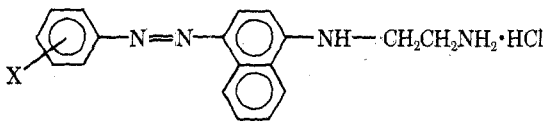

7

Rate constants at 30 °C (k_ψ) were obtained from a plot of log (Abs_t − Abs_∞) vs. time. Rate constants at 0 °C (k_P and k_D) were obtained as follows. The linear section of a plot of Abs_t vs. time was extrapolated to $t = 0$ to give an estimate of the amount of protection. Subtraction of this from A_0 gave the amount of decomposition and a value of R (where R = protection/decomposition) was obtained.

Now A_t = total *syn*- and *anti*-arylazo ether at time t and $(A_0 - A_t)$ = a measure of decomposition at time t (i.e., ArH). Therefore $R(A_0 - A_t)$ = protection at time t (i.e., *anti*-arylazo ether) and $A_t - R(A_0 - A_t)$ = *syn*-arylazo ether at time t. Now from a plot of log $[A_t - R(A_0 - A_t)]$ vs. time we get a measure of the total rate of reaction of *syn*-arylazo ether ($k_P + k_D$).

Knowing the fraction of protection and decomposition we obtain k_P and k_D from the total rate.

All solvents were chilled to 0 °C before the addition of reagents.

C. Kinetics Using Direct Uv Analysis (k_ψ). The rate of dediazoniation could also be measured by direct uv analysis of the reaction solution. The reaction was carried out in a thermostatically jacketed cuvette in the uv machine and the rate of decomposition was followed by monitoring the decrease in absorbance due to the *anti*-arylazo alkyl ether. The rate constant was obtained from a plot of log $(A_t - A_\infty)$ vs. time. Rate constants (k_ψ) measured by methods B and C are in Tables II and III.

Acknowledgments. We thank Professor J. F. Bunnett (University of California at Santa Cruz) and Drs. L. W. Deady and J. E. Rowe (La Trobe University) for stimulating discussions.

Registry No.—*p*-Nitrobenzenediazonium tetrafluoroborate, 456-27-9.

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Solvolysis of 3,4-Benzotricyclo[4.3.1.0^{1,6}]dec-3-en-2-yl *p*-Nitrobenzoates and Its Related System

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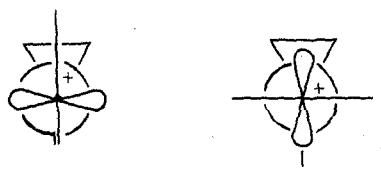
3,4-Benzotricyclo[4.3.1.0^{1,6}]dec-3-en-2- (*anti*- and *syn*-) yl *p*-nitrobenzoate (4-OPNB) and its homoallylic isomer (**5**-OBs) were prepared via 11- and 10-step synthesis, respectively, starting with 2-benzyl-2-methoxycarbonylcyclopentanone. Solvolysis of the syn **4s**-OPNB in 80% aqueous acetone proceeded at 25 °C with a rate of 1.73×10^{-4} s^{-1} which was two times faster than a rate of 0.86×10^{-4} s^{-1} for the anti **4a**-OPNB. Also, these rates were considerably fast (ca. $\times 10^2$) in comparison with ordinary cyclopropylphenylmethyl system. Brosylate **5**-OBs was solvolyzed with a rate of 0.65×10^{-4} s^{-1} at 25 °C. In the presence of base, **4a**-OPNB and **5**-OBs gave similar products, a mixture of **4a**-OH (13%), **4s**-OH (42%), and **6**-OH (45%). Treatment of **4a**-OH with acid catalyst or solvolysis of **4a**-OPNB in the absence of base afforded exclusively the tertiary alcohol, **6**-OH. The implications of these and other results are discussed together with available data.

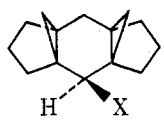
From enormous investigations by a number of forerunners[1-3] it has been established that solvolytic displacements of almost all cyclopropylmethyl systems proceed with remarkably accelerated rates in comparison with those of other alkyl systems. This is particularly enhanced when the geometric arrangement of the reactants favors the formation of such a transition state that the plane of a cyclopropane is orthogonal to that of an electron-deficient carbon atom. The interaction between these planes has been widely studied by NMR spectroscopy at low temperatures[4] or by molecular orbital calculation.[5]

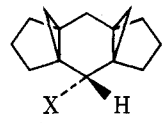
Recently the key discussion[6] in solvolysis of cyclopropylmethyl systems is to concentrate on character at the transition state. Winstein et al.[7] reported that the first-order rate constant of **1a**-OPNB in solvolysis in 80% aqueous acetone was 7.70×10^{-3} s^{-1} at 25 °C, the value being one-half the rate constant of **1s**-OPNB.

