4,5-Dimethyl-3-(1'-hydroxy)pentadecylveratrole (XIII).—To a solution of tetradecyl Grignard reagent prepared in the customary manner from 2.4 g of magesium metal (0.1 g-atom) and 25.5 g of 1-bromotetradecane (0.092 mole) in 85 ml of anhydrous ether was added 15.4 g of 5,6-dimethyl-*o*-veratraldehyde (0.08 mole) in 100 ml of ether. When the initial exothermic reaction had subsided, the mixture was heated at reflux for 20 hr. Hydrolysis was then accomplished by addition of 100 ml of 10% aqueous sulfuric acid and the phases were separated. After extracting with 100 ml of ether, the ethereal solutions were combined and washed with two 50-ml portions of 10% sodium bicarbonate, followed by four 50-ml portions of water. The ether solution was dried over magnesium sulfate and the solvent was removed to give a yellow oil which was dissolved in 50 ml of boiling ethanol. On cooling, 3.2 g of octacosane precipitated and was removed by filtration. The resulting solution was evaporated to give 25.7 g of crude 4,5-dimethyl-3-(1'-hydroxy)-pentadecylveratrole, which was used without further purification.

4,5-Dimethyl-3-pentadecylveratrole (VII).—The crude carbinol (XIII) from the previous reaction was dissolved in 150 ml of ethyl acetate containing 20 drops of sulfuric acid and the solution was hydrogenated in a Parr pressure reaction apparatus for 23 hr over 2.5 g of 10% palladium-on-carbon catalyst at an intial hydrogen pressure of 60.5 psi and about 60°. The catalyst was then removed by filtration and the solution was diluted with 100 ml of ether and then washed with 50 ml of 10% sodium bicarbonate, followed by four 50-ml portions of water. The residual oil obtained after drying the solution and removal of solvent was distilled at 0.4 mm to give 14.3 g of 4,5-dimethyl-3-pentadecylveratrole as a colorless oil (bp 215–235°) which became a white solid on cooling, mp 41.5–43°. The significant peaks in the nmr were singlets at τ 3.42 and 6.10 and a pair of singlets at 7.64 and 7.72 in the ratio 1:6:6.

Anal. Calcd for $C_{25}H_{44}O_2$: C, 79.73; H, 11.78. Found: C, 80.00; H, 11.81.

4,5-Dimethyl-3-pentadecylcatechol (II).—A solution of 10.4 g of 4,5-dimethyl-3-pentadecylveratrole in 50 g of pyridine was heated at reflux and a rapid stream of hydrogen chloride gas was passed through the reaction mixture. After about 45 min the solution stopped refluxing and the temperature of the reaction mixture rose slowly to about 225°. At that temperature refluxing began again with considerable frothing and the temperature was then maintained at 215–225° for 4.5 hr with continuous passage of hydrogen chloride. At the end of that time the contents of the flask were allowed to cool to 100°, and 50 ml of water was added, and after further cooling, 100 ml of ether was added as well. The phases were then separated, the water layer was extracted with two 100-ml portions of ether, and the combined ether solution was washed with three 100-ml portions of water and dried over magnesium sulfate. Removal of the solvent gave a tan solid which was recrystallized from hexane to yield 9.5 g (99%) 4,5-dimethyl-3-pentadecylcatechol as a white, noncrystalline solid, mp 77.0–78.2°. The hydroxyl peaks of the catechol appeared in the infrared in chloroform solution at 2.78 and 3.05 μ. A peak for methoxyl no longer was evident at ~9.3 μ.

Anal. Calcd for $C_{23}H_{40}O_2$: C, 79.26; H, 11.57. Found: C, 79.46; H, 11.60.

Registry No.—II, 7771-22-4; IVb, 7461-75-8; VIII, 7771-24-6; X, 7771-25-7; XII, 7732-10-7; V, 7732-11-8; XIII, 7771-26-8; VII, 7771-27-9.

