement with the work[2,3] previously cited. In the presence of cuprous chloride, the crude reaction mixture consisted of the alcohol III in 35% yield[5] resulting from normal addition and the ketone IV in 63% yield resulting from conjugate addition. The remaining 2% of the reaction mixture was material of lower volatility which was not characterized. The ketone IV had previously been prepared by Woods, *et al.*,[6] by another route. In the absence of cuprous chloride, the yield of alcohol III increased to 97% while that of ketone IV decreased to 3%. Both alcohol III and ketone IV were isolated by preparative gas chromatography and characterized by their infrared absorption, nmr spectrum, and elemental analysis.


III


IV

It is thus apparent that allylic Grignard reagents are insensitive to the usual effects of cuprous chloride in enhancing 1,4 addition to α,β-unsaturated ketones, and that the transition state I is more favorable than the alternative V.


V

Experimental Section[7]

β-Methallylmagnesium Chloride.—With cooling and rapid stirring, under a nitrogen atmosphere, 13.63 g (0.151 mole) of β-methallyl chloride in 50 ml of dry ether was added to 4.00 g (0.164 g-atom) of magnesium turnings suspended in 150 ml of dry ether at a rate to minimize gas evolution. The reaction mixture was stirred overnight and allowed to come to room temperature.

Reaction of β-Methylallylmagnesium Chloride with Δ^2-Cyclohexenone.—To the above suspension at room temperature was added 80 mg (0.81 mmole) of freshly prepared cuprous chloride.[8] The mixture was stirred for 45 min, after which it was cooled in an ice bath. To the rapidly stirred mixture was added a solution of 5.00 g (0.052 mole) of Δ^2-cyclohexenone in 50 ml of sodium-dried ether at a rate such that very little gas was evolved. The reaction mixture was stirred overnight, during which time it was allowed to warm slowly to room temperature. Decomposition of the reaction mixture was achieved at ice-bath temperature with a saturated aqueous solution of ammonium chloride. The ether solution was decanted, and the precipitated magnesium salts were washed with several small portions of ether. The ether solutions were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Gas chromatographic analysis[9] of the crude reaction mixture revealed the presence of alcohol V (95%). The remainder of the product mixture (5%) was material of lower volatility which was not characterized.

A pure sample of alcohol V,[9] n^{24}D 1.4901, exhibits infrared absorption[10] at 3625 (unassociated O-H), 1640 (*cis* CH=CH, C=CH$_2$), and 897 cm^{-1} (C=CH$_2$). The nmr spectrum[10] of the sample has a singlet at 5.54 ppm (CH=CH), two complex multi-

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(2) M. S. Kharasch and P. O. Tawney, *J. Am. Chem. Soc.*, **63**, 2308 (1941).

(3) H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 360 (1963).

(4) (a) W. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 649 (1946); (b) *ibid.*, **68**, 1472 (1946).

(5) The yields are reported as percentages of the volatile products detected by gas chromatography.

(6) G. F. Woods, P. H. Griswold, Jr., B. H. Armbrecht, D. I. Blumenthal, and R. Plapinger, *J. Am. Chem. Soc.*, **71**, 2028 (1949).

(7) The separation and purification of the reaction products was effected by collection from the gc column through the use of a 5.4-cm no. 21 hypodermic needle attached to the exit vent of the detector cell of an F & M Model 720 gas chromatograph. Repeated injections were made to isolate enough material for the analyses reported. The microanalyses were performed by Midwest Microlab., Inc., Indianapolis, Ind. The infrared spectra were determined with a Perkin-Elmer Model 137-B Infracord spectrophotometer. The nmr spectra were determined at 60 Mc with a Varian Model A-60 spectrometer. All nuclear magnetic resonances are reported in parts per million shift from tetramethylsilane as in internal reference.

(8) Prepared as described by W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1960, p 142.

(9) A gas chromatography column packed with 10% Apiezon L on 60–80 mesh Diatoport W was employed.

(10) Determined as a solution in carbon tetrachloride.

plets centered at 4.75 and 4.63 ppm ($>C{=}CH_2$), a singlet at 2.16 ppm ($-CH_2C{=}$), a broad singlet at 1.77 ppm (ring protons), a broad partially resolved singlet at 1.62 ppm ($CH_3C{=}$), and a singlet at 1.43 ppm (-O-H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.07; H, 10.53.

Preparation of Isobutylmagnesium Chloride.[11]—Magnesium turnings (1.17 g, 0.048 g-atom) were placed in the reaction flask, and after the system had been swept with dry nitrogen for several minutes, a solution of 0.18 g (0.002 mole) of isobutyl chloride in 10 ml of sodium-dried ether was added. Initiation of the reaction was effected by the addition of several drops of ethyl bromide followed by warming on a water bath. To the moderately stirred mixture was added a solution of 4.44 g (0.048 mole) of isobutyl chloride in 25 ml of sodium-dried ether at a rate such that gentle refluxing was maintained. Stirring was continued for 2 hr after the addition of halide had been completed, and the reaction mixture was allowed to stand overnight.