It is evident from these studies that the "bisected" conformation is more stable than the "perpendicular" one in the intermediate cyclopropylmethyl cation.[4,5,7,8]

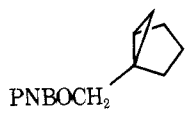


bisected perpendicular


1s-OAc


1a-OAc
1a-OPNB

In the similar study on the bicyclic *p*-nitrobenzoate **2**, greatly accelerated rate was observed in comparison with **3**.[9] Since the major product was 3-methylenecyclohexanol, relief of steric strain in the transition state was proposed for this high reactivity. The 1-bicyclo[3.1.0]hexyl group certainly exhibits a large accelerative effect in such solvolysis, aside from explanation.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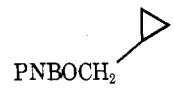
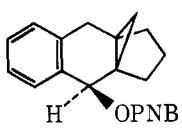
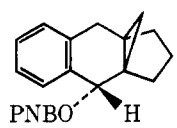
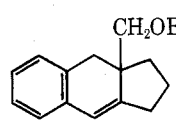

3

In this paper, the syntheses and the solvolysis of both 4-OPNB and 5-OBs are reported. The former may be adequate for the study on *intramolecular* competitive effects between two different modes of acceleration, σ-participation by a favorably rigid cyclopropane and π-conjugation by an aromatic ring.[10,24] The solvolytic behavior of the latter, a homoallylic isomer, may be inseparably related with the former.


4s-OPNB


4a-OPNB

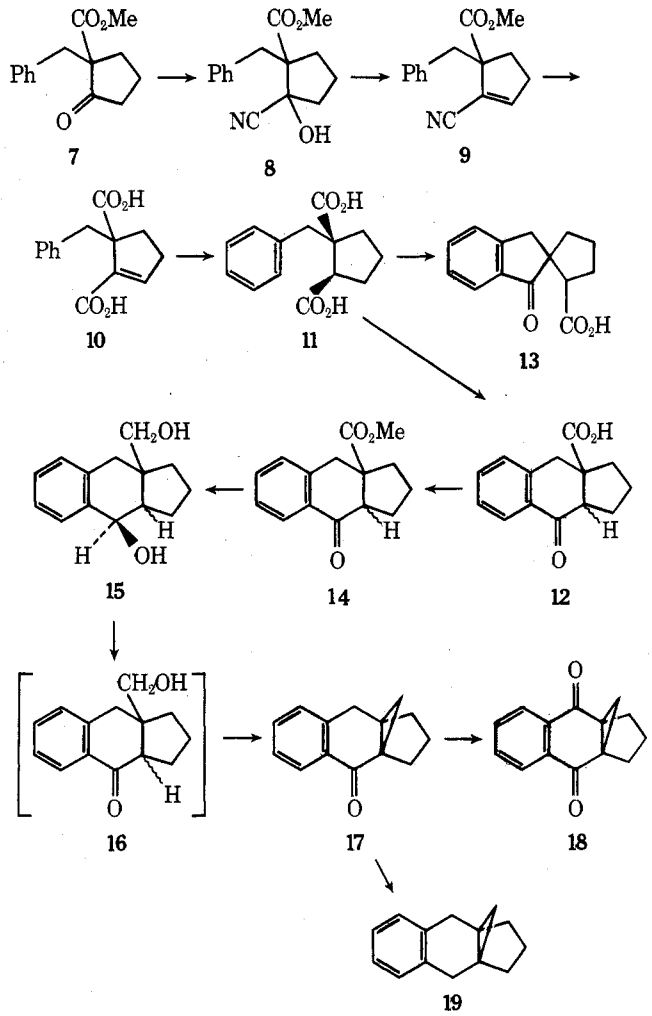

5-OBs

Results

Syntheses. The synthetic route of the important precursor, ketone **17**, of 4-OPNB is outlined in Scheme I.

