[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Isomerism in Diels–Alder Adducts. V. The Products of Hydroxylation of Norbornylene

BY HAROLD KWART AND WILLIAM G. VOSBURGH

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Three of the possible bicyclo[2.2.1]heptane diols have been prepared and their configurations identified by means of infrared measurement of their internal hydrogen bond distances. The significance of the configuration of the product of performic acid oxidation of norbornylene is discussed. Evidence is deduced confirming the fact that the cyclopentane ring system is puckered.

Introduction.—In previous papers[1c] in this series,[1] we have discussed the bromination of norbornylene (bicyclo[2.2.1]heptene-2) and demonstrated that under certain conditions of reaction a rearranged dibromide was the predominant reaction product. Our interest in determining the influence of substituents on the steric course of addition to the double bond in bicyclic systems in general led us to an investigation of the steric course of perhydroxylation of norbornylene. In particular we were interested to add this symmetrical reagent for the comparison it would afford with the previously reported addition of the similarly symmetrical halogen reagent.

It has been shown by Birch, Oldham and Johnson[2] that when norbornylene is oxidized by peracetic acid a glycol is obtained, which, when further oxidized with chromic acid, results in a mixture of di- and tricarboxylic acids. Direct oxidation of norbornylene with an excess of permanganate gave *cis*-cyclopentane-1,3-dicarboxylic acid. These authors have postulated a *trans*-2,3-diol structure for the product of peracetic acid oxidation on the basis of a most unusual postulated course of chromic acid oxidation involving an enolic intermediate which violates Bredt's rule.[3]

On the other hand, Gates and Malchik[4] have demonstrated that the glycol formed on perhydroxylation of dicyclopentadiene gives a negative periodate test for vicinal diol, indicating that the course of reaction must have involved a rearrangement of the bicyclic skeleton.

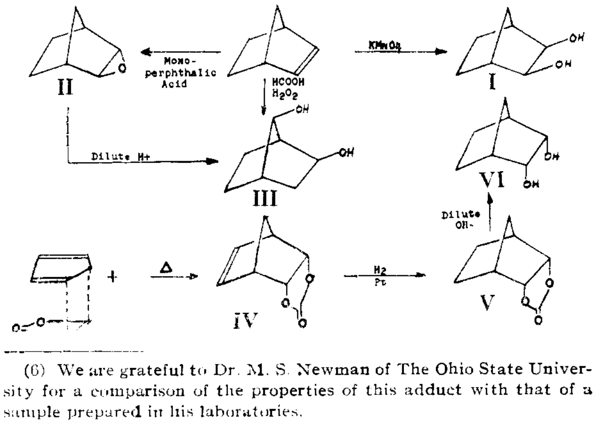
We are reporting here the results of the reaction of performic acid on norbornylene and a proof of structure of the reaction product that clarifies the observations of Birch, Oldham and Johnson and is consonant with the observations of Gates and Malchik on the analogous reaction of dicyclopentadiene.

Results.—When norbornylene was added to a solution of hydrogen peroxide in formic acid, in the usual procedure for perhydroxylation of an olefin,[5] an excellent yield of diol was obtained. Purification resulted in a product, III, which gave a negative periodic acid test for vicinal diols. In fact, none of the total crude product tested for the presence of vicinal diol, indicating that the course of addition to the double bond in norbornylene had been attended almost *exclusively* by rearrangement. The identical product also resulted from acid rearrangement of the 2,3-epoxide II, the latter obtainable by epoxidation of norbornylene with monoperphthalic acid.

Proof of the structure of III could be deduced by synthesis and identification of two of the vicinal diols of norcamphane and infrared measurement of the characteristic internal hydrogen bond distances for all three. The *endo-cis*-2,3-dihydroxy[2.2.1]-heptane (VI) was prepared by reduction of the Diels–Alder adduct[6] IV of vinylene carbonate and cyclopentadiene followed by dilute alkaline hydrolysis of the carbonate structure to the diol. The product of this series of reactions gave a periodic acid test and was assigned the *endo* structure in consistency with the Alder rules governing the configuration of bicyclic Diels–Alder adducts.[7] The *exo-cis*-2,3-dihydroxybicyclo[2.2.1]heptane (I) was obtained by reaction of norbornylene with dilute aqueous permanganate in the usual fashion for bring about *cis* hydroxylation of olefins.[8] I, like its isomer VI also gave a periodic acid test. The two vicinal diols were distinguished easily on the basis of infrared spectra and mixed melting point depression. The *exo* structural assignment of I was based on its distinguishability from the *endo* compound VI and the fact that both the *endo* and *exo* compounds showed almost identical internal hydrogen bonding distances. No other diol of norcamphane but one with the structure assigned to I could have this characteristic in common with VI.