Small-Ring Compounds. XV. The Dehydration of *trans*-$\alpha,\alpha,\alpha',\alpha'$-Tetramethyl-1,2-cyclopropanedimethanol

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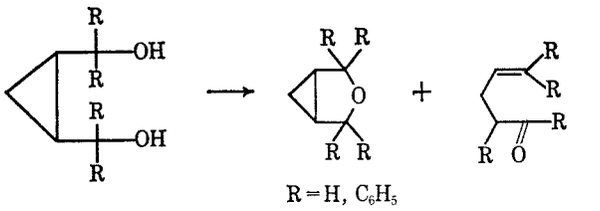
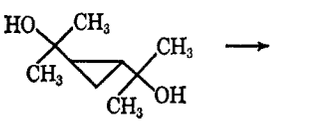
Received November 1, 1966

The dehydration of *trans*-$\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,2-cyclopropanedimethanol (1), catalyzed by *p*-toluenesulfonic acid yielded six products: two cyclic ethers (4 and 7), three unsaturated hydroxy compounds (2, 5, and 8), and one unsaturated ketone (9). The reaction routes were discussed on the basis of the structures of the products and the results of the gas chromatographic analysis.

The possibility of conjugative interaction of the cyclopropane ring with an adjacent unsaturated group or an carbonium ion has been of interest to many workers.[1] Especially, recent nuclear magnetic resonance (nmr),[2] electron diffraction,[3] or solvolysis studies[4] have strongly suggested the existence of such interaction. If such a prediction is correct, the solvolytic behavior of cyclopropylcarbinyl compounds bearing an unsaturated group on their 2 position might be affected by the substituent. In the present study, the syntheses of some cyclopropane derivatives having an unsaturated substituent were attempted for the purpose of the investigation of the above-mentioned effect.

In the previous paper[5] in this series, a study was made of the dehydration of some *cis*-1,2-cyclopropanedimethanol derivatives to a cyclic ether and a rearranged product. On the other hand, the dehydration of *trans*-$\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,2-cyclopropanedimethanol (1), synthesized from dimethyl *trans*-1,2-cyclopropanedicarboxylate by the Grignard method, might be expected to give *trans*-2-isopropenyl-α,α-dimethylcyclopropanemethanol (2) or *trans*-1,2-diisopropenylcyclopropane (3).





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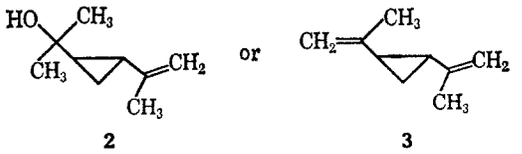


2 3

(1) For a summary of leading references, see P. von R. Schleyer and G. W. VanDine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).

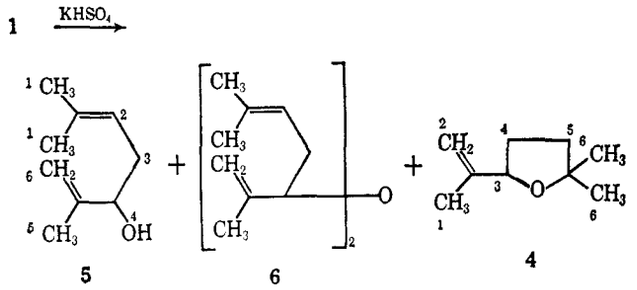
(2) G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965).

(3) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965).

(4) H. C. Brown and J. D. Cleveland, *J. Am. Chem. Soc.*, **88**, 2051 (1966).

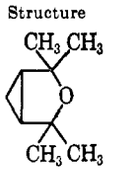
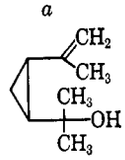
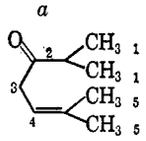
(5) T. Shono, A. Oku, T. Morikawa, M. Kimura, and R. Oda, *Bull. Chem. Soc. Japan*, **38**, 940 (1965).

The preliminary study[6] of the dehydration of **1** catalyzed by potassium bisulfate afforded an unexpected result; the main products were **4**, **5**, and **6**.



