

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 C₈H₈O₃: 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.

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

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 C₇H₁₂O₂: 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 P₂O₅ and stored over P₂O₅ 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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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

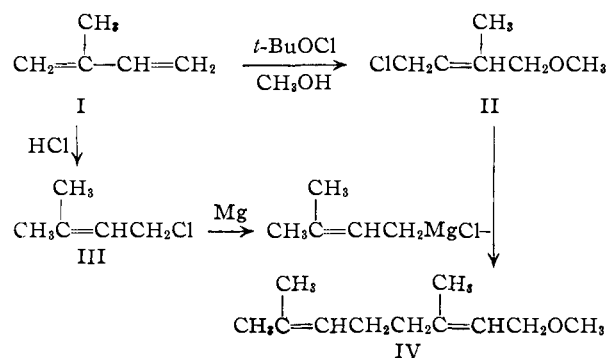
Allylic Rearrangement in the Reactions of 1-Chloro-3-methyl-2-butene; an Attempt at Total Synthesis of Geraniol

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 butenyl² Grignard.

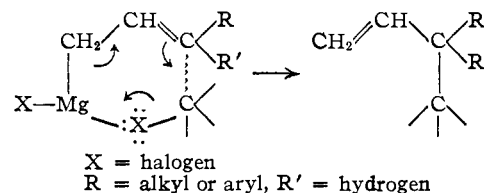
The work of Oroshnik and co-workers¹ on the synthesis of vitamin A has suggested to us the possibility of obtaining a total synthesis of geraniol starting from isoprene (I).



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 demonstrated² by Young and his co-workers that allylic Grignard reagents of the type RCH=CHCH₂MgX in coupling reactions with al-

lylic halides or addition reactions with carbon dioxide and carbonyl compounds behave without exception as though rearrangement to RCH(MgX)-CH=CH₂ had occurred prior to reaction. These observations have been reconciled³ with a cyclic mechanism of coupling or addition.



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 reagents² and reacted with carbon dioxide with the formation of 2,2-dimethyl-3-butenic acid (V) in good yield. Neither

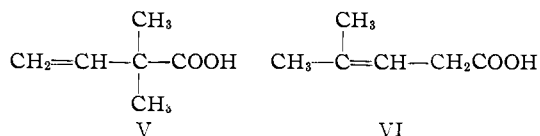
(1) (a) W. Oroshnik, *THIS JOURNAL*, **67**, 1627 (1945); (b) W. Oroshnik, G. Karmas and A. D. Mebane, *ibid.*, **74**, 295 (1952); (c) W. Oroshnik and R. A. Mallory, *ibid.*, **72**, 4608 (1950).

(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 -methylallyl 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).

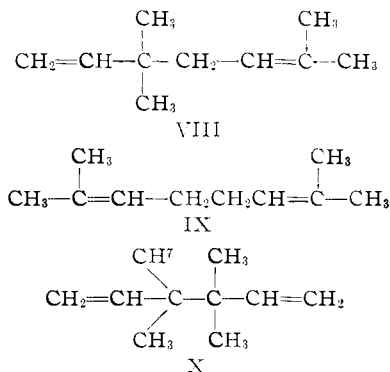
(4) This nomenclature is consistent with the name "prenol" given to 3-methyl-2-butene-1-ol by E. Späth and J. Bruck, *Ber.*, **71**, 2709 (1938).

the alternative product, 4-methyl-3-pentenoic acid (VI), nor any other product could be isolated.



The product V was identified by its dibromide and amide derivatives, and by hydrogenation to 2,2-dimethylbutanoic acid (VII), which in turn was characterized by its physical properties and the melting point of its amide. The properties of these acids and their derivatives clearly indicate that the product of carbonation of the prenyl Grignard reagent is the result of rearrangement.

When 1-chloro-3-methyl-2-butene (III) underwent the coupling reaction with magnesium the major product of the reaction was 3,3,6-trimethyl-1,5-heptadiene (VIII). The alternative products, diprenyl (IX) and 3,3,4,4-tetramethyl-1,5-hexadiene (X), could not be isolated, although they were probably present in very small amounts.