Reaction of Isobutylmagnesium Chloride with Δ^2-Cyclohexenone.[12]—To the above suspension was added, in turn, 50 mg (0.51 mmole) of freshly prepared cuprous chloride,[8] and a solution of 1.92 g (0.020 mole) of Δ^2-cyclohexenone in 50 ml of sodium-dried ether. After employing the previously described isolation procedure, gas chromatographic analysis[9] of the crude reaction mixture revealed the presence of alcohol VI (35%) and ketone VII (63%, components listed in order of increasing retention time). The remainder of the product mixture (2%) was material of lower volatility which was not characterized.

A pure sample of the alcohol VI,[9] $n^{25}D$ 1.4708, exhibits infrared absorption[10] at 3625 (unassociated O-H) and 1645 cm^{-1} (*cis* CH=CH). The nmr spectrum[10] of the sample has a singlet at 5.54 ppm (-CH=CH-), a broad singlet at 1.64 ppm (ring protons), a doublet at 1.41 and 1.33 ppm ($-CH_2CH<$), a singlet at 1.27 ppm (-O-H), and a doublet at 0.97 and 0.88 ppm [$-CH(CH_3)_2$].

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.98; H, 11.87.

A pure sample of the ketone VII,[9] $n^{24.5}D$ 1.4527 (lit.[6] $n^{25}D$ 1.4525), exhibits infrared absorption[10] at 1715 cm^{-1} (C=O). The nmr spectrum[10] of the sample has a broad multiplet centered at 1.81 ppm (ring protons) and a doublet at 0.91 and 0.81 ppm [$-CH(CH_3)_2$].

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.72; H, 11.95.

In the absence of cuprous chloride, gas chromatographic analysis[9] of the crude reaction mixture revealed the presence of alcohol VI (97%) and ketone VII (3%, components listed in order of increasing retention time).

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[11] The apparatus was identical with that used for the preparation of β-methylallylmagnesium chloride.

[12] The procedure was identical with that for the reaction of β-methylallylmagnesium chloride with Δ^2-cyclohexenone.

Ozonolysis of 1,2,3,4,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-diene

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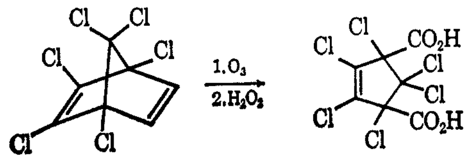
Received June 15, 1965

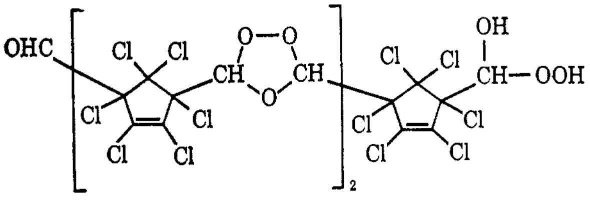
The present work was initiated with the desire of obtaining 1,2,2,3,4,5-hexachloro-4-cyclopentene-1,3-dicarboxylic acid (II) by oxidative ozonolysis[1] of 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2,5-heptadiene (I).



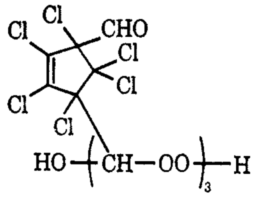
I II

There are numerous descriptions in the literature of this method for obtaining dibasic acids from cyclic aliphatic and aromatic olefins.[2-15] Although different intermediates can be isolated from ozonation in participating and in nonparticipating solvents, oxidation generally results in the same dibasic acid. In the present case the reaction did not give the expected high yields of II. However, several intermediate products were isolated which provide additional evidence for the Criegee[1b] mechanism of double bond ozonolysis.

Ozonation of I in either carbon tetrachloride at 0° or pentane at −78° gave a white solid which was determined to be the trimer III by the infrared spectrum (which has carbonyl and hydroxyl bands), nmr spectrum, elemental analysis, molecular weight determination, active oxygen determination, and polarogram. The polarogram shows two half-wave potentials (Table I) which probably correspond to reduction of the ozonide and hydroperoxide, respectively. The aldehyde would not be expected to give a half-wave poten-



III



IV

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[1] For reviews on ozonation, see (a) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958); (b) R. Criegee, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957); (c) R. Criegee, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 29–39.

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[10] P. S. Bailey, *Ind. Eng. Chem.*, **50**, 993 (1958).

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