trometer. The rate constant for the disappearance of vinyl protons was calculated in the usual manner.[43b]

Nucleophilic Reactivity of the Carbon–Carbon Double Bond. II. Solvolytic Ring Closure of 2-(3-Methyl- and 3,4-dimethyl-Δ³-cyclopentenyl)ethyl p-Nitrobenzenesulfonates[1]

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Contribution from the Converse Memorial Laboratory of Harvard University, Cambridge 38, Massachusetts. Received July 24, 1964

The two compounds in the title (XII and XIII), prepared according to Chart I, show acetolysis rates which are faster than that of the saturated reference compound XXXIII by factors of 600 and 3300, respectively. The similar accelerating effects of the first and second methyl groups show that the anchimeric assistance by the double bond is such as to place nearly equal amounts of positive charge simultaneously on the two originally doubly bonded carbon atoms. The products from XII and XIII, 2-methyl- and 1,2-dimethyl-exo-2-norbornyl acetates, respectively, have been isolated in good yield and their structures have been confirmed by synthesis. The effects of methyl substitution in solvolytic ring closure are compared with those in epoxidation and acid-catalyzed hydration as models for symmetrical and unsymmetrica ltransition states. 2-(2-Indanyl)ethyl p-nitrobenzenesulfonate (XIV) undergoes acetolysis more slowly than the saturated reference compound.

Introduction

In homoallylic (3-alkenyl) halides and sulfonates a carbon–carbon double bond often acts to accelerate ionization. In most such cases one end of the double bond (C-3) is nearer than the other to the seat of ionization, and it is the remote end of the double bond which appears (on the basis of product structure) to carry a good share of the charge. Examples are cholesteryl tosylate (I),[2] exo-2-norbornenyl bromide (III),[3] and 4-methyl-3-pentenyl tosylate (VI).[4] In these cases it has been inferred that the transition state and first intermediate in solvolysis involve an unsymmetrical participation of the double bond (II, IV, and VII, respectively). Although the norbornenyl cation readily undergoes rearrangements suggesting the symmetrical structure V[5] rather than IV, the incomplete redistribution of C-14 in the solvolysis of labeled norbornenyl derivatives[6] excludes V as the sole ionic intermediate, and even the representation V assigns different roles to the two carbon atoms of the double bond.

Among ionizable compounds which lead to cyclization by the π-route,[7] some of the greatest accelerations are noted in compounds having the double bond in the 5,6-position relative to the departing group and symmetrically placed, so that its two carbon atoms are equidistant from C-1 or nearly so. It is especially striking that the ratio of assisted to unassisted formolysis appears to be about 16 times as great for the symmetrically placed double bond of 2-(Δ³-cyclopentenyl)ethyl p-nitrobenzenesulfonate (VIII)[7] as for the unsymmetrically placed one of 3-(Δ²-cyclopentenyl)propyl p-nitrobenzenesulfonate (IX).[8] The most spectacular case of the effect of symmetry remains the contrast between the effect of the double bond on solvolysis rate in

anti-7-norbornenyl sulfonates $(k_{unsat}/k_{sat} = 10^{11})$[9] and in *exo*-2-norbornenyl sulfonates $(k_{exo}/k_{endo} = 10^3)$.[10]

(1) Presented at the 100th Annual Meeting of the National Academy of Sciences, Washington, D. C., April 22, 1963.
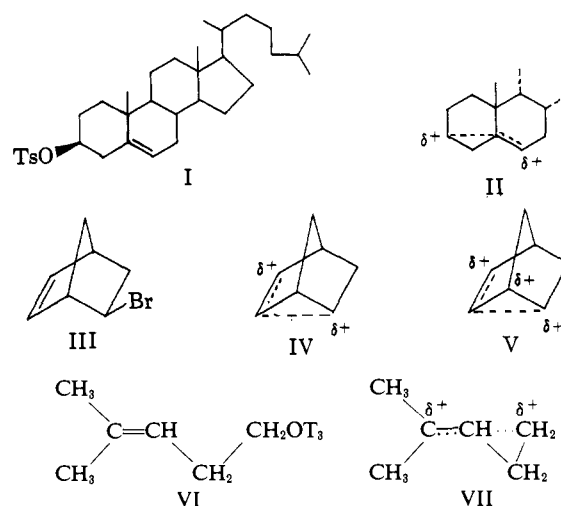(2) S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948).
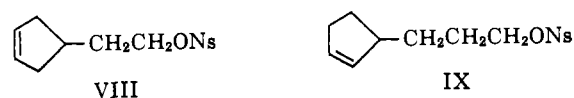(3) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).
(4) J. B. Rogan, *J. Org. Chem.*, **27**, 3910 (1962).
(5) C. H. DePuy, I. A. Ogawa, and J. C. McDaniel, *J. Am. Chem. Soc.*, **82**, 2397 (1960).
(6) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *ibid.*, **77**, 3034 (1955).

(7) For references see part I of this series: P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); P. D. Bartlett, *Ann.*, **653**, 45 (1962). For a definition of "π-route" see S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).
(8) W. D. Closson, *ibid.*, **86**, 1887 (1964).
(9) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).
(10) S. Winstein, H. M. Walborsky, and K. C. Schreiber, *ibid.*, **72**, 5795 (1950).

These facts make it appear that there must be conditions under which the nucleophilic reactivity of the C–C double bond involves direct, symmetrical attack through its π-electron pair upon the carbon bearing the anionic group. This is the mode of attack to be expected for direct formation of the symmetrical norbornyl bridged ion X, as opposed to the species with localized charge (XI) in the assisted solvolysis of VIII. In the present paper we report the preparation of three substitution products of 2-(Δ³-cyclopentenyl)ethanol (XII, XIII, and XIV) and the study of the products and rates of their solvolysis. As expected, the methyl groups increase the nucleophilic reactivity of the double bond
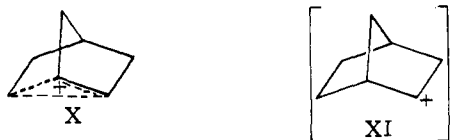

while the fused benzene ring diminishes it. The nearly equivalent effects of the first and second methyl groups provide information about the symmetry of the nucleophilic attack.

$$Ns = O_2SC_6H_4NO_2(p)$$
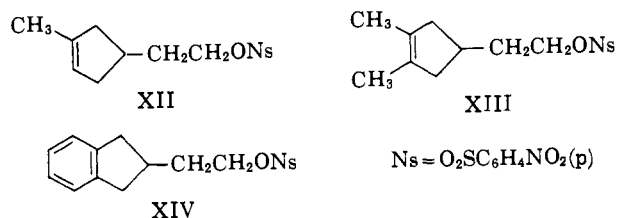
Preparation and Structure Proof. After much exploratory work the methylated compounds XII and XIII were prepared from isoprene and 2,3-dimethylbutadiene, respectively, by the sequence shown in Chart I.
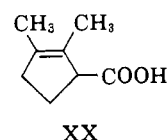
Chart I

a, R = H
b, R = CH₃
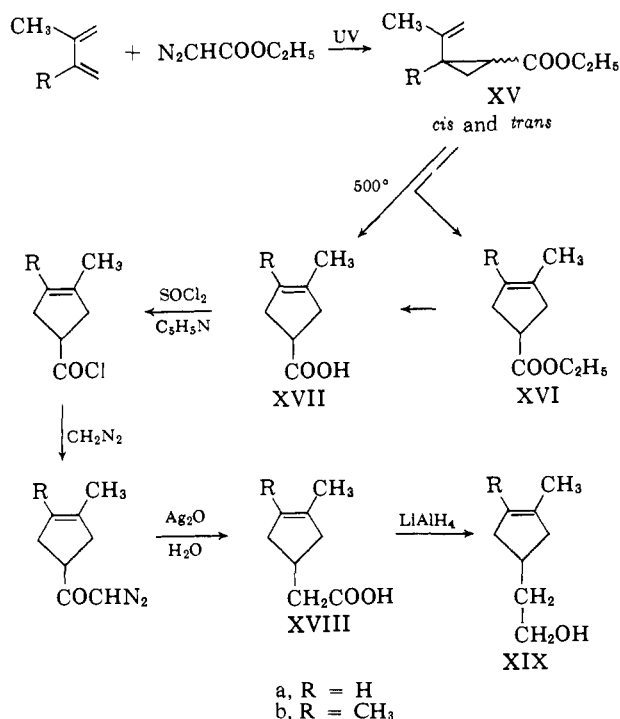
The ester XVb had been prepared by LaForge and co-workers[11a] using diazoacetic ester and copper powder. The use of ultraviolet irradiation proved advantageous, the yield based upon unrecovered starting material being 68% compared to 39% for the copper method. The structures of the cyclopropane esters were established by their n.m.r. spectra; a doubling of the signals due to the ethyl group indicated the presence of stereoisomers, in the ratio of 2:1, in the case of the dimethyl product XVb; in the case of XVa the proportions were 5:4. The structure assignment of XVa was based upon the absence of perceptible infrared absorption at 10.05–10.15 and 10.9–11.05 μ and the chemical shift and integrated peak intensity of the ethylenic proton absorption in the n.m.r. As little as 10% of the isomer with a terminal vinyl group would have been detectible by these criteria.[11b]

The thermal rearrangement of the isopropenylcyclopropane ester XV, patterned after some experiments of Vogel,[12a] proceeded smoothly to give, in the case of the dimethyl compound, a 74.5% yield of the combined acid and ester. It was observed that the unconverted ester XV underwent no elimination of ethylene, and product acid XVII could therefore be separated conveniently from accompanying materials by simple extraction with alkali.