2-Benzyl-2-methoxycarbonylcyclopentanone (**7**) was prepared by the condensation of 2-methoxycarbonylcyclopentanone with benzyl chloride according to "Organic Syntheses".[11] Addition of hydrogen cyanide to **7** gave cyanohydrin **8**, which, without further purification, was dehydrated by phosphorus oxychloride in dry pyridine to afford the unsaturated cyano ester **9** in 69% yield. Then the unsaturated dicarboxylic acid **10** was obtained by its hydrolysis. Hydrogenation of **10** with Adams' catalyst in ethyl acetate gave the saturated acid **11** in high yield. Since dehydration with acetic anhydride of **11** gave rise easily to acid anhydride, **11** could be characterized as the cis isomer. Intramolecular cyclization of **11** with concentrated sulfuric acid gave rise to the keto acid **12** (mp 129–130 °C) in 87% yield together with the minor spiro keto acid **13**. It was not determined whether the ring junction of **12** is cis or trans. The problem of these junctions, in any event, vanished in **17** or the primary alcohol (**5**-OH). On the other hand, Friedel–Crafts condensation of the acid anhydride of **11** afforded mainly **13** (mp 177–178 °C). Their structures were characterized by spectroscopic analysis and by the chemical transformations. Namely, concentrated sulfuric acid gave the cyclohexenone derivative **12** whereas anhydrous aluminum chloride gave the cyclopentenone **13**. Esterification with diazomethane converted **12** almost quantitatively into its ester **14**, which was reduced by lithium aluminum hydride

Scheme I



to give rise to a mixture of at least two diols (mp 156, 100 °C) in a good yield, the ratio being about 3:1. Contrary to the fact that the minor diol was not oxidized with active manganese dioxide, the major diol (mp 156–158 °C) (**15**) easily gave the keto alcohol **16** under the same conditions. Thus, it is deduced from the results and spectral data that the hydroxyl group at the benzyl position may be cis to the oxymethyl group in **15** and that the hydroxyl group may be trans in the minor diol. This conclusion is also consistent with the following facts. Sterically hindered carbinols were more readily oxidized by the above reagent than less hindered ones[12] and were predominantly produced by reduction of ketones with hydride reagents[13] owing to attack of a hydride ion from the less hindered side. Then, **16** was transformed to its tosylate, followed by heating it under reflux in dry pyridine to give **17** in 61% yield from **15**.

Spectroscopic and elemental analysis support the structure of assigned **17**. The NMR spectrum of **17** showed in $CDCl_3$ δ 1.05, 1.24 (AB q, J = 6.0 Hz, 2 H, cyclopropyl hydrogen), 3.02, 3.39 (AB q, J = 18.9 Hz, 2 H, benzyl hydrogen), and other signals.

In order to ensure the carbon skeleton, oxidation of the above ketone with chromic acid gave rise to a diketone, which was identical with the diketone (**18**) prepared from 1,4-dihydroxynaphthalene by an alternative route.[14] In addition, **17** was reduced with sodium in liquid ammonia into a hydrocarbon (**19**). The hydrocarbon (**19**) was also consistent with that of 3,4-benzotricyclo[4.3.1.0^{1,6}]dec-3-ene (**19**) prepared independently by Simmons–Smith reaction of 1,4-dihydro-2,3-trimethylenenaphthalene.[15]

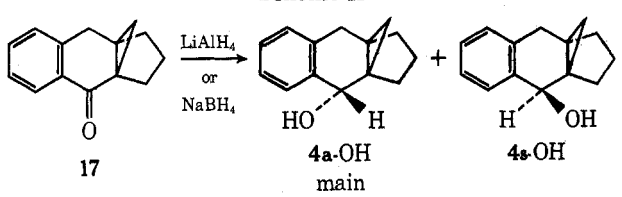
Table I. Observed α-Hydrogen Shifts and Their Differences Due to Neighboring Cyclopropane

	a	δ b	Δδ c	Ref
1-OH	Anti	3.48	0.69	d, e
	Syn	4.17		
Bicyclo[3.1.0]-hexan-2-ol	Anti	4.14	0.26	e
	Syn	4.40		
4-OH	Anti	4.83	0.21	Present study
	Syn	5.04		

a The relation in OH group and cyclopropane methylene. b Chemical shifts are listed in δ (ppm) relative to tetramethylsilane. c $\Delta\delta = \delta_{syn} - \delta_{anti}$. d Reference 16. e Reference 18.