In the present study, the dehydration of **1** under milder conditions was investigated to learn the detailed reaction routes. The reaction was performed in dioxane with *p*-toluenesulfonic acid as catalyst and was followed by gas chromatographic analysis where six major peaks were observed. (The peaks were numbered from 1 to 6 in the order of the increase in the retention time.) The compound corresponding to each peak (except peak 3) was separated and identified on the basis of elemental and spectroscopic analyses (Table I). All of the attempts to isolate or to synthesize the compound corresponding to peak 3 were unsuccessful, but the structure of this compound may be supposed to be **8**, as peak 3 was observed almost in parallel with peak 1 (**7**) and was easily rearranged to peak 4 (**2**) when it was heated under a neutral condition.[7] The relative intensity of each peak varied with the reaction time as shown in Figure 1, where the concentration of the catalyst was low and the peaks 2 (**4**) and 5 (**9**) were scarcely observed.

TABLE I
STRUCTURES OF PRODUCTS

Peak	Compd	Structure
1	7	
2	4	*a*
3	8	*cis* 
4	2	*a*
5	9	
6	5	*a*

[a] See the text.

Figure 1 suggests that under such a mild condition the reaction does not proceed beyond **5** and that **2**, **7**, and **8** are formed competitively, although **2** is the main product at a short reaction time and may collapse rapidly to the others. Compound **2** was synthesized according to the scheme shown and was dehydrated under conditions similar to those of the dehydration of **1** (Figure 2).

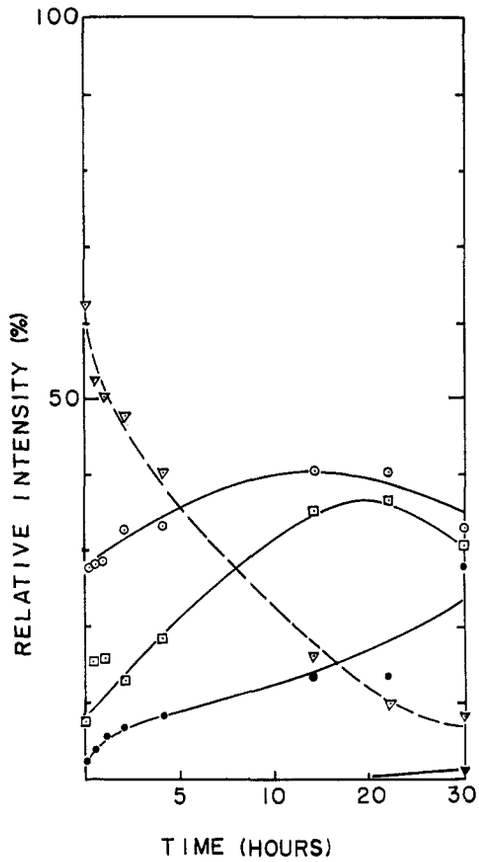


Figure 1.—Plot of relative intensity of each peak *vs.* reaction time: peak 1 (**7**), —○—○—; peak 3 (**8**) —□—□—; peak 4 (**2**), - -▽- -▽- -; peak 5 (**9**), —▼—▼—; and peak 6 (**5**), —●—●—.