The flow sheet depicts a comparison of the synthetic routes leading to each of the norcamphane diols discussed above. The accompanying table

FLOW SHEET



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[1] (a) H. Kwart and co-workers, THIS JOURNAL, **74**, 2094 (1952); (b) **75**, 3356 (1953); (c) **76**, 4072 (1954); (d) **76**, 4078 (1954).

[2] S. Birch, W. Oldham and E. Johnson, *J. Chem. Soc.*, 818 (1947).

[3] F. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

[4] A more complete discussion of the mechanism of the hydroxylation reaction is presented by these authors. See 1b for a further reference to the observations of Gates and Malchik, due to appear in THIS JOURNAL.

[5] H. R. Snyder, *Org. Synthesis*, **28**, 35 (1948).

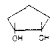
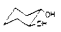
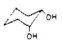
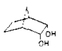
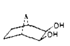
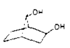
[6] We are grateful to Dr. M. S. Newman of The Ohio State University for a comparison of the properties of this adduct with that of a sample prepared in his laboratories.

[7] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[8] P. D. Bartlett and A. Bavley, THIS JOURNAL, **60**, 2416 (1938)

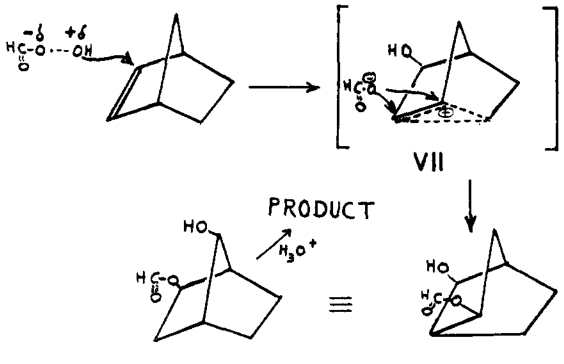
contains a summary of the hydrogen-bond data from which these structural assignments were inferred. Models are of considerable aid in perceiving that the value of 1.56 A. for the length of the internal hydrogen bond in III (when compared to the hydrogen bond values of the 2,3-vicinal diols) is almost exactly what one would expect for a 2,7-norcamphane diol. Furthermore, none of the other possible non-vicinal diols (including 1,3 and 1,4 possibilities) could have so short an internal hydrogen bonding distance, making the structural assignment for III both unique and compelling.

TABLE OF INTERNAL HYDROGEN-BONDING DATA FOR SEVERAL VICINAL DIOLS

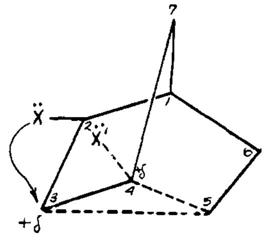
Compound	γOH cm.$^{-1}$ Free	γOH cm.$^{-1}$ Bonded	Δγ cm.$^{-1}$	Calcd. H...O distance, Å.
	3633	3572	61[a]	1.84
	3634	3602	32[b]	2.36
	3626	3587	39[b]	2.22
	3633	3531	102[c]	1.42
	3632	3529	103[c]	1.41
	3621	3545	86[c]	1.56

[a] Data provided by Dr. L. P. Kuhn. [b] Average values of several determinations made in these laboratories and those of Dr. L. P. Kuhn with samples kindly provided by Dr. Kuhn. [c] Average values of three determinations; maximum deviation less than 1.5%.