Reduction of 17 with lithium aluminum hydride or sodium borohydride gave the alcohol (4a-OH), in 90–95% yield, concomitant with a trace of another epimer (4s-OH, 2–3%) (Scheme II). In its NMR spectrum, 4a-OH in $CDCl_3$ showed

Scheme II



17 4a-OH main 4s-OH

signals at δ 0.36 (singlet, 2 H, cyclopropyl hydrogen), 3.15, 2.79 (AB q, J = 16.0 Hz, 2 H, benzylic hydrogen), and 4.83 (s, 1 H, α hydrogen) together with other signals. The following attempts were unsuccessfully carried out in order to isolate a pure sample of 4s-OH. Meerwein–Ponndorf reduction of 17, epimerization of 4a-OAc in acetic anhydride,[16] and substitution of 4a-OPNB with tetraethylammonium acetate[17] resulted in formation of a mixture of several compounds.

The assignment of stereochemistry at C_2 (reactive center) is based upon comparison of NMR spectra of both epimeric alcohols and upon the inference for the direction of hydride reduction of 17. Since it has been confirmed in NMR spectroscopy that a proton which is located above the plane of a cyclopropane ring should be shielded in contrast with a proton in the same plane as that of cyclopropane,[18] comparison of the chemical shifts of α-carbinyl protons in two epimers was made. The result is shown in Table I together with analogous data reported earlier. As seen, the anti geometry of the hydroxyl group relative to cyclopropane is assigned to the anti epimer, 4a-OH, in which the α proton was more shielded.

Anticipation of hydride reduction also leads to the same assignment to the alcohol. It may be expected that reduction of 17 with lithium aluminum hydride would give predominantly the anti-alcohol, 4a-OH, owing to hydride attack from less hindered side of the carbonyl group.[13] A similar result was reported.[16]

Finally the primary alcohol, 5-OH, was prepared in the sequence outlined in Scheme III. The hydroxy ester 20 was obtained by selective reduction of the keto ester 14 with sodium borohydride and dehydrated with p-toluenesulfonic acid in benzene to give the unsaturated ester 21. Reduction with lithium aluminum hydride converted this ester into the primary alcohol (5-OH) in 68% yield from 14.

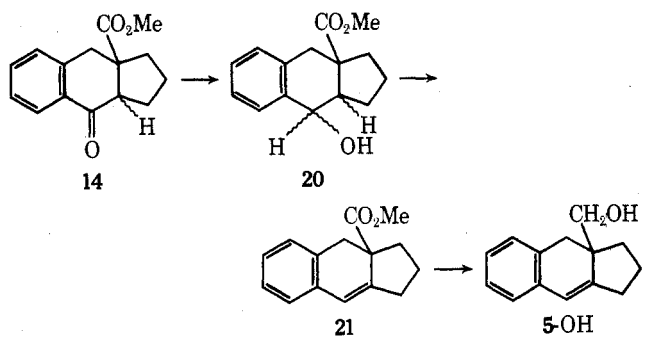
The structure of the final product was assigned as 5-OH from spectroscopic and elemental analysis. Its NMR spectrum in $CDCl_3$ showed a triplet at δ 6.35, J = 2.2 Hz, for a vinyl hydrogen, an AB quartet at δ 3.10, 2.65, J = 15.0 Hz, for benzylic methylene hydrogens, and a singlet at δ 3.28 for oxymethylene hydrogens together with other signals, and in

Table II. Rates of Solvolysis of Esters in 80% Aqueous Acetone

Compd	Temp, °C a	$10^4 k$, s^{-1} b	$\Delta H^{\ddagger}$, kcal/mol c	$\Delta S^{\ddagger}$, eu c
4a-OPNB	25.0	0.860 ± 0.05	20.6	−8.0
	30.0	1.51 ± 0.04		
	40.0	4.86 ± 0.03		
4s-OPNB	25.0	1.73 ± 0.06		
5-OBs	25.0	0.65 ± 0.006	22.7	1.6
	40.0	4.21 ± 0.04		

a ±0.03 °C. b Kinetic plots were linear to 75% conversion (2 half-lives). c Calculated from $\Delta H^{\ddagger} = R\,(T_1T_2/T_2 - T_1)\ln(T_1k_2/T_2k_1)$, $\Delta S^{\ddagger} = R \ln(k'h/kT_i) + H/T_i$; T_i, absolute temperature; h, Planck's constant; k, Boltzmann's constant.