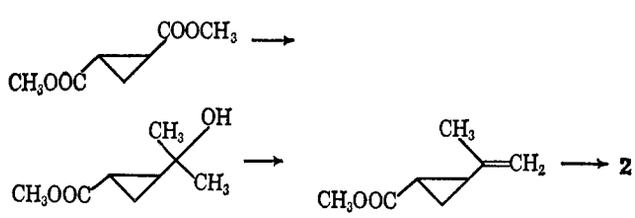
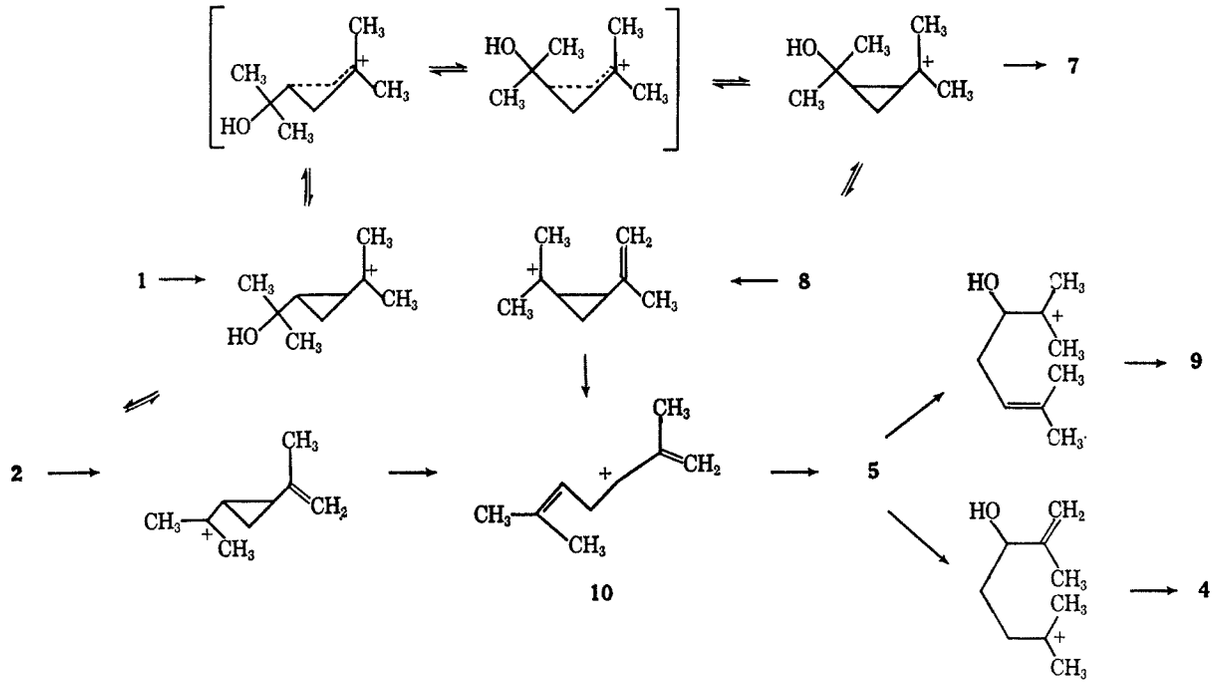


Figure 2, where the concentration of the catalyst was ten times that in Figure 1, may suggest that **9** and **4** arose from **2** and **8** passing through **5** as an intermediate. The formation of **7** and **8** requires the rearrangement of *trans* isomer to *cis* isomer and this rearrangement, in which an homoallyl-type carbonium ion would be assumed to the transition state, must occur in the early step of the reaction. All the evidence mentioned above suggest the reaction routes depicted in Scheme I. The absence of the methylenecyclopropane derivative **11** (Scheme II) or ketone **12** in the dehydrated products might indicate that **2** is fairly well stabilized by the conjugation between the isopropenyl group and the cyclopropane ring. That the ring-opened product **5** was obtained despite the expectation of the formation of the conjugatively stabilized **3** may be rationalized by the conjugative stability of the allyl cation **10**. It seems interesting that the dehydration of the *trans* isomer **2** yielding **10** may be faster than that of the *cis* isomer **8**.

(6) T. Shono, T. Yoshimura, and R. Oda, *J. Chem. Soc. Japan*, in press.
(7) That **8** arose from **2** (Figure 2) and that **5** arose from **8** (Figure 2) would be the additional facts to support the proposed structure of **8**.