VIII was identified by ozonolysis to α,α -dimethylsuccinic acid. VIII is entirely analogous to the product obtained under similar conditions by Young and co-workers² in the butenyl series. These authors, furthermore, have presented ample evidence to permit the supposition that VIII would also result from the reaction between the prenyl Grignard reagent and III and that the rearrangement observed here in coupling by means of magnesium is traceable to the initial formation of the prenyl Grignard reagent.⁵

Experimental⁶

1-Chloro-3-methyl-2-butene (III).—The method of Jones and Chorley⁷ was followed and gave, in 30% yield, product of b.p. 54–57° (105 mm.), n_{20}^D 1.4495.⁸

2,2-Dimethyl-3-butenic Acid (V).—The Grignard reagent was prepared by the slow addition of 52.5 g. (0.5

mole) of 1-chloro-3-methyl-2-butene, made up to 200 ml. in anhydrous tetrahydrofuran,⁹ to 60 g. (2.5 g. at.) of magnesium under 300 ml. of solvent. Acidimetric analyses¹⁰ of previous Grignards had shown quantitative yields of the reagent when tetrahydrofuran was used as solvent and the usual precautions against coupling¹¹ were observed. The reagent was filtered (to remove excess magnesium) directly onto 600 g. of crushed Dry Ice, as recommended by Lane, Roberts and Young.¹² After the excess Dry Ice had evaporated, the mixture was hydrolyzed by stirring in a solution of 75 ml. of concentrated hydrochloric acid in 125 ml. of water. The organic solvent was salted out, separated and the water layer extracted repeatedly with ether. The combined organic solutions were dried over sodium sulfate and the solvents distilled at ordinary pressure. Distillation of the residue at reduced pressure gave 36.6 g. (64% yield) of acid, b.p. 100–102° (28 mm.), n_{20}^D 1.4295.

The acid rapidly decolorized bromine in carbon tetrachloride. Evaporation of the solution from the bromination gave white crystals, m.p. 86–90°, which on recrystallization from carbon tetrachloride–petroleum ether had m.p. 89–91° (reported¹³ m.p. 91°).

A sample of the acid was converted to the amide by the method described by Shriner and Fuson.¹⁴ After recrystallizing from benzene–petroleum ether the derivative had a m.p. 97–98° (lit.¹⁵ m.p. 93°).

2,2-Dimethylbutanoic Acid (VII).—Thirty-four and seven-tenths grams of the unsaturated acid V dissolved in 150 ml. of ethyl acetate was hydrogenated over Adams catalyst at 50 lb. hydrogen pressure. After hydrogenation was complete the catalyst was filtered off and washed with ethyl acetate. The filtrate and washings were combined, and after distilling off solvent, 26.9 g. (76%) of acid, b.p. 101–105° (32 mm.), was obtained. The bulk of the product had a b.p. 104–105° (32 mm.) and n_{20}^D 1.4130. A small sample of the product had a b.p. 185–188° at atmospheric pressure (lit.¹⁶ b.p. 187° at atmospheric pressure), and gave a negative test with bromine in carbon tetrachloride and neut. equivs. 116.7, 116.4 (theoretical 116.2).

The amide of the hydrogenated acid was prepared in the usual way,¹⁴ and had a m.p. 101–102° (reported¹⁶ m.p. 103°) after recrystallization from benzene. The amide of authentic 2,2-dimethylbutanoic acid, prepared from *t*-amyl halide *via* carbonation of the Grignard reagent, was prepared in the same way and had a m.p. 101–102°. Mixed melting point of the two amides showed no depression.

The infrared spectrum of the saturated acid arising from this series of reactions was obtained (Baird double beam recording spectrophotometer) and found to be identical in every respect with the spectrum (run under identical conditions) of authentic 2,2-dimethylbutanoic acid prepared as indicated above.

3,3,6-Trimethyl-1,5-heptadiene (VIII).—Ninety grams (0.86 mole) of 1-chloro-3-methyl-2-butene reacted with 30 g. (1.2 g. at.) of magnesium under ether according to the method of Henne, *et al.*¹⁷ Reaction occurred readily; the mixture was worked up in the usual way, and, after removal of solvent, distillation of the product gave 25.4 g. (43%) of olefin, b.p. 65–71.5° (49 mm.), the major portion of which had b.p. 70–71.5° (49 mm.), n_{22}^D 1.4400.