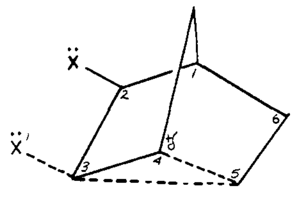
Discussion of the Addition Mechanism.—The mechanism of peracid oxidation of olefins has been discussed by Swern[9] as an acid-catalyzed reaction proceeding through ionic intermediates. Cope, Fenton and Spencer[10] in reporting the occurrence of rearrangement in the reaction of cyclooctene with performic acid have also described a mechanism involving ionic intermediates. In the chart we represent a mechanistic scheme for the reaction of performic acid with norbornylene in which bridged ion intermediates are written by analogy to that written by Gates and Malchik[4] for the case of dicyclopentadiene and to the bromination of norbornylene.[1c] A comparison of the perhydroxylation result with that of the bromination of norbornylene is very pertinent here. It would thus appear that the predominant product on addition of a symmetrical double bond reagent to the unsaturated bicyclic system in norbornylene has resulted from a course of rearrangement. An interesting point arises for consideration when one closely examines the question of why the bridged ion (or ion pair)[11] intermediate collapses with bond formation at C_4, and that none of that product obtained appears to arise by collapse in the direction of C_3. In the instance of norbornylene there exists no substituent influence on the initial bicyclic skeleton that could exert a directive effect on the course of addition. It is clear, furthermore, that the presence of a group with unshared pairs (either –Br or –OH) in the intermediate bridged ion VII, resulting from initial attack by the cationoid fragment of the addition reagent on the double bond, has produced a possible substituent influence that may direct the course of reaction leading to the transition state and thence to the final reaction products.[12] Formulas VIII and IX, where X = Br or OH and X′ = Br, HOH or formic acid, is a representation of the two possible transition states through which the bridged ion could proceed of the possible covalently bonded products. In state VIII where the anionoid fragment X′ is half bonded to C_4, bridging of the group $\ddot{X}$ at C_2 across to the adjacent C_3-position lowers the charge deficiency at C_3 and consequently lowers the energy of the complex as a whole. In state IX where the anionoid fragment X′ is half bonded to C_3-bridging of the group $\ddot{X}$ to the non-adjacent C_4 is not as probable. The stabilization therefore attributable to the bridging of the group at C_2 renders the transition state VIII the more probable course and accounts for the predominance of rearranged product in both bromination and perhydroxylation of norbornylene.



VII



VIII



IX

Significance of Results.—The data on internal hydrogen bonding (see Table I) of the several norcamphane diols prepared was obtained by the elegant method of Kuhn.[13] Comparison with data for several non-bicyclic vicinal diols permits some interesting conclusions. Thus, the O—H bond distances for both the *cis–exo* and *cis–endo*-bicycloheptane diols are the shortest ever observed in cyclic diols, being a tighter bond even than that in *cis*-cyclopentanediol. If the cyclopentane ring were planar, the *cis–vic*-hydroxyl groups would be

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[9] D. Swern, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 386.

[10] A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

[11] See for example D. J. Cram, *ibid.*, **74**, 2129 (1952), and S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952).

[12] This suggestion was made to the senior author in conversation with Dr. Saul Winstein.

[13] L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

eclipsed entirely and the maximum energy of internal hydrogen-bond formation would be realized in this configuration. Where the ring system is constrained in a single rigid configuration and the hydroxyl groups must perforce be eclipsed as in the bicyclic diols I and VI, the fact that a tighter hydrogen bond is observed than in *cis*-cyclopentanediol would seem to indicate that the maximum of hydrogen bond energy is not being realized in the latter case. The magnitude of the difference in hydrogen bond distance from that in the bicyclic cases suggests that the ring in cyclopentane diol is considerably puckered. In cyclopentane itself the extent of puckering of the ring due to non-bonded interaction of the ring hydrogen atoms[14] must be of even greater importance than in *cis*-cyclopentanediol, since the latter would be expected to derive hydrogen-bonding stabilization energy in proportion to the degree of planarity attained in the ring.

Of additional interest is the observation that the (non-vicinal) *cis*-2,7-bicyclic diol has a tighter hydrogen bond than both the vicinal and non-vicinal *cis*-cyclopentanediols. It appears that a C_7-substituent function on the bicycloheptane ring is so close in space to C_1 it conceivably could influence reactions at the C_1 center more strongly than in the corresponding relationship of a *cis* vicinal function on a cyclopentane ring.