For the ester and acid XVI and XVII to have the structure shown it is necessary that the cyclopropane ring in XV, in the course of the rearrangement, should have opened between the allylic carbon atom and the carbon atom bearing the carbethoxy group. That the n.m.r. spectrum of XVIIb shows a single unsplit methyl signal at τ 8.38, its area six times that of the carboxyl proton at τ −1.35, renders the alternative structure XX unlikely.[12b] The structure of the ester

XVIb was definitely established by the degradation shown in Chart II, yielding the known[13] di-n-propylacetamide, m.p. 123–124°. The structure XX would have yielded ethyl-n-butylacetamide, m.p. 101–102°, more than 20° lower than our product.
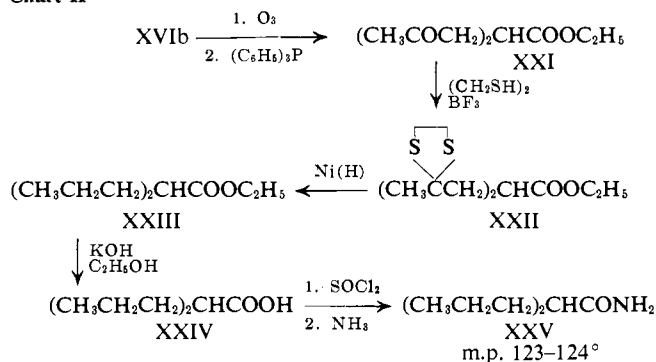
The identical location of the methyl group and double bond in XVIIa and XVIIb is shown by the fact that the n.m.r. spectra of the two are identical except that XVIIa, compared to XVIIb, shows half the intensity of the signal due to the methyl group on the double bond, and a new broad singlet at τ 4.8, attributable to a single ethylenic proton.

(11) (a) F. B. LaForge, W. A. Gerdsdorff, N. Green, and M. S. Schlechter, *J. Org. Chem.*, 17, 381 (1952). (b) The preference of the adding reagent, presumably carbethoxycarbene, for addition to the unsubstituted double bond of isoprene is unexpected. Either electrophilic attack by singlet carbenes (W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, 78, 3224 (1956); P. S. Skell and R. C. Woodworth, *ibid.*, 78, 4496 (1956); 81, 3383 (1959)) or formation of a biradical intermediate (P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, 86, 616 (1964)) from a triplet carbene might be expected to open the substituted double bond of the diene. Either cyclopropane could of course produce XVIa by rearrangement.
(12) (a) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, 1, 53 (1962); 2, 1 (1963); (b) XX or its ester would result from allylic migration of the CH₂ group of XVb instead of the CHCOOC₂H₅ group.
(13) E. Fischer and A. Dilthey, *Ber.*, 35, 844 (1902).

Chart II

XVIb $\xrightarrow[\text{2. (C}_6\text{H}_5)_3\text{P}]{\text{1. O}_3}$ (CH$_3$COCH$_2$)$_2$CHCOOC$_2$H$_5$

XXI $\downarrow$ $\overset{\text{(CH}_2\text{SH)}_2}{\text{BF}_3}$

(CH$_3$CH$_2$CH$_2$)$_2$CHCOOC$_2$H$_5$ $\xleftarrow{\text{Ni(H)}}$ (CH$_3\overset{\text{S S}}{\text{C}}CH_2$)$_2$CHCOOC$_2H_5$

XXIII   XXII

$\downarrow\overset{\text{KOH}}{_{\text{C}_2\text{H}_5\text{OH}}}$

(CH$_3$CH$_2$CH$_2$)$_2$CHCOOH $\xrightarrow[\text{2. NH}_3]{\text{1. SOCl}_2}$ (CH$_3$CH$_2$CH$_2$)$_2$CHCONH$_2$

XXIV   XXV
                                 m.p. 123–124°

The alcohols XIXa and XIXb, after a single distillation (b.p. 88–89° at 13 mm. and 66–66.5 at 0.35 mm.), were shown by vapor phase chromatography to be 97.8 and at least 99% pure, respectively. Their *p*-nitrobenzenesulfonates, m.p. 52.2–53.8° and 69.2–71°, the melt in the latter case being blood red, were prepared in average yields of 60% by treatment with 1.2 equiv. of *p*-nitrobenzenesulfonyl chloride in anhydrous pyridine at −10 to 0° for 45 min. in carefully dried apparatus.

The benzo analog of these compounds, 2-(2-indanyl)-ethyl *p*-nitrobenzenesulfonate (XIV), was prepared from 2-indanylmalonic ester by way of hydrolysis, decarboxylation, and reduction with lithium aluminum hydride. XIV melted at 126–127° after recrystallization from benzene–ligroin. The alcohol was shown by vapor phase chromatography to be at least 99% pure.
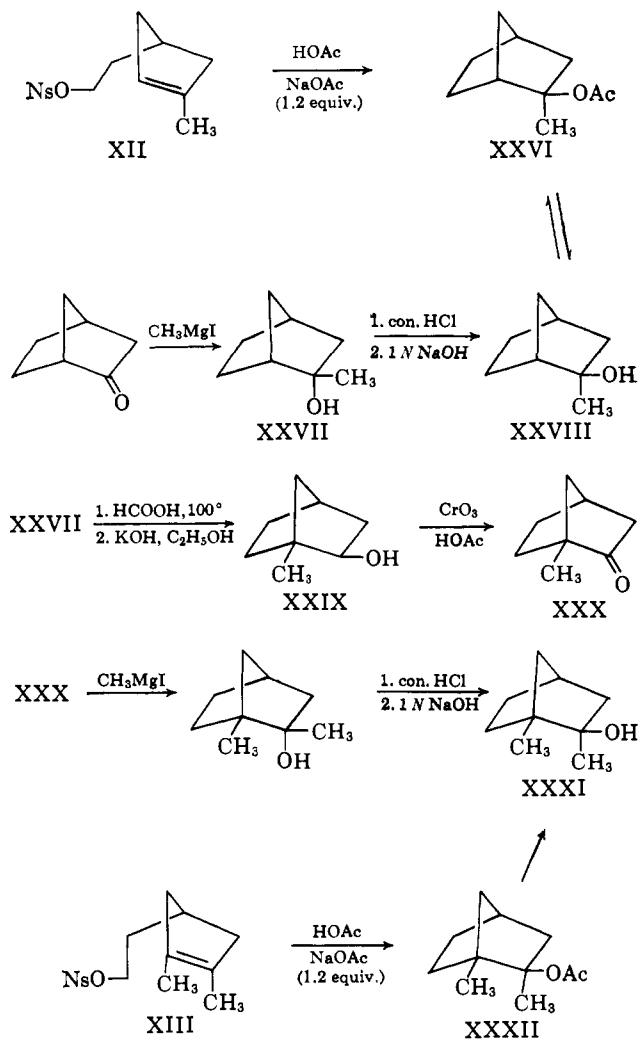
Product Studies. The monomethyl starting material (XII) was solvolyzed for 12 half-lives at 70° in acetic acid containing 1.2 equiv. of sodium acetate. The product, isolated in 94.5% yield, was a yellow oil with a camphor-like odor, which was saponified with alcoholic potassium hydroxide to the known *endo*-2-methyl-*exo*-2-norbornanol (XXVIII), m.p. and m.m.p. 84–85°. The 60-Mc. n.m.r. spectrum of the acetate XXVI contains sharp singlets at τ 8.13-(acetate) and 8.50, and no appreciable absorption at 8.92, the chemical shift attributed to the bridgehead methyl group of XXIX. The tertiary acetate XXVI could not be analyzed by vapor chromatography under any conditions found, without undergoing some decomposition in the injection port. The main peak was accompanied by variable amounts of two other peaks at lower retention times, which under the best conditions amounted to about 10% of the material. Under the same conditions, synthetic XXVI behaved identically. The product of solvolysis and the authentic material had identical infrared spectra.