Scheme III



14 20 21 5-OH

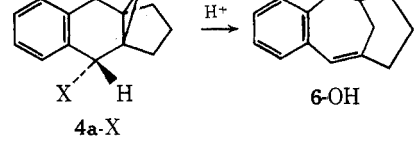
Me_2SO showed a triplet characteristic of a proton of hydroxyl group in primary alcohol.

Kinetic Studies. The p-nitrobenzoate of 4a-OH and the brosylate of 5-OH were prepared in high degree of purity by ordinary method, but the p-nitrobenzoate of 4s-OH was obtained by repeated recrystallization in the purity of ca. 95% analyzed by NMR spectroscopy because of very minor production from 17. The rates of solvolysis of these esters were determined by titration of p-nitrobenzoic acid in 80% aqueous acetone. The results are summarized in Table II.

The first-order rate constant of 4s-OPNB was about twice as high as that of 4a-OPNB at 25 °C. Since it was reported that a similar relative rate had been obtained in solvolysis of 1s-OAc and 1a-OAc under the same condition,[7] the above steric assignment for 4a and 4s-OH is not inconsistent with these kinetic data.

Products Studies. Solvolysis of 4a-OPNB in the absence of base clearly gave rise to the other alcohol 6-OH in 83% yield and the same alcohol was also produced by the treatment of 4a-OH with acid catalyst (p-nitrobenzoic acid) in 80% aqueous acetone (Scheme IV). The structural assignment of 6-OH is

Scheme IV



4a-X 6-OH

X = OPNB or OH

based upon its elemental and spectroscopic analysis. Its NMR spectrum in $CDCl_3$ showed a singlet at δ 6.17 for a vinyl hydrogen and an AB quartet at δ 2.40, 3.05 (J = 15.0 Hz) for benzylic methylene hydrogens together with other signals, and in Me_2SO showed a singlet characteristic of a proton of the hydroxyl group in tertiary alcohol. Uv spectra of 6-OH and

Table III. Uv Spectra of the Tertiary Alcohol 6-OH and Related Compounds in EtOH

	λ_{max}, nm	ϵ	Ref
6-OH	255	12 000	Present study
1,2-Benzo-4-methyl-cyclohepta-1,3-diene	258	86 000	*a*
1,2-Benzo cyclo-hepta-1,3-diene	280	41 900	*a*

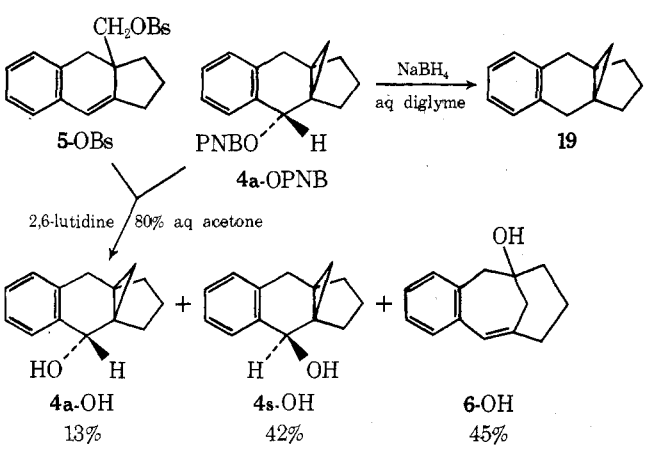
[a] Reference 19.

certain related compounds are listed in Table III, indicating that the molecular absorbance of **6**-OH is the lowest among three compounds. These results agree with the assigned structure for **6**-OH.

The study on the kinetic solvolysis products of 4-OPNB was carried out in 80% aqueous acetone in the presence of 2,6-lutidine or sodium hydrogen carbonate. After about 40 half-lives, the products were extracted by usual workup and analyzed by using NMR spectroscopy. Then, it was found from five runs that the solvolysis products were substantially a mixture of alcohols which consisted of **4a**-OH (13%) **4s**-OH (42%), and **6**-OH (45%). These alcohols (**4a**-OH, **5**-OH, and **6**-OH) were stable to the solvolysis conditions with 2,6-lutidine. The primary alcohol, **5**-OH, could not be detected by way of the extraneous singlet at δ 3.28 due to its hydroxymethyl protons. From the solvolysis of **5**-OBs under the same conditions there was obtained an almost identical product distribution with that of **4a**-OPNB.