The structure established here for III permits a clearer understanding of (the heretofore anomalous) oxidation products obtained by Birch, Oldham and Johnson with chromic acid (*vide supra*). Whereas oxidative cleavage of the intermediate vicinal diol (assumed to result initially from permanganate or norbornylene) would lead to cyclopentane-1,3-dicarboxylic acid, similar cleavage of the 2,7-diol III would be expected to result in the oxidation products observed, in which all the fused rings in the bicyclic system have been opened.

Finally, the *exo*-diol configuration of the permanganate reaction product I may be considered. The attack of the *cis*-perhydroxylating reagent is seen to have occurred at the *exo* side of the bicyclic double bond, in consonance with many analogous observations on the stereochemistry of addition to multiple bonds in bicyclic systems.[15] The present instance must be regarded as the first case (of known stereochemistry) in which other than a normally stepwise (*trans*) addition reaction has been observed to conform to the rule of *exo* addition.

Experimental[14a]

Bicyclo[2.2.1]hepta-2,3-diol (I).—Compound I was prepared following the directions of Bartlett and Bavley.[8] To a solution of 24.5 g. of norbornylene[16] in 50 ml. of acetone cooled in a Dry Ice–acetone-bath to − 10° was added over the course of 1 hour, with stirring, a solution of 47 g. of potassium permanganate in 100 ml. of water and 1 liter of acetone. After addition of the permanganate solution, the reaction was gradually (1 hour) allowed to warm to room temperature and the manganese dioxide filtered off. The reddish-brown solution was saturated with carbon dioxide and the small portion of potassium carbonate that precipitated was removed by filtration. The solution was decolorized with charcoal and the majority of the acetone removed from the now colorless filtrate under vacuum. The residue was extracted with ether and the ether solution dried with anhydrous sodium sulfate. After removal of the ether, vacuum sublimation (115–120° (30 mm.)) of the residue yielded 2.0 g. of shiny white plates melting sharply at 140.2–140.6°. This material gave a positive test for vicinal diol.[17] A discussion of the infrared spectra can be found in another section of this paper.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.62; H, 9.37. Found: C, 65.77, 65.52; H, 9.20, 9.17.

Bicyclo[2,2,1]-2,3-epoxyheptane (II).—To a solution of 43.7 g. (0.24 mole) of monoperphthalic acid[18] in 300 ml. of anhydrous ether was added in small portions, 19.6 g. (0.23 mole) of norbornylene. The reaction was maintained between 0 and 2° with slow stirring for 38 hours or until removal of an aliquot portion of the reaction mixture showed that no additional monoperphthalic acid was being used up. The reaction mixture was then extracted with two 500-ml. portions of 10% sodium hydroxide. The combined sodium hydroxide extracts were in turn extracted with three 500-ml. portions of ether; the ether then washed with water and dried over anhydrous sodium sulfate. After removal of the ether at atmospheric pressure the residue was sublimed slowly at 100° yielding 12 g. (25% yield based on starting material) of a white solid with a sharp penetrating odor. The solid melted with sublimation at 118–119°.

Anal. Calcd. for $C_7H_{10}O$: C, 76.36; H, 9.09. Found: C, 75.99, 75.93; H, 9.15, 9.01.

Oxidation of Bicyclo[2,2,1]heptene-2 to the 2,7-Diol (III).—Bicyclo[2,2,1]-2-heptene was oxidized using a procedure similar to that described in reference 5 for the preparation of *trans*-1,2-cyclohexadiol from cyclohexene. To a 500-ml. round-bottom flask fitted with a thermometer and mechanical stirrer was placed 35 ml. of 30% hydrogen peroxide and 150 ml. of 88% formic acid. Norbornylene (23.5 g., 0.25 mole) was added in small portions over a period of 25 minutes while the temperature of the reaction was maintained between 40 and 45°. The reaction was maintained at 40° for an additional hour and then allowed to stand at room temperature with a slow stirring overnight. The formic acid and water were removed under reduced pressure and to the residue was added 20 g. of sodium hydroxide dissolved in 40 ml. of water. This was added cautiously so as not to allow reaction temperature to rise above 45°. The resulting alkaline solution was then extracted six times with ethyl acetate at 45° and the extract dried with anhydrous sodium sulfate. After removal of the dry ethyl acetate the residue was sublimed at 160° (2 mm.) giving 24.8 g. of crude sublimate. Upon slow resublimation at 110° (1.5–2.5 mm.), 22 g. of a pure white solid was obtained (74% yield), melting with decomposition at 174–176°. This material gave a negative test for a vicinal diol.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.62; H, 9.37. Found: C, 65.32, 65.32; H, 9.24, 9.85.