In like fashion the solvolysis of the dimethyl compound XIII gave rise to the acetate XXXII, isolated as an oil after 16 solvolysis half-lives in a yield of 87%, and converted by lithium aluminum hydride in 91% yield into the alcohol XXXI, m.p. and m.m.p. 104–106° after sublimation. Under the most favorable conditions the v.p.c. analysis showed a single peak accounting for 93.8% of the material, the rest being two thermal decomposition products whose amounts varied with small changes in the conditions of the chromatography.

The n.m.r. spectrum of the solvolysis product, as in the previous case, had no absorption in the unsaturation region. There were three sharp singlets at τ 8.13

(acetate), 8.60 (2-methyl), and 8.92 (bridgehead methyl). The alcohol XXXI was identical in infrared and n.m.r. spectra with synthetic material. Chart III summarizes the preparation of the bicyclic alcohols XXVIII and XXXI by known methods.

Chart III. Synthesis of Solvolysis Products

NsO—[structure] $\overset{\text{CH}_3}{}$ $\xrightarrow[\text{(1.2 equiv.)}]{\overset{\text{HOAc}}{\text{NaOAc}}}$ [structure]—OAc, CH$_3$

XII   XXVI

[structure with O] $\xrightarrow{\text{CH}_3\text{MgI}}$ [structure]—CH$_3$, OH $\xrightarrow[\text{2. 1 N NaOH}]{\text{1. con. HCl}}$ [structure]—OH, CH$_3$

XXVII   XXVIII

XXVII $\xrightarrow[\text{2. KOH, C}_2\text{H}_5\text{OH}]{\text{1. HCOOH, 100°}}$ [structure] CH$_3$—OH $\xrightarrow[\text{HOAc}]{\text{CrO}_3}$ [structure] CH$_3$, O

XXIX   XXX

XXX $\xrightarrow{\text{CH}_3\text{MgI}}$ [structure] CH$_3$—CH$_3$, OH $\xrightarrow[\text{2. 1 N NaOH}]{\text{1. con. HCl}}$ [structure] CH$_3$, CH$_3$—OH

XXXI

NsO—[structure] CH$_3$, CH$_3$ $\xrightarrow[\text{(1.2 equiv.)}]{\overset{\text{HOAc}}{\text{NaOAc}}}$ [structure] CH$_3$, CH$_3$—OAc

XIII   XXXII

Kinetic Results. Table I summarizes the rate measurements at three temperatures on the acetolysis of the three *p*-nitrobenzenesulfonates XII, XIII, and XIV and, for comparison, the hydrogenation product of XIII, 2-(3,4-dimethylcyclopentyl)ethyl *p*-nitrobenzenesulfonate (XXXIII). The rates of the rapid solvolyses

$\overset{\text{CH}_3}{\underset{\text{CH}_3}{}}$[structure]—CH$_2CH_2$ONs

XXXIII
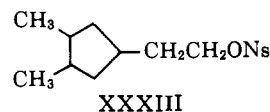
of XII and XIII were followed by conductivity, with the aid of a calibration curve which showed that at the concentrations used the conductance was a linear function of the concentration of *p*-nitrobenzenesulfonic acid. The solvolyses of XIV and XXXIII, which required higher temperatures and longer times, were followed by titration of the contents of sealed ampoules after different lengths of time.

Compounds XII and XIII are solvolyzed so much faster than their saturated analogs that a comparison can be made only by extrapolation to a common tem-

Table I. Rate Constants for Acetolysis of p-Nitrobenzenesulfonates

Compd.	Temp., °C.	$k_1 \times 10^4$ sec.$^{-1}$	ΔH^*, kcal./mole	ΔS^*, cal./deg. mole
XII	50.02	2.71		
		2.85		
	62.49	9.49	21.2 ± 0.2	−9.0 ± 0.5
		10.1		
	70.30	20.6		
		21.1		
	60.0 (interpolated)	7.69		
XIII	39.62	5.12		
		5.20		
	49.40	14.7	20.6 ± 0.5	−7.8 ± 1.6
		14.8		
	62.49	52.2		
		52.2		
	60.0 (interpolated)	42.3		
XXXIII	100.85	0.511		
		0.524		
	109.52	1.07	23.2 ± 0.2	−16.7 ± 0.5
		1.09		
	119.62	2.43		
		2.43		
	60.0 (extrapolated)	0.0127		
XIV	108.65	1.04		
		1.07		
		1.13		
	119.38	2.74	25.2 ± 1.1	−11.1 ± 2.6
		2.74		
	60.0 (extrapolated)	0.00747		

Table II. Relative Rates of Acetolysis at 60° of $RCH_2CH_2OSO_2C_6H_4NO_2$

R	Compd.	$k \times 10^4$ sec.$^{-1}$	k/k_{XXXIII}	k/k_{VIII}	Increment[a]
3,4-Dimethylcyclopentyl	XXXIII	0.0127	(1.00)		
Cyclopentyl	XXXIV	~0.0116[b]	~0.91		
Δ^3-Cyclopentenyl	VIII	1.10[b]	86.5	(1.00)	~95
3-Methyl-Δ^3-cyclopentenyl	XII	7.69	605.	7	7
3,4-Dimethyl-Δ^3-cyclopentenyl	XIII	42.3	3315.	38.5	5.5
2-Indanyl	XIV	0.00747	0.59	0.0084	

[a] k/k (preceding compound in table). [b] R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

perature. This is done in Table II for acetic acid solutions of six p-nitrobenzenesulfonates at 60°. The factor k_U/k_S is 605 for the monomethyl compound XII and 3315 for the dimethyl compound XIII. With the unsubstituted sulfonate VIII as a basis of comparison the first methyl group is seen to bring about an acceleration by a factor of 7, the second by a further factor of 5.5. The fused benzene ring of XIV not only produces no acceleration relative to the double bond, but lowers the rate to only 65% of that of the saturated compound XXXIV.

Discussion

If the bridged norbornyl cation X with delocalized charge is more stable than the localized "classical" structure XI, then the transition state in double bond assisted ionization should be symmetrical, with its primary carbon atom becoming bonded to the π-system of the double bond, and related similarly to its two carbon atoms. The charge, shared between these two carbon atoms, should be similarly stabilized at the transition state by methyl substitution at either site

or at both. Such cumulative acceleration by methyl substituents has been observed in the epoxidation of olefins by peracetic acid[14–16] and in the ionic bromination of olefins,[17] and has been used as a criterion for the mode of attack of carbenes upon the double bond.[18] A very different effect of methyl substitution is observed in the acid-catalyzed hydration of simple alkenes, where the rate-determining step appears to be the addition of a proton to a double bond to form a classical carbonium ion, with resultant concentration of charge upon *one* of the carbon atoms of the double bond.[19] In this reaction an olefin, such as isobutylene, which can yield a tertiary carbonium ion, reacts at least a thousand times as fast as an olefin, such as propylene, which can yield only a secondary carbonium ion. Further methylation of the less methylated end

(14) J. Stuurman, Thesis, Delft, 1936.
(15) J. Boëseken and J. Stuurman, *Rec. trav. chim.*, **56**, 1034 (1937).
(16) See D. Swern, *Chem. Rev.*, **45**, 1 (1949).
(17) C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2354 (1931); S. V. Anantakrishnan and C. K. Ingold, *ibid.*, 984, 1396 (1935).
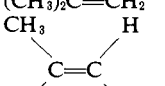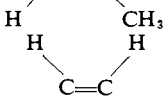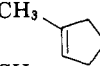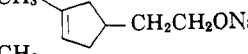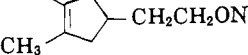(18) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, 78, 3409, 5430 (1956).
(19) P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *ibid.*, 79, 3724 (1957).

of the double bond produces no increase in the hydration rate of the compound.