SCHEME I



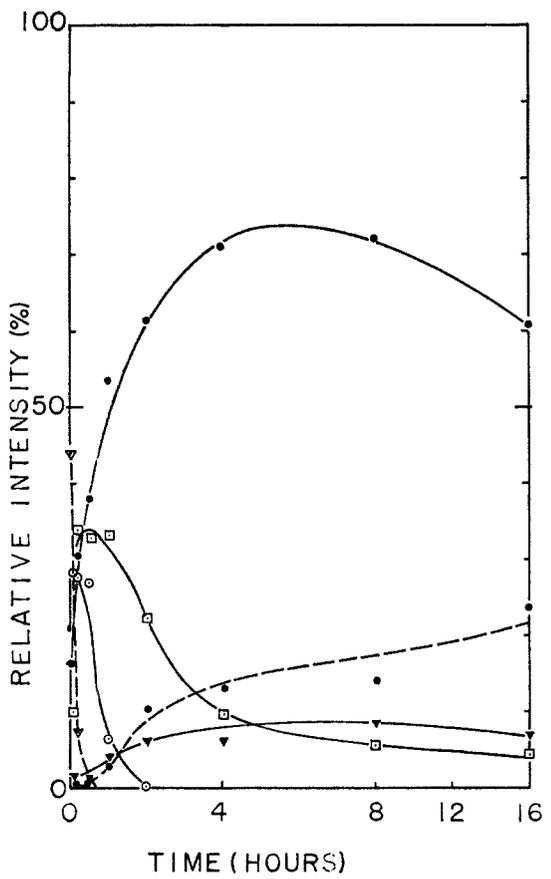


Figure 2.—Plot of relative intensity of each peak *vs.* reaction time: peak 1 (7), —○—○—; peak 2 (4), —●- - -●—; peak 3 (8), —□—□—; peak 4 (2), -▽- - -▽-; peak 5 (9), —▼—▼—; and peak 6 (5), —●—●—.

Experimental Section

***trans*-α,α,α',α'-Tetramethyl-1,2-cyclopropanedimethanol (1).**—To an ethereal solution of the Grignard reagent prepared from 426 g (3.0 moles) of methy iodide and 28 g (3.0 moles) of magnesium, 79 g (0.5 mole) of dimethyl *trans*-1,2-cyclopropanedicarboxylate was added dropwise to maintain the gentle boiling of the ether. After addition was completed, the reaction mixture was refluxed for an additional 1 hr and then allowed to stand at room temperature overnight. The mixture was worked up by usual method and **1**, mp 67.5–70° (recrystallized from ligroin–ether), was obtained as crystal after the ether was evaporated, the yield being 60 g (76.8%).

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.33; H, 11.28.

Methyl *trans*-2-(1-Hydroxyisopropyl)cyclopropanecarboxylate.—A solution of the Grignard reagent prepared from 56.8 g (0.2 mole) of methyl iodide and 10 g (0.22 mole) of magnesium in 200 ml of ether was added dropwise during 2 hr at 0–5° to a solution of 32 g (0.20 mole) of dimethyl *trans*-1,2-cyclopropanedicarboxylate in 100 ml of ether. After the addition was completed, the reaction mixture was stirred for 30 min at room temperature and then was refluxed for an additional 2 hr. The mixture was treated in usual way and 12.6 g (39.4%) of methyl *trans*-2-(1-hydroxyisopropyl)cyclopropanecarboxylate (bp 114–116° at 19 mm) was obtained.

Methyl *trans*-2-Isopropenylcyclopropanecarboxylate.—To powdered potassium bisulfate in a distilling flask, 32 g (0.23 mole) of methyl *trans*-2-(1-hydroxyisopropyl)cyclopropanecarboxylate was added dropwise at 180°. The organic layer of the distillate was separated, dried, and distilled to give methyl *trans*-2-isopropenylcyclopropanecarboxylate, yield being 23 g (71.7%), bp 166–167°. The structure is supported by nmr data τ 7.8–9.2 (ring protons), 8.4 ($CH_3\overset{|}{C}=$), 6.4 ($COOCH_3$), and 5.3 ($=CH_2$).

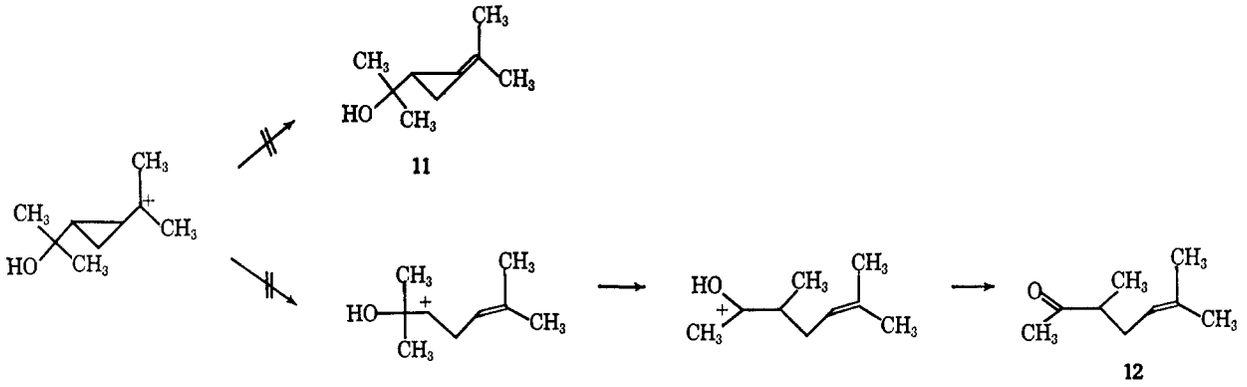
Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.84; H, 8.83.