Ozonolysis of the Decadiene VIII.—Eight and one-tenth grams of hydrocarbon from the center fraction of the coupling product (above) was dissolved in 100 ml. of ethyl acetate and ozonized oxygen was bubbled through the solution at 0° until no more ozone was absorbed. The ozonized solution was then poured into a mixture of 100 ml. of water,

(9) R. N. Lewis and J. R. Wright, *ibid.*, **74**, 1253 (1952).

(10) H. Gilman, *et al.*, *ibid.*, **45**, 150 (1923).

(11) W. G. Young, A. N. Prater and S. Winstein, *ibid.*, **55**, 4908 (1933).

(12) J. F. Lane, J. D. Roberts and W. G. Young, *ibid.*, **66**, 543 (1944).

(13) L. Bouveault, *Bull. soc. chim. France*, [3] **21**, 1062 (1899).

(14) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 132.

(15) A. Courtot, *Bull. soc. chim. France*, [3] **35**, 111 (1906).

(16) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds, Order I," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 192–193.

(17) A. L. Henne, H. Chanan and A. Turk, *THIS JOURNAL*, **63**, 3473 (1941).

(5) It is our belief, since the reaction of the prenyl Grignard reagent in each case leads to predominantly a single product, that the Young mechanism provides the only satisfactory explanation of the course of these reactions. Reasoning by analogy to the behavior of the butenyl Grignard reagent studied by Young and co-workers, we feel sufficient evidence is available to support the conclusion that the prenyl Grignard reagent exists entirely in the primary covalent form in non-polar media.

(6) Melting points, unless otherwise indicated, were taken in an air-bath melting point apparatus as described by A. May, *Anal. Chem.*, **21**, 1427 (1949), and are uncorrected.

(7) W. J. Jones and H. W. T. Chorley, *J. Chem. Soc.*, 832 (1950).

(8) W. G. Young, S. Winstein and H. L. Goering, *THIS JOURNAL*, **73**, 1958 (1951).

50 ml. of 30% hydrogen peroxide and 5 ml. of concentrated sulfuric acid, and the mixture refluxed until it gave a negative Schiff test (3.5 hr.). The excess peroxide was decomposed by the addition of manganese dioxide and the solution filtered. The filtrate was concentrated under vacuum to yield 1.29 g. of a solid acid, m.p. 120–130°. Recrystallization from water gave white crystals, m.p. 139–140°. The melting point of α,α -dimethylsuccinic acid given in the literature¹⁸ is 140–141°. The product gave neut. equivs. 72.5, 71.7; calcd. for $C_4H_8(COOH)_2$, 73.1.

The anilic acid derivative of the product was prepared by the method of Bone and Sprankling.¹⁸ After recrystallizing from 25% alcohol the derivative had a m.p. 208–210° in the air-bath melting apparatus, and m.p. 186° with decomposition (slow heating) in a capillary melting point tube. This is in accord with the reported¹⁸ melting characteristics of this derivative of α,α -dimethylsuccinic acid.

(18) W. A. Bone and C. H. G. Sprankling, *J. Chem. Soc.*, **75**, 839 (1899).

Attempted Syntheses of Geranyl Methyl Ether.—1-Chloro-2-methyl-4-methoxy-2-butene (II), prepared by the method of Oroshnik and Mallory,¹⁶ b.p. 77–79° (30 mm.), n_D^{20} 1.4605, was added to prenyl Grignard, prepared as previously described, under various conditions of temperature and time of reaction. Work-up of the reaction mixtures was carried out in the usual way, the product being (finally) distilled repeatedly at reduced pressures. In all cases a considerable amount of unreacted II was recovered and only small amounts of high boiling material could be found. Thus, in a typical experiment, out of 96 g. of product only 3.4 g. of material was obtained boiling at 90° (5 mm.), n_D^{20} 1.4646 and giving a positive silver nitrate test for halogen. Infrared spectra of the higher boiling fractions from several runs indicated terminal as well as internal unsaturation. These fractions are obviously complex mixtures, and, since their properties are not near those expected for geranyl methyl ether, no further attempt was made to identify the components.