Table III summarizes some relative rates of differently methylated alkenes in these two reactions. The assisted solvolysis closely resembles the epoxida-

Table III. Effect of Methyl Substitution on Reactivity of Carbon–Carbon Double Bond

Compd.	Peracetic acid epoxidation (Böeseken and Stuurman)[b]	Hydration (Taft)[c]	Acetolysis
$CH_3CH=CH_2$	22	...	
$(CH_3)_2C=CH_2$	22	10^3–10^4	
CH₃ ... H (C=C) H ... CH₃	(22)	0.71	
H ... H (C=C) CH₃ ... CH₃		1.68	
$(CH_3)_2C=CHCH_3$	10.5	{ 0.67[d] 10^3–10^{4e}	
CH₃ cyclopentene CH₃	11–12		
CH₃ ... CH₃ cyclopentenyl–CH_2CH_2ONs			7
CH₃ ... CH₃ cyclopentenyl–CH_2CH_2ONs			5.5

[a] k_n/k_{n-1} is the rate constant for the compound indicated, relative to the compound with one less methyl group. [b] J. Stuurman, Thesis, Delft, 1936. [c] R. W. Taft, Jr., private communication. See also P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *J. Am. Chem. Soc.*, **79**, 3724 (1957). [d] Relative to isobutylene. [e] Relative to 2-butene.

tion; methyl groups on adjacent carbon atoms simultaneously accelerate the reaction by similar factors. Hence the transition state resembles X, not XI, in structure. Figure 1 shows these relationships graphically.

In view of the difficulty of examining the structures of short-lived ions, and the greater difficulty of examining transition states, the effect of substitution at different sites may be the best available criterion of the nature of the transition state in an ionization. Examination of the data on hydration suggests that, for the transition state in unsymmetrical attack on a double bond, methyl substitution is completely ineffective except at the atom where the ionic charge is concentrated. In analogous free-radical reactions, the σ-attack of a radical on a double bond is actually retarded by methyl substitution on the atom to which the new bond is being formed (for example, such substitution in styrene, vinyl acetate, or methyl methacrylate produces monomers not readily susceptible to polymerization). This retarding effect, probably steric in nature, has been estimated to amount to a factor of about 20 in the biradical mechanisms for 1,2-cyclo-addition.[20] The effect near zero in the hydration rate

(20) P. D. Bartlett and L. K. Montgomery, *J. Am. Chem. Soc.*, **86**, 628 (1964).
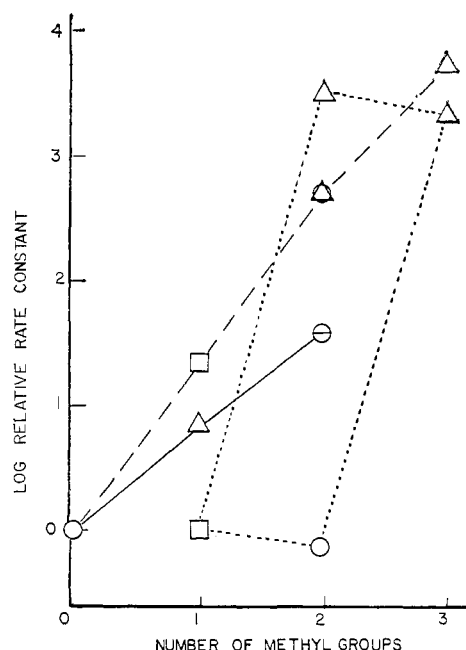

Figure 1. Comparison of effect of methyl substitution on rate constant in three reactions of the carbon–carbon double bond: solid line, acetolysis of 2-(Δ^3-cyclopentenyl)ethyl p-nitrobenzenesulfonates; dashed line, epoxidation of ethylenes; dotted lines, acid-catalyzed hydration of ethylenes. The type of point indicates whether olfin is symmetrically or unsymmetrically substituted, and whether the most branched charge-localized carbonium ion derivable from it is secondary or tertiary: O, symmetrical secondary; $\ominus$, symmetrical tertiary; $\square$, unsymmetrical secondary (propylene); $\triangle$, unsymmetrical tertiary. The ordinates are log (k/k_0) where k_0 is the rate constant for the least methylated member of each series which has been reported.

probably represents opposing effects of a small steric retardation and a small general inductive acceleration.

In any event, the direct formation of a charge-localized ("classical") ion would not seem to profit by methyl substitution at more than one site in an ionizable compound. By this criterion the participation of the double bond in ionization involves a transition state of the type of X even when, as in homoallylic cases, the geometry of the molecule forces this transition state to be unsymmetrical. The 3.7-fold acceleration produced by the double bond in the formolysis of allylcarbinyl tosylate[21] (compared to n-butyl tosylate) is multiplied 3.5-fold by methyl substitution at position 3, but 45- and 210-fold, respectively, by cis- and trans-methyl substitution at position 4.[22] Thus the dimensions of the transition state are favorable to quite unequal amounts of positive charge at C-3 and C-4, but this case does not reach the limiting conditions where methyl substitution at C-3 would be of zero or slightly negative effect.

The products of solvolysis are determined by kinetic competition at a later stage than the ionization. The factors involved in their formation may be complicated. In most cases the kinetically determined products, under conditions of re-ionization, are converted into other products representing a closer approach to equilibrium. Nevertheless, the acetolysis products of methylcyclopentenylethyl sulfonates can be covered by

(21) K. L. Servis and J. D. Roberts, *ibid.*, **86**, 3773 (1964).
(22) J. D. Roberts, private communication, Jan. 10, 1964.

a simple generalization already recognized[23-25] in the study of the ion from XII when it was produced by the σ-route. The kinetically determined product is entirely that acetate which results from attack at the tertiary carbon atom. Re-ionization affords a "thermodynamically determined" product from attack at the other position, presumably because this product has a much lower ionization constant than the tertiary acetate has.

Some of the recent discussions of anchimeric assistance to ionization have sounded as if there were no connection between the structure of a carbonium ion and that of the transition state leading to it. Let us recall that the transition state is an attempted conceptual snapshot of a system in the middle of a leap from one position of rest to another. Identically, then, the transition state must lie on the *direct path* of lowest energy between two adjacent intermediates, or in this case between starting material and first intermediate. In the present instance, if a symmetrical starting material (VIII or XIII) jumps to a symmetrical (bridged) ion, the direct path must lie over a symmetrical transition state; if to an unsymmetrical (charge-localized) ion, it must go over an unsymmetrical transition state. Because of the demonstrable symmetry of the starting material, this relationship must hold for reasoning in both directions; if the symmetrical starting material goes over a symmetrical transition state, it must be headed for a symmetrical first intermediate. We cannot exclude at present the possibility that, *after* the formation of a bridged cation, a charge-localized ion may in some cases prove stabler and be formed. However, should the introduction of such a species into the reaction scheme prove necessary, it will constitute a complication (something of which nature is quite capable) and not a simplification.

The lack of assistance to ionization by the benzo group in XIV is in accord with the observation of Bartlett and Giddings[26] that a benzo group assisted ionization from the 7-position of the norbornene ring 7,000,000 times less well than a carbon–carbon double bond.

Experimental

1. Dimethyl Series. 1-Methyl-1-isopropenyl-2-carbethoxycyclopropane (Mixture of cis and trans Isomers). Columbia Chemicals 2,3-dimethylbutadiene was redistilled through a 60-cm. vacuum-jacketed, Heli-Pak column. After a considerable forerun, b.p. 50–68°, pure 2,3-dimethylbutadiene, b.p. 69.5°, was obtained. To 60 ml. (44.7 g., 0.545 mole) of material thus obtained, contained in a 250-ml. round-bottom flask, was added 40 g. (0.35 mole) of Aldrich Chemical Co. ethyl diazoacetate. The flask was equipped with a water-cooled reflux condenser and a bubble counter for evolved gas. The flask was irradiated with a G.E. 275-w. sun lamp, placed approximately 2 cm. directly beneath the flask. The heat from the lamp caused the reaction mixture to reflux at a moderate rate. Irradiation was carried out until the reaction mixture became

deep orange in color (approximately 30 hr.). If irradiation was continued until nitrogen was no longer evolved, the reaction mixture became very black and viscous, and distillation led to greatly reduced yields of the desired product. The combined product of two such irradiations was fractionally distilled through a 20-cm. vacuum-jacketed Podbielniak Heli-Pak column. The third fraction, a nearly colorless oil weighing 58.6 g., distilled at 39–50° (2.3 mm.). It showed strong infrared absorption at 5.78, 6.05, and at 11.12 μ. The last two absorptions are characteristic of unsymmetrically disubstituted double bonds.[27] The n.m.r. spectrum indicated that the material was a mixture of the two possible *cis* and *trans* isomers. The over-all yield was 68.2%, corrected for recovered ethyl diazoacetate.

