(25,000), 288 (21,800), and 278 (20,800). The n.m.r. spectrum (dry CH_3CN) had a peak at δ 4.28 (area 1) and a multiplet near 7.9 (area 20); in CF_3CO_2H, with 5% benzene, the phenyl multiplets were centered 0.5 p.p.m. below benzene, and the single proton 3.16 p.p.m. above benzene.

The perchlorate XI (1.59 g.) was stirred with 0.55 g. of $LiAlD_4$ in 30 ml. of anhydrous ether overnight. Aqueous work-up and chromatography yielded IX-*d*, identical in melting point and infrared spectrum with IX. In the n.m.r., the singlet at δ 2.38 was only $^1/_{20}$ the area of the phenyl protons. Treatment of this compound with triphenylmethyl perchlorate, as above, afforded partially deuterated XI whose n.m.r. spectrum (in CH_3CN) had the peak at δ 4.28 with an area roughly $^1/_{40}$ that of the phenyl protons.

Reaction of IX with Potassium Amide. A solution of 0.15 g. of IX in 60 ml. of dimethoxyethane was added to potassium amide (from 0.8 g. of potassium) in 60 ml. of liquid ammonia. After standing overnight, aqueous work-up and chromatography afforded 1,2,3,4-tetraphenylbenzene (XII, 0.030 g., 20%) as the only crystalline product. No other isomer could be detected.

Thermal Rearrangement of IX. Four separate samples of the dimer IX (150–440 mg.) in 60 ml. of purified ethoxyethanol (b.p. 133–135°) were heated under reflux (N_2) for 7 days. In one run the reaction was followed by periodic sampling and quantitative ultraviolet determination; good isosbestic points at 275 and 355 mμ were observed, the final spectrum being that of a mixture of tetraphenylbenzenes. The solvent was removed *in vacuo* and the total product was taken up in CCl_4 and analyzed by vapor phase chromatography (5-ft. 5% SE-30 on 60–80 mesh Firebrick with N_2 carrier, column at 300°). 1,2,4,5-Tetraphenylbenzene (IV) and 1,2,3,4-tetraphenylbenzene (XII) were identified by identical retention times (14.5 min. for IV and 9 min. for XII) with those of authentic samples. Quantitative analysis by comparing peak areas with those from authentic mixtures gave ratios of IV/XII in the four separate runs of (average of at least three measurements on each): 11 ± 1, 13 ± 1.5, 4.2 ± 0.4, and 8.4 ± 0.8. In a preliminary run, IV and XII were separated and identified by melting point and spectral criteria. In four separate runs, rearrangement of IX by injection directly into the 300° v.p.c. column gave a ratio IV/XII of 3.5 ± 0.5.

Photochemical Rearrangement of IX. A stirred solution of 3.78 g. of IX in 500 ml. of anhydrous ether was irradiated for 41 hr. under N_2 (Hanovia 450-w. medium-pressure lamp in an immersion well with a Pyrex filter). The ether was evaporated and the crude product was analyzed by vapor phase chromatography, as above. The ratio of the two tetraphenylbenzenes, XII/IV, was 2.2 ± 0.3. Alumina chromatography of the crude product afforded only 0.300 g. of the mixture of IV and XII, whose infrared spectrum was a composite of those of the authentic compounds. Analysis of this purified fraction by vapor phase chromatography gave a ratio XII/IV of 2.8 ± 0.3. The mixture was also identified by thin layer chromatography (silica gel, CCl_4, H_2SO_4 spray; IV R_f 0.51, blue spot; XII R_f 0.46, pink-purple spot). A control irradiation of IV under the same conditions gave quantitative recovery of the starting material.