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

Stereochemistry of Allylic Rearrangements. I. The Synthesis, Assignment of Configuration and Resolution of *cis*- and *trans*-5-Methyl-2-cyclohexenol¹

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RECEIVED MARCH 5, 1954

The diastereoisomeric 5-methyl-2-cyclohexenols have been prepared by reduction of 5-methyl-2-cyclohexanone and the configurations have been established unequivocally by reduction to the corresponding 3-methylcyclohexanols. Lithium aluminum hydride reduction of the ketone gives a mixture of alcohols consisting of 93% of the *cis* and 7% of the *trans* isomer. The product from the aluminum isopropoxide reduction contains 60% of the *cis* and 40% of the *trans* isomer. Physical properties of the alcohols and derivatives and the resolution of the acid phthalates are described.

The diastereoisomeric 5-methyl-2-cyclohexenols described in this paper were of interest in connection with a stereochemical study of replacement reactions and rearrangements in cyclic allylic systems. The stereochemistry and kinetics of the rearrangements of the acid phthalates of these alcohols are reported in the following paper.³

The diastereoisomeric 5-methyl-2-cyclohexenols (I and II) were obtained as mixtures from the reduction of 5-methyl-2-cyclohexanone.⁴ Reduction of the ketone with lithium aluminum hydride gave a 96% yield of a mixture consisting of 93% of the *cis*-(I) and 7% of the *trans*-(II) isomer. The composition of the product, which was isolated in such a way as to avoid fractionation, was determined from the percentage transmission at 9.80 and 13.61 μ (bands present in the spectrum of I but not in that of II) and at 10.66 and 13.28 μ (bands present in the spectrum of II but not in that of I).

The pure *cis* isomer was obtained readily from the lithium aluminum hydride reduction product by recrystallization of the *p*-nitrobenzoate to constant melting point.⁵ Hydrolysis of *cis*-5-methyl-

2-cyclohexenyl *p*-nitrobenzoate with concentrated base with removal of the allylic alcohol as formed by steam distillation yielded pure I as demonstrated by reconversion to the *cis*-*p*-nitrobenzoate. The *cis* configuration was established by reduction of the alcohol to 3-methylcyclohexanol, a reaction which does not affect the configuration of the asymmetric centers. Comparison of the infrared spectra and melting points of derivatives showed the 3-methylcyclohexanol to be identical with authentic *cis*-3-methylcyclohexanol.⁶

The preponderant formation of the *cis* isomer in the lithium aluminum hydride reduction of 5-methyl-2-cyclohexanone parallels the stereochemistry of the reduction of 3-methylcyclohexanone.^{6a} This is especially interesting in view of the fact that for 3,5-disubstituted cyclohexenes the *cis* and *trans* isomers are of similar stability,⁷ whereas for 1,3-disubstituted cyclohexanes the *cis* isomer is the more stable one.^{6a,8}

Reduction of 5-methyl-2-cyclohexanone with aluminum isopropoxide by the method of Macbeth and Mills⁹ for highly reactive carbonyl compounds gave a mixture of isomers in 70% yield. Infrared

(1) This work was supported in part by the Office of Ordnance Research, Contract No. DA-11-022-ORD-1158, Project No. TB2-0001 (630) and in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(2) Allied Chemical and Dye Company Fellow, 1952–1953; du Pont summer research assistant 1953.

(3) H. L. Goering, J. P. Blanchard and E. Silversmith, *THIS JOURNAL*, **76**, 5409 (1954).

(4) J. P. Blanchard and H. L. Goering, *ibid.*, **73**, 5863 (1951).

(5) A good criterion of homogeneity in this case since a binary melting point diagram shows that the melting point of each isomer is depressed considerably by a small amount of the other diastereoisomer.

(6) (a) H. L. Goering and C. Serres, *THIS JOURNAL*, **74**, 5908 (1952); (b) see also D. S. Noyce and D. B. Denney, *ibid.*, **74**, 5912 (1952), and S. Siegel, *ibid.*, **75**, 1317 (1953).

(7) In acetonitrile at 100° the equilibrium mixture of the 5-methyl-2-cyclohexenyl acid phthalates consists of 63–65% of the *trans* and 35–37% of the *cis* isomer (reference 3). The equilibrium mixture of the 5-methyl-2-cyclohexenols (obtained by acid-catalyzed equilibration) in aqueous acetone at 100° consists of 55% of the *cis* and 45% of the *trans* isomer (unpublished results from these laboratories).

(8) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(9) A. K. Macbeth and J. A. Mills, *ibid.*, 2646 (1949).