Thermal Rearrangement of 1-Methyl-1-isopropenyl-2-carbethoxycyclopropane.[12] A total of 58.0 g. (0.345 mole) of 1-methyl-1-isopropenyl-2-carbethoxycyclopropane was introduced dropwise from a dropping funnel into a glass-packed Pyrex column heated to 500° in an electric combustion furnace. A stream of dry nitrogen swept the vapors through the furnace, through an air condenser, and into a 300-ml., three-necked, round-bottom flask equipped with a Dry Ice condenser and beyond it a mineral oil gas counter. During the pyrolysis the nitrogen flow rate and the rate of introduction of liquid into the column were adjusted to minimize refluxing and the formation of aerosols. Pyrolysis of the 58 g. required just under 1 hr. The product was taken up in ether, and the ether solution was extracted with 10% aqueous sodium bicarbonate until a further extraction produced no gas evolution. The ether solution was then washed twice with water and dried over anhydrous sodium sulfate. The combined aqueous extracts were acidified with 10% aqueous hydrochloric acid and extracted three times with ether. These combined ether solutions were then washed twice with water and dried over anhydrous sodium sulfate.

3,4-Dimethyl-Δ^3-cyclopentenecarboxylic Acid. Evaporation of the ether from the acidic extract yielded 28.6 g. (60%) of a light yellow oil. Distillation through a 30-cm. Vigreux column gave as a single fraction, b.p. 108° at 2.5 mm., 27.8 g. of a colorless oil which solidified to a white, waxy solid in the receiver, m.p. 42–43°. The infrared spectrum showed no band at 11.12 μ, showing that the unsymmetrically substituted double bond was no longer present. The n.m.r. spectrum in deuteriochloroform showed a six-proton singlet at τ 8.38, a four-proton unresolved multiplet at τ 7.22–7.50, a one-proton multiplet consisting of at least five peaks at τ 6.70–7.25, and a one-proton singlet at τ -1.35. The neutralization equivalent (in 95% ethanol to bromothymol blue) was calcd. 140, found 139. The anilide melted at 126–127° after four recrystallizations from ethanol.

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.12; H, 7.98; N, 6.36.

From the nonacidic fraction of the product, the ester was obtained by distillation through a 20-cm. vacuum-jacketed Podbielniak Heli-Pak column at 3 mm.; 8.4 g. was obtained, b.p. 67° (3 mm.). Earlier

(23) S. Beckmann, R. Schaber, and R. Bamberger, *Ber.*, 87, 997 (1954).
(24) N. J. Toivonen, E. Siltanen, and K. Ojala, *Ann. Acad. Sci. Fennicae, Ser. A. II*, No. 64 (1955).
(25) P. von R. Schleyer, Thesis, Harvard University, 1956.
(26) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, 82, 1240 (1960).

(27) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2d Ed., Methuen and Co., Ltd., London, 1958, p. 51.

fractions were contaminated with unrearranged material, and later fractions were contaminated with an unidentified impurity. The n.m.r. spectrum, determined without solvent, showed a triplet at τ 8.82, $J = 7$ c.p.s. (relative area, 3.42), a singlet at 8.43 (5.70), an unresolved multiplet at τ 7.32–7.68 (3.70), a multiplet at τ 6.75–7.30 (1.08), and a quartet at τ 5.92 with $J = 7$ c.p.s. (2.10).

This ester (2 g.) was saponified with 10% ethanolic potassium hydroxide to a nearly quantitative yield of the corresponding acid which had an infrared spectrum identical with that obtained directly from the pyrolysis.

Proof of Structure of 1,2-Dimethylcyclopentene-4-carboxylic Acid. a. Ozonization of 4-Carbethoxy-1,2-dimethylcyclopentene. A solution of 5.04 g. (0.03 mole) of the ethyl ester in 50 ml. of methylene chloride was treated with ozone at −70° until 10 drops of the solution no longer decolorized 1 drop of a 5% solution of bromine in carbon tetrachloride. The cold solution was then purged of excess ozone with oxygen and added to a solution of the equivalent quantity, 7.85 g., of triphenylphosphine in 50 ml. of ether.[28] The solution was allowed to warm to room temperature, and the solvent was stripped on a rotary evaporator. The residue, a mixture of colorless oil and white solid, was triturated with several portions of ether and the ether-insoluble triphenylphosphine oxide was filtered off. The ether solution was concentrated to a small volume, transferred to a 10-ml., round-bottom flask for distillation through a micro Podbielniak Heli-Grid column. Of three fractions collected, the second and third had identical n.m.r. spectra, resembling that of the starting material except for a downfield shift of 32 cycles in the sharp singlet arising from the methyl groups. The yield of product of b.p. 101–101.5° at 0.23 mm. was 5.42 g. (90.5%).

b. Reduction of Ketonic Carbonyl to Methylene. The bisethylene dithioketal (XXII) was prepared by the procedure given by Pettit and van Tamelen[29] and by Fieser.[30] It was a colorless oil weighing 7.23 g. or 82% of the theoretical. The infrared spectrum of this oil revealed the loss of the carbonyl stretching band at 5.80–5.85 μ, which was present in the keto ester, and contained only the sharp ester band at 5.77 μ. The n.m.r. spectrum showed a 25-cycle unfield shift in the sharp peak arising from the two nonester methyl groups. A sharp singlet attributable to the eight equivalent methylene protons appeared at τ 6.7.

A solution of 7.05 g. (0.02 mole) of the bisethylene dithioketal in 500 ml. of absolute ethanol was refluxed for 4 hr. in the presence of 28 g. of Raney nickel T-1 prepared by the method of Dominguez and Lopez.[31] The solution was cooled to room temperature and filtered to remove the catalyst with precautions against its self-ignition. The product (XXIII) was isolated by distillation at atmospheric pressure. Its b.p. was 182–182.5° (lit.[32] for ethyl di-n-propylacetate, 183°).

c. Saponification to the Acid. Saponification of 1.44 g. of the saturated ester by conventional methods

led to the isolation of an oil which was distilled in a micro Claisen apparatus at atmospheric pressure, b.p. 218.8° (lit.[32] for di-n-propylacetic acid, 219.5°).

d. Di-n-propylacetamide. The amide prepared in the normal fashion[33] melted at 123.4–124.2° after one recrystallization from aqueous ethanol (lit.[13], for di-n-propylacetamide, 123°).

1,2-Dimethylcyclopentene-4-carboxylic acid chloride was prepared from the acid by means of purified[34] thionyl chloride. The yield was 9.51 g. (80%) of a colorless oil, b.p. 40–42° at 0.90 mm. The infrared spectrum showed strong carbonyl absorption at 5.58 μ, but no trace of a band at 5.85 μ.

3,4-Dimethyl-Δ^3-cyclopentenyldiazomethyl Ketone. A solution containing from 0.19 to 0.21 mole of diazomethane in approximately 350 ml. of anhydrous ether was prepared from Dupont N,N'-dimethyl-N,N'-dinitrosoterephthalamide by the procedure of Moore and Reed.[35] While the solution was stirred magnetically and maintained at 5–10° by external cooling, a solution of 9.50 g. (0.06 mole) of 1,2-dimethylcyclopentene-4-carboxylic acid chloride in 50 ml. of anhydrous ether was added dropwise over the course of about 20 min. Nitrogen evolution commenced immediately. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Excess diazomethane and ether were removed at aspirator pressure, the temperature never being allowed to rise above room temperature. The remaining 9.81 g. of dark orange oil had intense infrared bands at 4.78 and 6.06 μ, characteristic of diazoketones. This oil was used in the succeeding reaction without purification.

Methyl 3,4-dimethyl-Δ^3-cyclopentenylacetate was prepared by the rearrangement of the diazoketone with silver oxide in anhydrous methanol by the method of Bachmann, Cole, and Wilds.[36] The yield of crude material, boiling at 41–48° at 0.42 mm. and showing strong absorption at 5.76 μ, was 46% over-all from the lower acid.

3,4-Dimethyl-Δ^3-cyclopentenylacetic acid was similarly obtained in 48% over-all yield when the rearrangement was conducted in dioxane–water containing sodium carbonate and sodium thiosulfate. This acid, a yellowish oil with intense absorption at 5.85 μ, was used in the subsequent reduction without purification.