***trans*-2-Isopropenyl-α,α-dimethylcyclopropanemethanol (2).**—To a solution of the Grignard reagent prepared from 85 g (0.6 mole) of methyl iodide and 14 g (0.58 mole) of magnesium in 300 ml of ether, 28 g (0.2 mole) of methyl *trans*-2-isopropenylcyclopropanecarboxylate was added dropwise at room temperature. After the reaction mixture was refluxed for 2 hr, it was treated in usual manner to give **2**, yield being 20 g (71.4%); bp 74° at 15 mm; nmr data τ 8.6–9.6 (ring protons), 8.85 ($(CH_3)_2\overset{|}{C}CH_3$, singlet), 8.4 ($CH_3\overset{|}{C}=$, singlet), 7.5 (OH, singlet), and 5.5 ($=CH_2$, doublet); infrared spectrum 1630, 880 ($C=CH_2$), 3340, and 1150 cm^{-1} (COH).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.89; H, 11.73.

Dehydration of 1 or 2.—The dehydration of **1** or **2** was carried out in anhydrous dioxane using *p*-toluenesulfonic acid as catalyst.

SCHEME II



The molar ratios of the catalyst to **1** or **2** were 1 and 0.1. The reaction was followed by vapor phase chromatographic analysis on a 2-m Silicon DC 550 column at 120°. Two of the results are shown in Figures 1 and 2.

Separation and Identification of the Products. A. Compound 4.—A solution of 10 g (0.063 mole) of **1** and 2.18 g (0.013 mole) of *p*-toluenesulfonic acid in 40 g of anhydrous dioxane was allowed to stand at room temperature for 7 days. After the reaction mixture was neutralized with sodium bicarbonate, it was distilled to give 1 g of **4** (11.4%): bp 61–62° at 39 mm; nmr data τ 8.77 (C_6 protons, singlet), 8.3 (C_1, singlet with small coupling), 7.85–8.42 (C_4 and C_5, multiplet), 5.63 (C_3, triplet), and 4.99 and 5.21 (C_2, doublet); infrared spectrum 1650, 900 (C=CH_2), 1370, 1390 [C(—CH_3)CH_3], and 1060–1080 (COH).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.89; H, 11.36.

B. Compound 5.—A solution of 6.32 g (0.04 mole) of **1** and 6.88 g (0.04 mole) of *p*-toluenesulfonic acid in 28 ml of dioxane was allowed to stand at room temperature for 5 hr. The reaction mixture was neutralized with sodium bicarbonate, dried, and distilled to yield 1.7 g of **5** (30%): bp 91° at 23 mm; nmr data τ 8.32 (C_1 protons, singlet), 8.4 (C_5, singlet), 7.82 (C_3, triplet), 6.46 (OH, singlet), 6.05 (C_4, triplet), 5.15 and 5.27 (C_6, doublet), and 4.9 (C_2, triplet); infrared spectrum 3360, 1020–1040 (COH), 1650, 890 (C=CH_2), and 830 (CH=C).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.97; H, 11.54.

C. Compound 9.—A solution of 5.6 g (0.04 mole) of **2**, 3.44 g (0.02 mole) of *p*-toluenesulfonic acid, and 0.72 g (0.04 mole) of water in 28 g of dioxane was allowed to stand at 20° for 30 min. After the reaction mixture was neutralized with sodium bicarbonate, **9** was separated by preparative vapor phase chromatograph (column, Apiezon L): nmr data τ 8.9 (C_1 protons, doublet), 8.25 (C_5, singlet), 7.2–7.8 (C_2, multiplet), 6.91 (C_3, doublet), and 4.65 (C_4, triplet). The 2,4-dinitrophenylhydrazone of **9** melted at 113–115°.