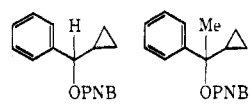
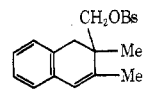
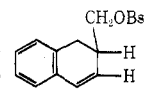
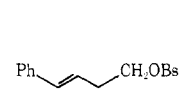
In addition, trapping[31] a carbonium ion with sodium borohydride in aqueous diglyme has been tried for **4a**-OPNB to afford the hydrocarbon **19** in 90% yield. Its structure was established by a comparison of the NMR spectrum and the VPC retention time with those of an authentic sample prepared independently as stated above. Further, it was confirmed experimentally that **4a**-OPNB was not epimerized into **4s**-OPNB in kinetic conditions after 0.5 half-life. The isomerization of **4a**-OPNB into **4s**-OPNB or the homoallylic tertiary ester (**6**-OPNB) is excluded. These results are summarized in Scheme V.

Scheme V



Although the rate of acetolysis of **4a**-OPNB was not measured, the product analysis was carried out in the presence of potassium acetate at 40 °C. The acetates obtained as the product under such acetolysis conditions were converted by lithium aluminum hydride reduction into a mixture of the corresponding alcohol followed by analysis with NMR spectroscopy. It was then found that the mixture consisted of the primary alcohol (**5**-OH) and the tertiary alcohol (**6**-OH) in ratio of 4:1. Neither **4a**-OH nor **4s**-OH could be found by this analytical procedure. The secondary acetate (**4a**-OAc) was independently prepared and subjected to the same acetolysis as above. Since almost all **4a**-OAc was converted into the tertiary acetate (**6**-OAc) under the conditions, secondary acetates produced by acetolysis of **4a**-OPNB may be transformed into **6**-OAc even if the former were the initial products in acetolysis. Thus, there was observed a large difference in products between the acetolysis and 80% aqueous acetone solvolysis of **4a**-OPNB.

Table IV. Relative Rates of Solvolysis of Ester in 80% Aqueous Acetone at 25 °C

	4s-OPNB	4a-OPNB	1s-OPNB[b]	1a-OPNB[b]
k_{rel}	2.0	1.0	8 × 10	4 × 10
				
	22[c]	23[d]	24[b]	25[b]
k_{rel}	~10^{-2} [a]	2.4	~3	~3
	5-OBs			
		26[e]	27[e]	28[f]
k_{rel}	1.0	0.25	0.05	0.1[a] or *b*

[a] Extrapolated from (22) in 60% aqueous acetone; (28) naphthalene sulfonate in EtOH at 60 °C. [b] Reference 7. [c] Reference 23. [d] Reference 24. [e] Reference 25. [f] Reference 26.

Discussion

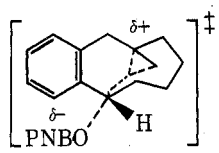
Rate Comparison. The rate comparison in solvolysis of **4s**-OPNB, **4a**-OPNB, **5**-OBs, and certain related esters is made in Table IV. The marked rate enhancement is observed for both **4s**-OPNB and **4a**-OPNB compared with the simple cyclopropylphenylmethyl *p*-nitrobenzoate (**22**), the magnitude of the rate constant being 10^2 times. The enhanced rate for these secondary esters is also as high as that of the tertiary **23**. A similar large accelerative effect was reported setting **1s**-OPNB and **1a**-OPNB against **24** and **25**. Now, the rate of ionization of **1s**-OPNB or **1a**-OPNB was about 40 times faster than that of **4s**-OPNB or **4a**-OPNB. Namely, the biscyclopropylmethyl system is more reactive than the cyclopropylphenylmethyl system when both secondary systems are composed of an analogous aliphatic carbon skeleton. In other words, a cyclopropyl group proves more effective for the stabilization of the transition state than a phenyl group, so far.