2-(3,4-Dimethyl-Δ^3-cyclopentenyl)ethanol was prepared in normal fashion by the lithium aluminum hydride reduction of both the ester and the acid. A product from reduction of the acid was shown by vapor phase chromatography to be at least 99% pure. The infrared spectrum showed that it was free of carbonyl compounds. A 60-Mc. n.m.r. spectrum was very similar to that of 2-(Δ^3-cyclopentenyl)ethanol (part I[7]) except for the presence of the sharp six-proton singlet at τ 8.51 and the absence of the ethylenic proton absorption at τ 4.38; yield 3.12 g. or 62%.

(28) L. Horner and H. Hoffmann, *Angew. Chem.*, 68, 473 (1956).
(29) G. R. Pettit and E. E. van Tamelen, *Org. Reactions*, 12, 356 (1962).
(30) L. F. Fieser, *J. Am. Chem. Soc.*, 76, 1945 (1954).
(31) X. A. Dominguez and I. C. Lopez, *J. Org. Chem.*, 26, 1625 (1961).
(32) R. S. Burton, *Am. Chem. J.*, 3, 390 (1882).

(33) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds, 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956.
(34) L. F. Fieser, "Experiments in Organic Chemistry," 3d Ed. (revised), D. C. Heath and Co., Boston, Mass., 1957, p. 345.
(35) I. A. Moore and D. E. Reed, *Org. Syn.*, 41, 16 (1962).
(36) W. E. Bachmann, W. Cole, and A. L. Wilds, *J. Am. Chem. Soc.*, 62, 824, (1940).

2-(3,4-Dimethyl-Δ³-cyclopentenyl)ethyl p-Nitro-benzenesulfonate. We found the yields of p-nitro-benzenesulfonates to show an unusual degree of variation with the purity of the acid chloride and the dryness of the apparatus. A 50-ml. erlenmeyer flask and a 0.5-in. teflon-coated magnetic stirring bar were dried in the oven at 140° for several hours and cooled under protection by a calcium chloride drying tube. A solution of 1.40 g. (0.01 mole) of 2-(3,4-dimethyl-Δ³-cyclopentenyl)ethanol in 10 ml. of anhydrous pyridine (distilled from barium oxide and stored over potassium hydroxide, b.p. 119.5° at 762 mm.) was placed in the flask which was then chilled in an ice–salt bath for 30 min. To the cold, stirred solution was then added 2.66 g. (0.012 mole) of Eastman p-nitrobenzenesulfonyl chloride, m.p. 73–77°. After stirring at −10 to 0° for 45 min., the solution was poured into 70 ml. of ice and 5% aqueous HCl. A solid precipitated in clumps. The clumps were broken up and the mixture was stirred as vigorously as possible until all the ice had melted, then filtered through a sintered glass funnel. The solid was washed with ice-cold 3% aqueous HCl and then with several portions of water. The crude p-nitrobenzenesulfonate was then pumped dry *in vacuo*. When dry, it was dissolved in 10 ml. of anhydrous ether, and a small amount of insoluble material was removed by filtration. Crystallization was induced by adding about 5 volumes of petroleum ether and chilling the resulting solution to −25°. The p-nitrobenzenesulfonate crystallized in pale yellow flakes. A total of three crops yielded 1.85 g. (57%); it melted at 69.2–71° to a blood red melt.

The infrared spectrum had nitro bands at 6.54 and 7.44 μ and sulfonate absorption at 7.28 and 8.42 μ. The n.m.r. spectrum in carbon disulfide showed a methylene triplet at τ 5.9 and the methyl singlet at τ 8.4. The n.m.r. spectrum in chloroform solution, at first identical with that of the carbon disulfide solution, changed with time. After a series of color changes in the solution, both the singlet at τ 8.47 and the triplet at τ 5.83 declined in intensity and eventually disappeared altogether, and a broad envelope of largely unresolved absorption appeared, stretching upfield to approximately τ 9.4. We were not successful in isolating any characterizable material from this reaction.

The p-nitrobenzenesulfonate decomposes noticeably at room temperature in 24 hr. It was stored in a tightly stoppered bottle, placed inside a second tightly closed bottle, containing anhydrous calcium sulfate, and kept in the freezer at −25°.

Anal. Calcd. for $C_{15}H_{19}NO_5S$: C, 55.36; H, 5.89; N, 4.30; S, 9.85. Found: C, 55.29; H, 5.91; N, 4.16; S, 8.88.

Acetolysis Product of 2-(3,4-Dimethyl-Δ³-cyclopentenyl)ethyl p-Nitrobenzenesulfonate. A solution containing 0.650 g. (0.002 mole) of the sulfonate and 0.197 g. (0.0024 mole) of anhydrous sodium acetate in 30 ml. of anhydrous acetic acid was placed in a constant temperature bath at 62.5° and allowed to remain there for 45 min. (more than 16 half-lives). The solution was cooled, diluted with twice its volume of water, and extracted with three 30-ml. portions of Philips' n-pentane. The combined pentane extracts were washed with 10% aqueous sodium carbonate and with water and dried over anhydrous magnesium sulfate. Evap-

oration of the pentane left 0.317 g. (87% recovery) of a light yellow oil with a camphor-like odor. The complex infrared spectrum showed strong carbonyl absorption at 5.78 μ. The n.m.r. spectrum had no absorption below τ 7.68. It was characterized by three very sharp singlets rising from an envelope of unresolved absorption stretching from τ 7.68 to 9.3. The three singlets occurred at τ 8.92, 8.60, and 8.13.

V.p.c. analysis of the oil was carried out first on a 6 ft. × 0.25 in. column, packed with 25% diethylene glycol adipate and 2% of 85% phosphoric acid by weight on 80–100 mesh acid-washed Chromosorb W, at 135° with a helium carrier flow rate of approximately 85 ml./min. The resultant chromatogram contained two peaks, whose retention times were 1.52 and 8.0 min., and whose relative integrated areas were 63.8 and 36.2, respectively. Varying the temperature of the injection port from 222 to 155° did not significantly affect either the retention times or the relative integrated peak areas.

A sample of 1-methylcyclopentyl acetate,[37] known to be more than 99.5% pure, injected onto the column under conditions identical with those of the analysis of the solvolysis product, gave a similar chromatogram. In this case the two peaks had retention times of 0.8 and 7.6 min. with relative integrated areas of 58.5 and 41.5, respectively.

V.p.c. analysis of the solvolysis product on an 8 ft. × 0.25 in. column packed with 5% silicone oil 710 on 60–80 mesh Haloport F at 135° with a helium carrier flow rate of approximately 90 ml./min. gave a chromatogram containing three peaks. These arose at retention times of 0.48, 1.20, and 6.24 min., and possessed relative integrated peak areas of 10.9:43.2:45.9, respectively. Varying the column and injection port temperatures was found to produce a considerable variation in the relative integrated peak areas of the three peaks. This indicated that the two peaks of shortest retention time arose from decomposition in the injection port. The decomposition appeared to be autocatalytic, since repeated injections under identical conditions led to progressively smaller relative areas for the peak with longest retention time. It proved to be impossible to find conditions that would totally eliminate the two peaks at low retention times, but with the column at 90° and the injection port at 120°, a chromatogram was obtained in which the three peaks, occurring at retention times of 1.0, 2.5, and 25.0 min., had relative integrated peak areas of 1.37:4.80:93.8, respectively.

Reduction to the Alcohol. The solvolysis product resisted attempts to hydrolyze it with 10% ethanolic KOH on the steam bath for 4 hr., and it was accordingly reduced with lithium aluminum hydride in anhydrous ether. The reaction mixture was refluxed for 4 hr. The excess lithium aluminum hydride was destroyed by the dropwise addition of water to the cooled reaction mixture. The dimethylnorbornanol was isolated by extraction with ether, washing with aqueous sodium chloride, drying over anhydrous magnesium sulfate, and stripping to leave a 91% yield of nearly white crystals. The m.p. of 94–97° was raised by sublimation from KOH to 104–106° (lit.[38] for 1,2-dimethyl-*exo*-2-norbornanol, 105–108°, 112–

(37) Kindly supplied by Mr. T. J. Cogdell.
(38) H. Toivonen, *Suomen Kemistilehti*, 33B, 66 (1960).

113° after chromatography over alumina), mixture melting point with synthetic 1,2-dimethyl-*exo*-2-norbornanol, m.p. 101–103.5, was 101.5–105°.