Hydrolysis of II to the 2,7-Diol (III).—Compound II (2.44 g.) was shaken with 13.2 ml. of perchloric acid solution (7 drops of 72% perchloric acid in 330 ml. of water) for 20 minutes while maintaining the reaction temperature at about 60°. The acid solution was then neutralized with 0.1 *M* NaOH and extracted with ether. The ether extract was dried with anhydrous sodium sulfate, and upon removal of the ether the residue was sublimed at 118–122° (5 mm.) yielding 2.3 g. (80% yield) of a white crystalline solid. This material gave a negative test for vicinal diol. Its infrared spectrum was identical with the spectrum of the product III.

Vinylene Carbonate.—This substance was prepared following the directions of Newman and Addor[19] and obtained as a colorless liquid boiling at 59.8–60° (18 mm.), n^{25}D 1.4212.

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(14) J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2483 (1947).

(14a) K. Alder and G. Stein, *Ann.*, **515**, 191 (1935); **525**, 183 (1936).

(15) The infrared spectra referred to in this paper have been deposited as Document number 4235 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm, payable to: Chief, Photoduplication Service, Library of Congress.

(16) L. M. Joshel and L. W. Butz, THIS JOURNAL, **63**, 3350 (1941).

(17) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1940.

(18) H. Böhme, *Org. Syntheses*, **20**, 70 (1940).

(19) M. S. Newman and R. W. Addor, THIS JOURNAL, **75**, 1263 (1953).

Diels–Alder Adduct from Vinylene Carbonate and Bicyclo[2,2,1]heptene-2 (IV).—Vinylene carbonate (5 g., 0.058 mole), twice distilled cyclopentadiene (4 g. 0.06 mole) and anhydrous benzene (18 g.) were heated at 200° in a sealed glass tube for six hours. Upon removal of the benzene 10.2 g. of a light yellow semi-solid was obtained. This material was sublimed slowly at 130–140° (0.5 mm.) giving 6.4 g. of a white sweet-smelling solid. Upon crystallization of this sublimate from *n*-hexane there was obtained 5 g. of white needles melting sharply at 113.2–113.5°. This material gave a negative test for vicinal diol.

Anal. Calcd. for $C_8H_8O_3$: C, 63.16; H, 5.26. Found: C, 63.34, 63.27; H, 5.32, 5.47.

Reduced Vinylene Carbonate–Cyclopentadiene Adduct (V).—Compound IV was reduced in ethyl acetate solution using Adams catalyst and low pressure hydrogen by a procedure similar to that described by Vogel.[20] The residual product after removal of catalyst and evaporation of the ethyl acetate was not characterized but hydrolyzed directly to VI.

***endo*-Bicyclo[2,2,1]hepta-2,3-diol (VI).**—Compound V, 1.1 g., was hydrolyzed with 30 ml. of 5% sodium hydroxide. The alkaline solution was extracted with ether and the ether solution dried with anhydrous sodium sulfate. Upon vacuum sublimation (80–95° (15 mm.)) of the residue, 0.7 g. (77% yield) of a white crystalline powder was obtained. This material gave a positive test for a vicinal diol. It sublimed around 110° and melted sharply between 201.2–201.7°.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.62; H, 9.37. Found: C, 65.60, 65.66; H, 9.25, 9.17.

Intra- and Intermolecular Hydrogen Bonds in I, III and VI.—The above compounds were purified by resublimation prior to infrared examination. The carbon tetrachloride used as the solvent was distilled over P_2O_5 and stored over P_2O_5 until used. The measurements were taken with a Perkin–Elmer model 21 spectrophotometer equipped with a lithium fluoride prism. The solutions of the compounds were made up according to the procedure of Kuhn.[13] The frequencies of all the bands studied are given in the table.