Recently a number of studies on the relative ability to stabilize an adjacent cationic center to a cyclopropyl and a phenyl group have been reported in NMR measurement of the ions in superacidic media and in solvolytic behavior. There are several different elucidations for the above phenomena.[6] Of these, strain relief from the bent-bond[8b,9,27] and "vertical"[6a,b,g] electronic effect without changing the geometry are representative for the effect of a cyclopropyl group. On the other hand, coplanarity of phenyl group attached to the central carbon atom is important for the accommodation of the positive charge in the ions or in the intermediate in solvolysis.

The carbon skeleton of the present system has been intentionally designed so that both an benzene ring and an 1-bicyclo[3.1.0]hexyl group are capable of favorable conjugation with or participation in the reaction center. As shown in rate acceleration, this has been proved to be quite effective. Also, it seems that the competitive effect of a phenyl and a cyclopropyl group may be examined intramolecularly by such planning in solvolysis of a secondary system. The relative rate ratio between syn (**4s**-OPNB) and anti isomer (**4a**-OPNB) was

found to be ca. 2, the value being very close to that for other examples[7,29] in which benzylic type stabilization is lacking. If π-conjugation of the benzene ring would dominate in the rate-determining step of the present solvolysis, the difference between the rates of two epimeric esters should be much smaller than the observed value, so that σ-participation of the cyclopropyl group might exert a larger influence on the transition state.

From the above discussion the following transition state (**29**) could be proposed for the solvolysis of **4a**-OPNB as an example. It is emphasized that the transition state is more like



29

transition state

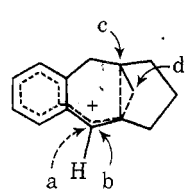
the cyclopropylcarbinyl cation than the benzylic cation or the fully delocalized cyclopropylphenylcarbinyl cation. However, further investigation for the substituent effect on the benzene ring should be necessary with regard to the magnitude of π-conjugation from an aromatic nucleus,[30] though the smaller ρ^+ value would be anticipated in comparison with the other analogous systems.

In the similar reaction of a homoallylic isomer (**5**-OBs), the rate was 4–20 times larger than that of the related systems (**26**, **27**, and **28**). The rigidity of the benzobicyclic system in **5**-OBs again assists the solvolysis in comparison with a more fluxional system. Thus, π-participation of the double bond may lead to a similar transition state to the above. This is also deduced from the analogous $\Delta H^{\ddagger}$ values (20.6 and 22.7 kcal/mol) in both the solvolyses of **4a**-OPNB and **5**-OBs.

Products. The product distribution in solvolysis is shown in Scheme V. Since the sufficient amount of **4s**-OPNB could not be prepared, product analysis from this ester was not carried out. The relative rate of **4s**-OPNB to **4a**-OPNB is very close both to that of **1s**-OAc to **1a**-OAc[7] and that of Gassman's system,[29] and also in these cases the product distribution for syn isomer was identical with that for anti isomer. Further, the same product distribution was observed in the reaction of **5**-OBs. It could, therefore, be assumed that the products were very similar to those from the anti ester. On account of the result, a common intermediate may be expected in the solvolyses starting from all three esters (**4s**-OPNB, **4a**-OPNB, and **5**-OBs).

Another characteristic of the present result is production of the tertiary alcohol (**6**-OH) in considerable portion (45%) in the presence of a base. In the absence of the base, this alcohol was the predominant product. It is interesting that, in acidic solvolysis media, the sole product was **6**-OH among four isomers, **4a**-OH, **4s**-OH, **5**-OH, and **6**-OH, in spite of the presence of an unfavorable double bond at the bridgehead in the small bicyclic system.[20-22] Since classical carbonium ions at the bridgehead in such small bicyclic systems are generally unstable,[31] those ions could not be adopted as an intermediate.

On these evidences, a homoallylically conjugated carbonium ion such as **30** is proposed for the sole common intermediate.



30

reaction intermediate

In aqueous media this intermediate carbocation might undergo discharge by water from the side of a, b, and c in the formula to be converted into the final product. In acetolysis neighboring participation by back-side σ-bonding electrons may be more important during ionization than in aqueous acetone because of lower degree of solvent polarity and nucleophilicity.[33] Then, the attack of acetic acid on the intermediate (**30**) from the side of d might coincide with the participation of the cyclopropane during C–O heterolysis. This resulted in formation of **5**-OAc as the main acetolysis product together with tertiary acetate (**6**-OAc). The configurational assignment for **4a**-OH is also consistent with these facts.