Both the alcohol here described and the synthetic 1,2-dimethyl-*exo*-2-norbornanol gave identical chromatograms on v.p.c. analysis with an 8 ft. × 0.25 in. column packed with 5% Carbowax 20 M on 60–80 mesh Haloport F, at 200° with a nitrogen carrier flow of approximately 80 ml./min. The material (81%) was in a single peak with a retention time of 15.1 min., and the remaining 19% appeared to consist of decomposition products. Under these conditions the same column resolved an authentic mixture of the epimeric *exo*- and *endo*-1,2-dimethylnorbornanols. The *endo* epimer showed the longer retention time, 16.2 min., and gave no decomposition on the column when injected singly.

2-(3,4-Dimethylcyclopentyl)ethanol. A solution of 2.0 g. (0.0143 mole) of 2-(3,4-dimethyl-Δ^3-cyclopentenyl)ethanol in 40 ml. of anhydrous Fisher methanol and 100 mg. of Adams catalyst were shaken together in a Parr apparatus for 12 hr. at a hydrogen pressure of 30 p.s.i. After filtration and solvent stripping, the residue consisted of 1.89 g. (93.4%) of a colorless oil. The product was homogeneous to vapor phase chromatography to the extent of at least 99%. The n.m.r. spectrum revealed the loss of the sharp singlet at τ 8.51 and the appearance of a partially resolved triplet at τ 9.12. *p*-Nitrobenzenesulfonate had m.p. 68.3–69.5°.

Anal. Calcd. for $C_{15}H_{21}NO_5S$: C, 55.03; H, 6.47; N, 4.28; S, 9.79. Found: C, 55.04; H, 6.49; N, 4.30; S, 9.75.

2. Monomethyl Series. The preparations leading to 2-(3-methyl-Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate were carried out in the same manner as just described for the dimethyl series. The photochemical reaction between isoprene and ethyl diazoacetate led to the *ethyl ester of 2-isopropenylcyclopropane-1-carboxylic acid.* This structure was shown by the n.m.r. spectrum in which the integrated intensities of absorption in the unsaturated region and at the methylene group of the ester ethyl were identical. The infrared spectrum had strong ester absorption at 5.78, vinyl proton streching at 3.23, and peaks at 5.07 and 11.2 μ. The absence of perceptible absorption at 10.05–10.15 and at 10.9–11.05 μ also indicated that addition had taken place primarily at the unsubstituted double bond of the isoprene.

1-Methylcyclopentene-4-carboxylic acid, b.p. 69–70° at 0.55 mm., was obtained in 51% crude yield by thermal rearrangement of the photoaddition product. The n.m.r. spectrum of the acid was identical with that of the dimethyl acid with two exceptions: (1) The singlet at τ 8.32 had only half the relative intensity shown by the dimethyl acid and (2) a new one-proton peak appeared at τ 4.8. The infrared had a peak at 12.6 but none at 11.0–11.2 μ. The *anilide* had m.p. 88–89° (from aqueous ethanol).

Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.70; H, 7.68; N, 6.74.

The *acid chloride* had b.p. 47° at 3.6 mm.; yield 74%.

2-(3-Methyl-Δ^3-cyclopentenyl)ethanol, b.p. 88–89° at 13 mm., was obtained by lithium aluminum hydride reduction of the corresponding acid from the Arndt-Eistert reaction. Its infrared spectrum was free of carbonyl group absorption. The alcohol was shown by vapor chromatography to be 97.8% pure, the main fraction having a retention time of 10.1 min., on a 10-ft. column packed with 5% Ucon LB550X on 60–80 mesh acid-washed Chromosorb P at 180° with a helium carrier flow rate of approximately 90 ml./ min. The single impurity had a retention time of 6.0 min. under these conditions.

p-*Nitrobenzenesulfonate, M.p. 52.2–53.8°.* The melt, initially colorless, turned red at 66°. The *p*-nitrobenzenesulfonate was stored with the same precautions as were used for the dimethyl compound. The infrared and n.m.r. spectra were consistent with the structure assigned.

Anal. Calcd. for $C_{14}H_{17}NO_5S$: C, 54.01; H, 5.50; N, 4.50; S, 10.30. Found: C, 54.12; H, 5.52; N, 4.64; S, 10.24.

Acetolysis Product of 2-(3-Methyl-Δ^3-cyclopentenyl)-ethyl p-Nitrobenzenesulfonate. This acetolysis was conducted at 60.0° for 3 hr. (approximately 12 half-lives), and the product was worked up as in the dimethyl example. The solvolysis product, isolated in 94.5% yield, had an infrared spectrum identical with that of an authentic synthetic sample of 2-methyl-*exo*-2-norbornyl acetate. The n.m.r. spectrum, also identical with that of synthetic material, consisted of two very sharp peaks at τ 8.50 and 8.13, rising from a broad envelope stretching from τ 7.4 to 9.2.

Again vapor chromatography gave rise to variable proportions of three peaks. A 10 ft. × 0.25 in. column was used, packed with 5% silicone oil 710 on 60–80 mesh Haloport F, with a helium flow rate of 85 ml./ min. The retention times of these peaks were identical with those from authentic 2-methyl-*exo*-2-norbornyl acetate. With the injection port temperature at 110° and the column programmed from 90 to 135° at a rate of 6.4°/min. commencing from the time of injection, the three peaks (now at retention times of 0.6, 2.0, and 12.3 min.) had relative areas 2.5, 7.5, and 90.0, respectively.

This acetate, unlike its homolog previously described, could be saponified by heating with 10% ethanolic KOH on the steam bath for 1 hr. After work-up and sublimation from potassium hydroxide, the alcohol was obtained as pure white, waxy needles, m.p. 84–85° (lit.[39] for 2-methyl-*exo*-2-norbornanol, 86°). The mixture melting point with authentic synthetic material of m.p. 84.4–85.5° was 84.0–84.8°. The infrared spectra of the alcohol from solvolysis product and the synthetic alcohol were identical. There was no absorption at 10.44 or at 10.59 μ where the *endo* epimer has intense sharp bands. Studies of synthetic mixtures showed that as little as 5% of *endo* mixed with *exo* alcohol could be detected in the infrared spectrum.

The n.m.r. spectrum, which was also identical with that of synthetic 2-methyl-*exo*-2-norbornanol, had a sharp singlet at τ 8.75 and no absorption at τ 8.92.

(39) N. J. Toivonen, E. Siltanen, and K. Ojala, *Ann. Acad. Sci. Fennicae, Ser. A. II*, No. **64**, (1955).

V.p.c. gave a pattern of a main peak and 23% decomposition products of which proportions and retention times were the same for the isolated and synthesized material. The main peak had a retention time of 10.0 min., and there was no peak for 2-(3-methyl-Δ^3-cyclopentenyl)ethanol whose retention time under these conditions was 19.6 min. Synthetic *exo*- and *endo*-2-methyl-2-norbornanols could be distinguished in v.p.c. by the fact that the *endo* epimer gave no decomposition. The *endo* and *exo* isomers, however, could not be separated from an artificial mixture by v.p.c.

2-Indanone. 2-Indanone was prepared from Rütgerwerke, A.G., 97% pure indene (obtained from the Beacon Chemical Co., and used without redistillation) by the method of Horan and Schiessler[40] in 74% yield. The product obtained by steam distillation melted at 57–58°.

2-Indanol was prepared in the usual manner by lithium aluminum hydride reduction of 2-indanone. After one recrystallization from aqueous ethanol, the 2-indanol crystallized in pure white needles, m.p. 69–70° (lit. 69°[41] and 70°,[42] yield 59.07 g. or 88%).

2-Indanyl p-toluenesulfonate was prepared in the usual manner.[43] The crude product, obtained in 78% yield, was used in the succeeding reaction without purification.

2-Indaneacetic acid was prepared from the above tosylate by the malonic ester synthesis. The crude acid melted at 88–90° (lit.[44] 84–86° crude and 91–92° recrystallized from methanol), yield 5.90 g. or 65%. This material was used directly for reduction.

2-(2-Indanyl)ethanol was obtained by reduction of 4.90 g. (0.0278 mole) of 2-indaneacetic acid with 1.70 g. (0.179 equiv.) of LiAlH₄ in the usual manner. The product was obtained as a colorless oil, which was distilled through a micro Podbielniak Heli-Grid column at reduced pressure, b.p. 80° at 1.0 mm., yielding 3.55 g., 74.5%. This product was homogeneous to v.p.c. to the extent of at least 99%.

p-Nitrobenzenesulfonate had m.p. 126–127° after three recrystallizations from benzene–ligroin.