Small-Ring Compounds. XLIV. Interconversion of Cyclopropylcarbinyl and Allylcarbinyl Grignard Reagents[1]

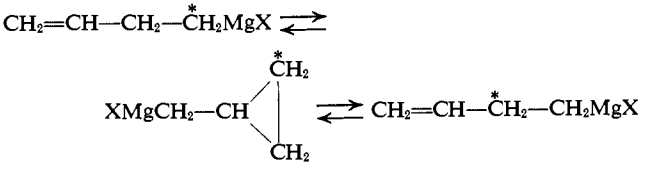
Dinshaw J. Patel, Carole L. Hamilton, and John D. Roberts

Contribution No. 3255 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. *Received July 6, 1965*

The previously postulated rapid conversion of the cyclopropylcarbinyl Grignard reagent to the allylcarbinyl Grignard reagent has been confirmed by partial trapping of cyclopropylcarbinylmagnesium chloride prepared in refluxing diethyl ether in the presence of benzoic acid as methylcyclopropane and formation of cyclopropylcarbinylmagnesium bromide at −24° from the corresponding bromide and magnesium in dimethyl ether. The rearrangement of cyclopropylcarbinylmagnesium bromide to allylcarbinylmagnesium bromide appears to be a first-order reaction and has a half-life of 121 min. at −24°.

Introduction

In recent years, there has been considerable interest in interconversions of cyclopropylcarbinyl, allylcarbinyl, and cyclobutyl compounds in reactions involving a potential anionic center. It has been shown that Grignard reagents prepared in the ordinary way from both cyclopropylcarbinyl and allylcarbinyl halides possess the allylcarbinyl structure to the extent of more than 99%.[2,3] The allylcarbinylmagnesium halides, however, were found to undergo an extraordinary rearrangement in which the α- and β-carbons exchange positions. This reaction was presumed to occur



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

(2) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(3) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960).

Table I. Acidolysis Products of Grignard Reagents from Cyclopropylcarbinyl Halides

Starting halide	Acid	Lifetime	Refluxing solvent	RX/Mg	Isomer distribution: ▷—CH_3, %	Isomer distribution: 1-Butene, %
▷—CH_2Cl	CF_3CO_2H	*In situ*	Et_2O	1.5	10	90
	$C_6H_5CO_2H$	*In situ*	Et_2O	1.5	9	91
		In situ	Et_2O	0.25	4	96
		5 hr.	Et_2O	0.25	0.1	99.9
		42 hr.	Et_2O	0.25	0.1	99.9
▷—CH_2Br	CF_3CO_2H	*In situ*	Et_2O	1.0	32	68
		In situ	Et_2O	0.25	33	67
	$C_6H_5CO_2H$	*In situ*	Et_2O	1.0	28	72
		In situ	Et_2O	0.25	29	71
		1 hr.	Et_2O	1.0	0[a]	100
		8 hr.	Et_2O	1.0	Trace[a]	~100
		20 hr.	Et_2O	1.0	Trace[a]	~100
▷—CH_2I	$C_6H_5CO_2H$	*In situ*	Et_2O	1.0	15	85
	CF_3CO_2H	*In situ*	Me_2O	1.0	47	53
		In situ	Me_2O	0.25	41	59
▷—CH_2Br	$C_6H_5CO_2H$	*In situ*	Me_2O	1.0	55	45
		In situ	Me_2O	0.25	47	53
		0.5 hr.	Me_2O	1.0	47	53
		1 hr.	Me_2O	1.0	43	57
		1.5 hr.	Me_2O	1.0	39	61
		24 hr.	Me_2O	1.0	2	98
		48 hr.	Me_2O	1.0	Trace	~100
▷—CH_2I	$C_6H_5CO_2H$	*In situ*	Me_2O	1.0	40	60

[a] Formation of less than 0.1% would have escaped detection.

through an intermediate cyclopropylcarbinyl structure[3] and raises the question as to whether or not the cyclopropylcarbinylmagnesium halides have only a fleeting existence or are relatively stable molecules.

Evidence that anionic cyclopropylcarbinyl species may be found and not rearrange has been demonstrated by the Sommelet–Hauser rearrangement of cyclopropylcarbinylbenzyldimethylammonium bromide to cyclopropyl-*o*-tolylcarbinyldimethylamine,[4] and the Wittig rearrangement of phenylcyclopropylcarbinyl ether which yields predominantly phenylcyclopropylcarbinol.[5] Stronger indication that cyclopropylcarbinyl Grignard reagents should be expected to be relatively stable entities is provided by the stability of cyclopropylcarbinyllithium at low temperatures.[6]

At this time, we report direct evidence on the formation and stability of cyclopropylcarbinylmagnesium halides.