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[20] A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1949, p. 460.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

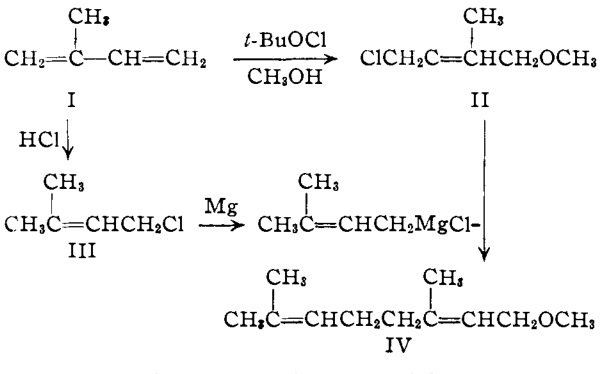
Allylic Rearrangement in the Reactions of 1-Chloro-3-methyl-2-butene; an Attempt at Total Synthesis of Geraniol

BY HAROLD KWART AND ROBERT K. MILLER

RECEIVED APRIL 29, 1954

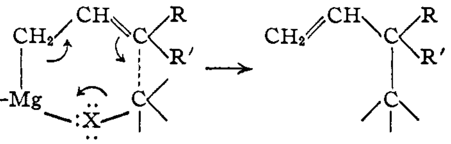
The failure of an attempted total synthesis of geraniol starting from isoprene has prompted an investigation of the reactions of the Grignard reagent obtainable from 1-chloro-3-methyl-2-butene. The reactions of the so-called prenyl Grignard reagent are compared with the reactions of the butenyl[2] Grignard.

The work of Oroshnik and co-workers[1] on the synthesis of vitamin A has suggested to us the possibility of obtaining a total synthesis of geraniol starting from isoprene (I).



This series of reactions, however, failed to yield a product which could be identified as geranyl methyl ether (IV). Since successful coupling reactions of II have been reported,[1a] these results have prompted an investigation of the reactions of the Grignard from III.

It has been demonstrated[2] by Young and his co-workers that allylic Grignard reagents of the type $RCH{=}CHCH_2MgX$ in coupling reactions with allylic halides or addition reactions with carbon dioxide and carbonyl compounds behave without exception as though rearrangement to $RCH(MgX)\text{-}CH{=}CH_2$ had occurred prior to reaction. These observations have been reconciled[3] with a cyclic mechanism of coupling or addition.



X = halogen

R = alkyl or aryl, R' = hydrogen

A similar representation can be used for X = carbonyl oxygen. However, among the allylic halides studied by these workers there were no examples with disubstitution in the *α*- or *γ*-position of the allylic halide. It seemed possible that such cases might afford steric or electronic influences to alter the cyclic course of reaction. Using the Grignard reagent obtained from 1-chloro-3-methyl-2-butene (III) we undertook to examine a coupling and an addition reaction of a case where both R and R' were methyl.

The Grignard reagent from III (designated as the "prenyl"[4] Grignard reagent) was prepared in the manner usual for allylic reagents[2] and reacted with carbon dioxide with the formation of 2,2-dimethyl-3-butenoic acid (V) in good yield. Neither

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[1] (a) W. Oroshnik, THIS JOURNAL, **67**, 1627 (1945); (b) W. Oroshnik, G. Karmas and A. D. Mebane, *ibid.*, **74**, 295 (1952); (c) W. Oroshnik and R. A. Mallory, *ibid.*, **72**, 4608 (1950).

[2] W. G. Young, J. D. Roberts and H. Wax, *ibid.*, **67**, 841 (1945), and articles therein referred to. It has been the practice in these articles to use the non-committal term "butenyl" in referring to the Grignard obtained from either crotyl or *α*-methallyl halide and this is the nomenclature we have adopted throughout this paper.

[3] W. G. Young and J. D. Roberts, *ibid.*, **68**, 649 (1946); W. G. Young and J. D. Roberts, *ibid.*, **68**, 1472 (1946).

[4] This nomenclature is consistent with the name "prenol" given to 3-methyl-2-butene-1-ol by E. Späth and J. Bruck, *Ber.*, **71**, 2709 (1938).