Anal. Calcd. for C₁₇H₁₇NO₅S: C, 58.78; H, 4.93; N, 4.03; S, 9.23. Found: C, 58.94; H, 5.14; N, 4.02; S, 9.26.

2-Methyl-endo-2-norbornanol was prepared as described by Beckmann, Schaber, and Bamberger[23] from 110 g. (1.0 mole) of Columbia Chemicals' norcamphor and a solution of methyl Grignard reagent prepared from 38.6 g. (2.0 moles) of magnesium and 288 g. (2.0 moles) of methyl iodide. The crude product, distilled through a 30-cm. Vigreux column, boiled at 77.5° (21 mm.), gave 106.1 g. (84.2% yield) of a colorless oil which solidified on standing to a solid mass of long, white needles, m.p. 31–32° (lit. 34°,[39] 33.5–34.5°[25] after sublimation). The infrared spectrum of the product was identical with that recorded by Schleyer.[25] The largely unresolved n.m.r. spectrum showed a characteristic sharp singlet at τ 8.75.

(40) J. E. Horan and R. W. Schiessler, *Org. Syn.*, **41**, 153 (1961).
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2-Methyl-endo-2-norbornyl p-Nitrobenzoate. Very pale yellow needles were obtained with m.p. 101–101.5° (lit. 100.5–101°[23] and 101.6–102.1°[25] (Schleyer)).

2-Methyl-exo-2-chloronorbornane was prepared by the procedure of Toivonen, Siltanen, and Ojala.[39] 2-Methyl-*endo*-norbornanol (12.6 g.) was stirred vigorously with 75 ml. of concentrated HCl at room temperature for 2 hr. Petroleum ether was added, and the organic layer was separated, washed once with saturated aqueous CaCl₂, and dried over CaCl₂. Removing the petroleum ether on the rotary evaporator left 14.2 g. (98.2%) of a colorless oil which did not solidify. The infrared spectrum showed it to be free of hydroxyl groups.

2-Methyl-exo-2-norbornanol was prepared from the above chloride by the procedure of Toivonen, Siltanen, and Ojala.[39] Ice-cold, aqueous 1 *N* NaOH (175 ml.) was added to the flask containing the crude chloride prepared in the preceding reaction, and the mixture was allowed to warm to room temperature. After vigorous stirring for 12 hr., ether was added and the organic phase was separated. Work-up at this point yielded a product whose infrared spectrum showed the presence of a large amount of unreacted chloride. After warming to 95° for 0.5 hr. with the original NaOH solution and then stirring for 16 hr. at room temperature, a white, flaky solid was obtained on evaporation of the ether. Recrystallization from pentane yielded fine white needles, m.p. 84–85°. Sublimation from KOH raised the melting point to 84.4–85.5° (lit.[39] 86°); yield 11.0 g., 87.4%. The infrared spectrum of this alcohol was totally different from that of its epimer, but the n.m.r. spectra were very similar with the characteristic strong singlet arising from the methyl group coming at τ 8.75.

2-Methyl-exo-2-norbornyl acetate was prepared using acetyl chloride in anhydrous pyridine. Distillation of the product yielded four fractions containing increasing amounts of 2-methyl-*exo*-2-norbornanol as revealed by their infrared and n.m.r. spectra. The main fraction of acetate boiled at 79.0–79.2° (14 mm.). Its n.m.r. spectrum was characterized by two sharp singlets at τ 8.13 and 8.50, rising from the broad envelope of unresolved absorption.

1-Methyl-exo-2-norbornanol was prepared by the method of Schleyer by refluxing 2-methyl-*endo*-2-norbornanol with 97% formic acid for 4 hr. Standard work-up was followed by distillation of the alcoholic product through a 15-cm. Vigreux column at atmospheric pressure. Using a steam-heated condenser, 49.8 g., 79%, of colorless oil distilled over at 175–177° and rapidly solidified to a colorless amorphous mass in the receiver. The second fraction, b.p. 177–181°, consisted of colorless oil which did not solidify even on standing for several days. The infrared spectrum of this oil was quite different from that of the solid alcohol.

The solid alcohol, m.p. 65–68°, showed an infrared spectrum identical with that reported by Schleyer for 1-methyl-*exo*-2-norbornanol. The n.m.r. spectrum had a sharp singlet at τ 8.92, rising from an envelope of unresolved absorption stretching from τ 7.7 to 9.3, and an unresolved multiplet at τ 6.31.

1-Methyl-exo-2-norbornyl nitrate was isolated as a stable, yellow oil in an attempt to oxidize 1-methyl-

exo-2-norbornanol (28.53 g.) by slowly adding it to a magnetically stirred mixture of 67.2 ml. of Dupont concentrated nitric acid and 16.8 ml. of fuming nitric acid over the course of 90 min. The infrared spectrum of the oil showed no carbonyl or OH absorption, but did possess an intense band at 6.12 μ and two very intense bands at 7.82 and 11.6 μ, the latter being very broad. Brown[45] has found that 21 nitrate esters all possess intense bands at 6.06–6.15 and 7.79–7.85 μ. The n.m.r. spectrum of the nitrate closely resembled that of the starting alcohol except for a general displacement toward lower field. The sharp singlet attributable to the methyl group now occurred at τ 8.83 τ and the one-proton multiplet attributable to hydrogen at C-2 was now at τ 5.27.

After refluxing for 16 hr. with 1 N aqueous NaOH the nitrate yielded a mixture still showing a moderately intense infrared band at 6.12 μ and weak bands at 7.83 and 11.63 μ. Inflections at 9.4 and 9.85 μ admitted the possibility of the presence of a small amount of 1-methyl-*exo*-2-norbornanol. In all other respects the spectrum was identical with that of authentic 2-methyl-*exo*-2-norbornanol.

1-Methyl-2-norbornanone was prepared by the method of Schleyer by oxidizing 1-methyl-*exo*-2-norbornanol with an aqueous solution of chromic anhydride. The ketone was isolated by distillation in fractions from 62 to 69° at 16 mm. totaling 7.99 g., whose infrared spectra were identical with each other and to the spectrum recorded by Schleyer for 1-methyl-2-norbornanone. The n.m.r. spectrum showed the sharp singlet at τ 8.91 characteristic of the bridgehead methyl group in this series.

1,2-Dimethyl-endo-2-norbornanol was prepared in the normal manner from 1-methyl-2-norbornanone and methyl magnesium iodide. The product was isolated by extraction, and that part boiling from 61 to 62.5° at 5 mm. (5.62 g., 67%) was used in the succeeding reaction. It was shown by v.p.c. to have a purity greater than 94%. A small sample of the fraction,

(45) J. F. Brown, Jr., *J. Am. Chem. Soc.*, 77, 634 (1955).

b.p. 61–61.5° at 5 mm., was sublimed from KOH to give a white, waxy solid, m.p. 30–33° (lit.[38] 34.5–36°, and after purification *via* its hydrate, 37–38°).[39] The infrared spectrum of the sublimed material did not differ from that of the oil from which it was obtained.

1,2-Dimethyl-exo-2-chloronorbornanone was prepared as described by Toivonen in 91% yield, m.p. 122.5–124° (lit.[38] 123–124°). The infrared spectrum was free from any OH peak.

1,2-Dimethyl-exo-2-norbornanol, prepared by the procedure of Toivonen, melted at 101–103.5° after sublimation from KOH (lit.[38] 105.5–108°, and after chromatography over alumina, 112–113°).[39] No conditions were found for vapor phase chromatographic analysis without the occurrence of decomposition on the column. The n.m.r. spectrum of the alcohols showed two sharp singlets at τ 8.93 and 8.75 rising from a broad envelope of unresolved absorptions stretching from τ 7.6 to 9.1.

Kinetic Procedures. The acetolyses of 2-(3,4-dimethyl-Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate and the corresponding monomethyl compound were followed by the conductometric technique as described in part I, a tape recorder being used for the rapid runs at 62.45 and 70.30°. In order to obtain a distinct null point with the conductivity bridge, both the bridge and the constant temperature bath had to be effectively grounded.

The acetolyses of 2-(3,4-dimethylcyclopentyl)ethyl *p*-nitrobenzenesulfonate and 2-(2-indanyl)ethyl *p*-nitrobenzenesulfonate were followed by the standard ampoule titration technique, the acid generated being titrated with a stock sodium acetate solution in acetic acid to bromophenol blue end point.