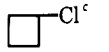
Results

Acidolysis of C_4H_7MgCl is a rapid, apparently straightforward reaction providing hydrocarbon products that can be easily analyzed by means of vapor phase chromatography (v.p.c.). The composition of the products are expected to reflect the nature of the Grignard species trapped by the reaction provided that there are no skeletal rearrangements in the acidolysis reactions. There is no special problem with the Grignard reagents derived from allylcarbinyl halides; acidolysis of the organomagnesium halide, either immediately after formation or on long standing, gives 1-butene containing only traces of methylcyclopropane. The situation with cyclopropylcarbinyl halides is more complex since Grignard reagents prepared in the conventional way produce 1-butene and but traces of methylcyclopropane on treatment with acids. Our initial work was therefore undertaken with the idea of establishing whether or not acidolysis leads to rearrangement products. When cyclopropylcarbinyl chloride (contaminated with 2% of cyclobutyl chloride) was allowed to react with magnesium in the presence of benzoic acid, the hydrocarbon products consisted of 92% 1-butene, 6% methylcyclopropane, and 2% cyclobutane. With this encouraging evidence for the formation of at least some cyclopropylcarbinylmagnesium chloride, we initiated a study of the interconversion of allylcarbinyl and cyclopropylcarbinyl Grignard reagents under varying conditions. We shall assume in the sequel that acidolysis of cyclopropylcarbinylmagnesium halide produces methylcyclopropane and no 1-butene. We have no compelling evidence for this except for results obtained with other cyclopropylcarbinyl organometallic compounds of known structure.[7] The consequence is to assume that cyclopropylcarbinyl halides react with magnesium to give substantial amounts of allylcarbinylmagnesium halides because so far we have obtained no more than 55% of methylcyclopropane from acidolysis of Grignard reagents prepared directly from cyclopropylcarbinyl halides. The reasonableness of this assumption will be discussed later.

Table I shows the acidolysis products of Grignard reagents prepared from cyclopropylcarbinyl halides in refluxing dimethyl ether (−24°) and diethyl ether (36°). Distributions of hydrocarbons obtained from the Grignard reactions of allylcarbinyl and cyclobutyl halides and subsequent acidolysis are given in Table II. Experiments in which the Grignard reagents were refluxed for some time before cleavage showed that some

(4) C. L. Bumgardner, *J. Am. Chem. Soc.*, **85**, 73 (1963).
(5) P. T. Lansbury and V. A. Pattison, *ibid.*, **84**, 4295 (1962).
(6) P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. Sidler, *ibid.*, **86**, 2247 (1964).
(7) A. Maercker and J. D. Roberts, *ibid.*, in press.

Table II. Acidolysis Products of Grignard Reagents from Allylcarbinyl and Cyclobutyl Halides

Starting halide	Acid	Lifetime	Refluxing solvent	RX/Mg	Isomer distribution: ▷—CH_3, %	Isomer distribution: 1-Butene, %	Isomer distribution: □, %
	$C_6H_5CO_2H$	*In situ*	Et_2O	1.50	0.2	99.8	...
		In situ	Et_2O	0.25	2	98	...
		8 hr.	Et_2O	0.25	0.2	99.8	...
		24 hr.	Et_2O	0.25	0.1	99.9	...
		42 hr.	Et_2O	0.25	0.2	99.8	...
	CF_3CO_2H	*In situ*	Et_2O	1.0	0[b]	100	...
	$C_6H_5CO_2H$	*In situ*	Et_2O	1.0	0[b]	100	...
		8 hr.	Et_2O	1.0	0[b]	100	...
	CF_3CO_2H	*In situ*	Me_2O	1.0	0[a]	100	...
	$C_6H_5CO_2H$	*In situ*	Me_2O	1.0	0[a]	100	...
		14 hr.	Me_2O	1.0	0[a]	100	...
 [c]	$C_6H_5CO_2H$	*In situ*	Et_2O	0.25	0	1	99
		24 hr.	Et_2O	0.25	0	1	99

[a] Formation of less than 1% would have escaped detection. [b] Formation of less than 0.1% would have escaped detection. [c] Starting material was 0.5% allylcarbinyl chloride.