Anal. Calcd for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.09. Found: C, 56.48; H, 5.96.

D. Compound 7 was synthesized by the method reported earlier[5] and identified by vapor phase chromatographic analysis.

Registry No.—**1**, 7731-99-9; methyl *trans*-2-(1-hydroxyisopropyl)cyclopropanecarboxylate, 7732-00-5; methyl *trans*-2-isopropenylcyclopropanecarboxylate, 7732-01-6; **2**, 7732-02-7; **4**, 7771-20-2; **5**, 7775-88-4; **9**, 5782-75-2; 2,4-dinitrophenylhydrazone of **9**, 7771-21-3.

Kinetics of the Addition of Alcohols to Activated Vinyl Compounds

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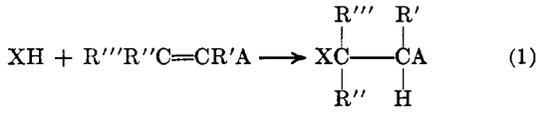
Received July 1, 1966

The kinetics of the base-catalyzed addition of alcohols to 29 compounds containing activated carbon–carbon double bonds of the type R'''R''C=CR'A, where A is a strongly electron-attracting group, have been investigated. The effects of varying the activating group A and the groups R', R'', and R''' were explored. The rate-enhancing effect of the activating group was found to increase in the order CONHR < $CONH_2$ < $CONR_2$ < CO_2R < SO_2NR_2 < CN < SO_2R < COR ≤ $^+PR_3$, where R is the same lower alkyl group. A methyl group on either vinyl carbon lowers the rate compared with that of the unsubstituted activated vinyl compound, with α substitution producing the greater effect. Two β substituents produce a greater rate reduction than monosubstitution in either position.

The addition of nucleophiles to carbon–carbon double bonds activated by an adjacent electron-attracting group (A) is widely recognized and utilized in preparative organic chemistry. Kinetic studies of the Michael reaction and the activated vinyl reaction[1] have been reported, primarily for reaction with active hydrogen compounds other than alcohols.[2] Ogato, *et al.*,[2c] were the first to carry out a kinetic study of the base-catalyzed addition of an alcohol to an activated vinyl compound. These authors studied the kinetics of



(1)

(1) In accordance with present custom, the authors restrict the term Michael reaction to those additions involving carbon nucleophiles where a new carbon–carbon bond is formed, and prefer the term activated vinyl reaction (or addition) for noncarbon nucleophiles, *e.g.*, alcohols, amines, thiols.

(2) (a) W. J. Jones, *J. Chem. Soc.*, **105**, 1547 (1914); (b) M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.*, **78**, 4556 (1956); (c) Y. Ogato, M. Okano, Y. Furuya, and I. Tabushi, *ibid.*, **78**, 5426 (1956); (d) R. Oda and T. Shono, *Nippon Kagaku Zasshi*, **78**, 1683 (1957); (e) V. G. Ostroverkhov, *Ukr. Khim. Zh.*, **23**, 474 (1957); *Chem. Abstr.*, **52**, 6196 (1958); (f) J. F. Bunnett and J. J. Randall, *J. Am. Chem. Soc.*, **80**, 6020 (1958); (g) U. Schmidt and H. Kubitzek, *Chem. Ber.*, **93**, 866 (1960); (h) J. Hine and L. A. Kaplan, *J. Am. Chem. Soc.*, **82**, 2915 (1960); (i) T. I. Crowell and A. W. Francis, Jr., *ibid.*, **83**, 591 (1961); (j) N. Ferry and F. J. McQuillin, *J. Chem. Soc.*, 103 (1962); (k) M. L. Bender and K. A. Connors, *J. Am. Chem. Soc.*, **84**, 1980 (1962); (l) T. O. Crowell, G. C. Helsley, R. E. Lutz, and W. L. Scott, *ibid.*, **85**, 443 (1963); (m) M. Friedman and J. S. Wall, *J. Org. Chem.*, **31**, 2888 (1966).