C_4H_8 hydrocarbons were formed prior to the decomposition step. These materials amounted to only to a few percent of the total volatile hydrocarbons produced in acidolysis and therefore did not significantly affect the isomer distributions.

Unreacted chloride was recovered unchanged from the reactions of cyclopropylcarbinyl chloride and allylcarbinyl chloride with magnesium in the presence of benzoic acid and refluxing ethyl ether with magnesium in excess. Under the same conditions with chloride in excess, a net rearrangement of cyclopropylcarbinyl chloride to cyclobutyl chloride of 5% was observed. Cyclopropylcarbinyl chloride was shown to be stable to refluxing with benzoic acid in ethyl ether. Furthermore, cyclopropylcarbinyl and cyclobutyl chlorides did not appear to rearrange when refluxed with magnesium bromide or with magnesium chloride and magnesium in ethyl ether.

Measurement of the rate of conversion of cyclopropylcarbinylmagnesium bromide to allylcarbinylmagnesium bromide at −24° was accomplished by following the time dependence of the fraction of methylcyclopropane formed upon acidolysis (Table III). The rearrangement followed first-order kinetics with a half-life of 121 min. which corresponds to a free energy of activation of 19 kcal.

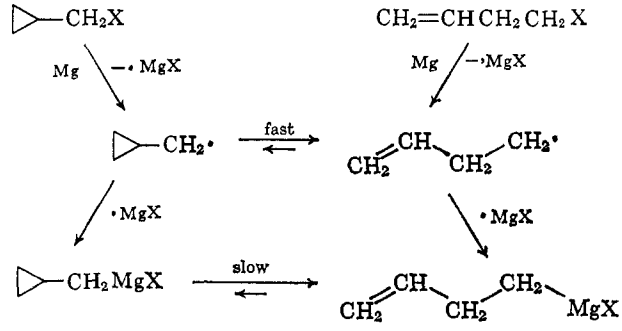
Table III. Rate of Isomerization of Cyclopropylcarbinylmagnesium Bromide at −24°

Time, min.	Isomer distribution: ▷—CH_3, %	Isomer distribution: 1-Butene, %	$[▷—CH_3]_t / [▷—CH_3]_0$
0	44	56	1
25	40	60	0.91
50	33	67	0.75
80	28	72	0.64
105	24	76	0.55
130	22	78	0.50

Discussion

The data in Tables I and II indicate that in ether solutions the allylcarbinyl and cyclopropylcarbinyl Grignard reagents exist in equilibrium with each other. The position of the equilibrium seems to depend on the nature of the halogen but, in any case, the open-chain isomer is strongly favored. The free-energy difference between allylcarbinylmagnesium chloride and cyclopropylcarbinylmagnesium chloride appears to be on the order of 4 kcal. Taking the value of the activation energy for interconversion of the positional isomers of allylcarbinylmagnesium bromide, 26 kcal.,[3,8] as representing the barrier to transformation of the open-chain compound to its cyclic isomer, and using 19 kcal. for the free energy of activation for opening the ring, leads (with neglect of entropy effects) to an expected difference of 7 kcal. for the two C_4H_7MgBr isomers. If this calculation is valid, the equilibrium concentration of cyclic Grignard reagent would be considerably below the limits of detection and, in fact, no more than traces of methylcyclopropane were observed in the acidolysis of C_4H_7MgBr after equilibrium was established.

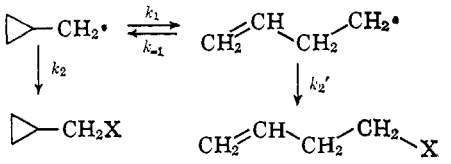
It is interesting that the *in situ* acidolysis of the Grignard reagent prepared from allylcarbinyl chloride and excess magnesium produced more methylcyclopropane than at equilibrium. Furthermore, the extent of formation of 1-butene formed upon *in situ* acidolysis of the Grignard reagents from cyclopropylcarbinyl halides appears to exceed the amount to be expected from formation and isomerization of the cyclopropylcarbinyl Grignard reagent to its allylcarbinyl isomer. The initial product in Grignard formation from either a cyclopropylcarbinyl halide or an allylcarbinyl chloride appears to contain substantial amounts of both the cyclic and the open-chain com-



(8) This value was erroneously reported[3] to be 23 kcal.

pounds. This behavior is expected if the Grignard reagents are formed by way of radical intermediates.[9,10]

Substantial evidence for rapid, but not instantaneous, ring opening of cyclopropylcarbinyl radicals is available from studies of the chlorination of cyclopropane,[2,11] the decarbonylation of cyclopropylacetaldehyde,[12] and cyclopropyldimethylacetaldehyde.[12,13] Ring closure of the allylcarbinyl radical itself is not so well documented, although analogous ring closures of bicyclic unsaturated radicals have been extensively studied.[14] However, reduction of allylcarbinyl bromide with tributyltin hydride does give traces of methylcyclopropane,[13] presumably by a free-radical mechanism.[15] Somewhat more ring closure, but still less than 0.25%, occurs with γ,γ-dimethylallylcarbinyl bromide.[13] There are no data at present that can be regarded as giving anything but a qualitative impression that the cyclopropylcarbinyl radical is less stable than the allylcarbinyl radical, *i.e.*, that $K = k_1/k_{-1} > 1$.



It is not clear yet in which experiments (if any) equilibrium is actually established between the radicals, and we still have no definite idea as to whether in general we should expect the reactivities of the radicals with various substrates (k_2 and k_2') to be very different or nearly the same. It is hoped that current investigations of reactions of substituted cyclopropylcarbinyl and allylcarbinyl radicals will clarify some part of these difficulties.

Experimental Section

Boiling points are uncorrected. Nuclear magnetic resonance (n.m.r.) spectra were taken on a Varian Associates A60 spectrometer. Analyses by vapor phase chromatography (v.p.c.) were performed with a Perkin-Elmer vapor fractometer, Model 154-B, and were not corrected for variations in thermal conductivities or volatilization.

Cyclopropylcarbinyl Chloride. The product from treatment of cyclopropylcarbinol with thionyl chloride and tri-*n*-butylamine[16] was fractionated through a center-rod column. In a typical preparation, a 74% yield of material, b.p. 82.5–86.2° (745 mm.) was collected; of this, 37% had b.p. 85.9–86.2° and consisted of 98% cyclopropylcarbinyl chloride and 2% cyclobutyl chloride. Fractions were analyzed by v.p.c. (diisodecyl phthalate on diatomaceous earth, 75°).

Cyclopropylcarbinyl Bromide. Cyclopropylcarbinol was treated with phosphorus tribromide following the method of Meek and Rowe.[17] Fractionation of the product through a center-rod column gave cyclopropylcarbinyl bromide in 64% yield, b.p. 109° (lit.[2] b.p. 111.6–112.0°). Analysis by v.p.c. and n.m.r. indicated the material contained 3% of cyclobutyl bromide.

Cyclopropylcarbinyl Iodide. Treatment of cyclopropylcarbinyl bromide with sodium iodide in acetone gave cyclopropylcarbinyl iodide, b.p. 48–49° at 38 mm. (lit.[18] b.p. 88–90° at 150 mm.). The product was identified from its n.m.r. spectrum, and contained less than 3% cyclobutyl iodide.

Allylcarbinol was prepared from 3-butenoic acid using the same procedure as for the synthesis of cyclopropylcarbinol. A 70% yield was obtained, b.p. 111.5–112.5° at 744 mm. (lit.[19] b.p. 112.5–113.5° at 748 mm.), $n^{25}D$ 1.4191 (lit.[16] $n^{25}D$ 1.4182).

Allylcarbinyl chloride from allylcarbinol and thionyl chloride in the presence of pyridine[16] was distilled through a center-rod column and had b.p. 73–75° (lit.[19] b.p. 75.0°). Analysis by v.p.c. showed the product to be greater than 99.9% pure.

Allylcarbinyl bromide was prepared by treatment of allylcarbinol with phosphorus tribromide according to Juvala[19] and, after distillation through a center-rod column, had b.p. 97° (lit.[19] b.p. 98.5–99°). V.p.c. analysis indicated a purity of 99.9%.

Grignard Reactions in Dimethyl Ether. The procedure of Hall, Piccolini, and Roberts[20] was followed for Grignard reactions in dimethyl ether. In a three-necked, 100-ml., round-bottomed flask equipped with a mechanical stirrer, Dry Ice condenser, and dropping funnel was placed magnesium (0.01 g.-atom) and 10 ml. of diethyl ether. A few drops of methyl iodide were added and the magnesium surface was scratched with a glass rod. The preparation was carried out under an atmosphere of high-purity nitrogen. The flask was cooled in Dry Ice–acetone, and dimethyl ether (50 ml.) was condensed in it. The dimethyl ether was allowed to heat to the reflux temperature (−24°) and the halide (0.01 mole), dissolved in 5 ml. of diethyl ether, was added to the flask. After the specified reaction times, the hydrolyzing agent (0.01 mole) in 10 ml. of ether was introduced through a serum stopper and the gaseous products were collected in a container cooled in Dry Ice–acetone. The gaseous samples were analyzed by v.p.c. (tetraisobutylene on diatomaceous earth, room temperature). The peaks due to 1-butene and methylcyclopropane had retention times on the tail of the methyl ether peak and were identified by comparison of retention times with authentic samples. In the reactions involving *in situ* cleavage, the acidolysis agent was added before the dimethyl ether was introduced into the flask. Most of these experiments required 8–12 hr. of reaction times.

(9) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954.
(10) (a) C. Rüchardt and H. Trautwein, *Ber.*, **95**, 1197 (1962); (b) H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3288 (1964).
(11) E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *ibid.*, **83**, 1987 (1961).
(12) D. I. Schuster, Ph.D. Thesis, California Institute of Technology, 1960.
(13) A. J. Rosen, Ph.D. Thesis, California Institute of Technology, 1964.
(14) See D. J. Trecker and J. P. Henry, *J. Am. Chem. Soc.*, **85**, 3204 (1963), for references and discussion.
(15) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *ibid.*, **84**, 3584 (1962).
(16) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).
(17) J. S. Meek and J. W. Rowe, *J. Am. Chem. Soc.*, 77, 6675 (1955).
(18) P. T. Lansbury and V. A. Pattison, *ibid.*, **85**, 1886 (1963).
(19) A. Juvala, *Ber.*, **63**, 1989 (1930).
(20) G. Hall, R. Piccolini, and J. D. Roberts, *J. Am. Chem. Soc.*, 77, 4540 (1955).

Bromides were found to be more reactive than chlorides at low temperatures.

Grignard Reactions in Diethyl Ether. A. Chlorides. Magnesium turnings were amalgamated by treatment in several portions with a solution of mercuric bromide in ether,[21] washed well with ether, and placed in an oven-dried, 50-ml., two-necked flask fitted with a water-cooled reflux condenser to which was attached an acetone–Dry Ice cooled trap. The system was flushed with helium that had been passed through Fieser's solution[22] and concentrated sulfuric acid. The reaction flask was then charged with the appropriate proportion of C_4H_7Cl, a drop or two of methyl iodide, any addend desired, and 5–7 ml. of dry ether. Liquid reagents were added from a 1-ml. hypodermic syringe graduated to 0.01 ml.; about 5 mmoles of C_4H_7Cl was customarily used.

When the Grignard reaction had been initiated, the mixture was warmed to the reflux temperature. If an addend was present, the reflux period extended until all hydrocarbon products were driven into the Dry Ice trap (48–72 hr.). If an addend was not used, the mixture was transferred after the desired reflux time through a glass wool plug to a nitrogen-filled dropping funnel. This was attached to an identical apparatus containing an ether solution of hydrolyzing agent, the Grignard solution was added, and the mixture was heated to reflux with a water-cooled condenser until all hydrocarbons had been collected in the cold trap. The products and the unreacted chloride were analyzed by v.p.c.

B. Bromides and Iodides. Magnesium (0.01 g.-atom) in 30 ml. of ether was placed in a 100-ml., three-necked, round-bottomed flask equipped with a mechanical stirrer, dropping funnel, and reflux condenser. The magnesium was activated by scratching the surface in the presence of a few drops of methyl iodide. The flask was swept with a steady flow of purified nitrogen, then heated at such a rate as to maintain gentle reflux. The halide (0.01 mole) in 10 ml. of ether was added to the flask, and the reaction was allowed to proceed for the required time. The hydrolyzing agent (0.01 mole) in 10 ml. of ether was added through a serum stopper and the gaseous products were collected in a Dry Ice cooled trap and analyzed by v.p.c. In the Grignard reactions involving *in situ* hydrolysis, the hydrolyzing agent was added to the refluxing ethyl ether before addition of halide.

Kinetic Experiments. The kinetic runs were carried out in refluxing dimethyl ether in a system flushed with purified nitrogen. The Grignard reagent from cyclopropylcarbinyl bromide was prepared in dimethyl ether as described above and filtered through a sintered-glass disk into another flask. Portions of this Grignard reagent were then withdrawn at intervals and hydrolyzed with benzoic acid in refluxing dimethyl ether. Analysis of the hydrocarbons was carried out by v.p.c.

(21) J. E. Nordlander, Ph.D. Thesis, California Institute of Technology, 1961.
(22) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955.

Olefinic Cyclizations. VIII.[1] The Butenylmethylcyclohexenol System

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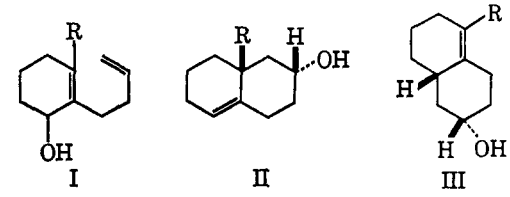
Contribution from the Department of Chemistry, Stanford University, Stanford, California. *Received July 11, 1965*

The dienol I (R = CH_3), prepared by the sequence IV → V → VI → I (R = CH_3), was cyclized readily by formic acid at room temperature. The product was shown to consist of approximately 30% of the methyloctalol VII, 35% of the diol VIIIa, and 22% of the C-1 epimeric diol VIIIb. None of the product with an angular methyl group was found. The isomeric dienol XI (R = CH_3) was prepared by the sequence m-cresyl methyl ether → XIII → XIV → XV → XVI → XI (R = CH_3). Cyclization with formic acid gave, in almost quantitative yield, the product XII (R = CH_3) with an angular methyl group.

In a previous study[2] it was shown that 2-(Δ^3-butenyl)-2-cyclohexenol (I, R = H), on mild treatment with formic acid, underwent rapid, stereoselective cyclization to give, after hydrolysis of the formates, *syn*-$\Delta^{1,9}$-6-octalol (II, R = H) in 80% yield along with some of the C-6 epimeric octalol and small amounts of olefins. In anticipation of the possible use of this reaction for the synthesis of fused-ring systems containing the angular methyl group,[3] it was considered of interest to examine the cyclization of the homolog I (R = CH_3), in order to ascertain if this system was suitable for producing the desired substance II (R = CH_3), or to what extent cyclization would proceed in the opposite possible sense so as to produce the isomeric



I II III

(1) Part VII: W. S. Johnson and J. K. Crandall, *J. Org. Chem.*, **30**, 1785 (1965).
(2) W. S. Johnson, W. H. Lunn, and K. Fitzi, *J. Am. Chem. Soc.*, **86**, 1972 (1964).
(3) *Cf.* W. S. Johnson, *Pure Appl. Chem.*, **7**, 317 (1963).