In conclusion, the rate of solvolysis of **4s**- and **4a**-OPNB in 80% aqueous acetone was highly accelerated in comparison with the cyclopropylphenylmethyl system, essentially owing to σ-participation from the rigid tricyclo[4.3.1.$0^{1,6}$] system rather than π-conjugation from the aromatic nucleus.[30] The relative rate for **4s**- and **4a**-OPNB was quite similar to that of analogous syn and anti isomeric pairs of cyclopropylmethyl systems.[7,29] The solvolysis product in the presence of base was a mixture of **4a**-OH (13%), **4s**-OH (42%), and **6**-OH (45%); **4a**-OH was isomerized into **6**-OH under acidic conditions. The same mixture was obtained as the product for similar solvolysis of **5**-OBs, which was solvolyzed faster than referred homoallylic primary brosylates. The common cationic intermediate **30** was proposed for the solvolysis of **4s**-OPNB, **4a**-OPNB, and **5**-OBs in order to explain the above experimental results.

Experimental Section

All the melting points are uncorrected. Infrared spectra were recorded with a Hitachi 215 grating ir spectrophotometer. NMR measurements were carried out on a Hitachi R-20 spectrometer, using tetramethylsilane as an internal reference.

2-Benzyl-1-hydroxy-2-methoxycarbonylcyclopentanecarbonitrile (8). 2-Benzyl-2-methoxycarbonylcyclopentanone (**7**,[11] 37 g, 0.16 mol) dissolved in 120 ml of ether was added to an aqueous solution (90 ml) of sodium cyanide (37 g, 0.75 mol) with vigorous stirring under cooling by an ice bath. Concentrated hydrochloric acid (45 ml) was added to the above mixture at such a rate that the temperature was maintained between 5 and 10 °C. Vigorous stirring was continued for 30 h at that temperature. The crude cyanohydrin **8** (35.6 g) was obtained in 86% yield by the ordinary method for extraction of the reaction product, and used for the following dehydration without further purification. A pure sample was obtained by recrystallization from carbon tetrachloride. It melted at 119–120 °C: ir (Nujol) 3380 (OH), 2250 (CN), 1735 (CO_2Me), 1190, 1090, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.42–7.02 (m, 5 H, aromatic), 3.70 (s, 3 H, methyl), 3.30 and 2.70 (AB q, J = 13.5 Hz, 2 H, benzyl), 2.40–1.70 (m, 7 H, aliphatic, OH).

Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.67; H, 6.60; N, 5.26.

5-Benzyl-5-methoxycarbonylcyclopent-1-enecarbonitrile (9). To the solution of **8** (24.7 g, 0.1 mol) in 100 ml of anhydrous pyridine was added phosphorus oxychloride (45.9 g, 0.3 mol) with vigorous stirring and cooling below 10 °C. The stirring was continued for 3 h in an ice bath, for 12 h at room temperature, then for 2 h under reflux. After the reaction mixture was poured onto a mixture of crushed ice (100 g) and concentrated hydrochloric acid (100 ml), 19.4 g of **9** (80% yield) was obtained by ordinary workup process: bp 170–175 °C (5 mm); ir (neat) 2230 (CN), 1730 (CO_2Me), 1250, 710 cm^{-1}; NMR ($CDCl_3$) δ 7.28 (s, 5 H, aromatic), 6.69 (t, J = 2.5 Hz, 1 H, vinyl), 3.78 (s, 3 H, methyl), 3.25 and 2.95 (AB q, J = 13.5 Hz, 2 H, benzyl), 2.60–1.85 (m, 4 H, aliphatic).

5-Benzylcyclopent-1-ene-1,5-dicarboxylic Acid (10). A mixture of **9** (19.4 g, 0.08 mol), concentrated hydrochloric acid (200 ml), and glacial acetic acid (100 ml) was heated under reflux with vigorous stirring for 10 h. The crude **10** (14 g, 71% yield) was obtained by cooling the reaction mixture, mp 208–210 °C. The pure sample was recrystallized from 50% aqueous methanol: mp 220–221 °C; ir (Nujol) 1690 (CO_2H), 1670 (CO_2H), 1620 cm^{-1}. Its treatment with diazomethane gave the methyl ester, mp 35–36 °C, quantitatively: NMR for methyl ester (CCl_4) δ 7.15 (s, 5 H, aromatic), 6.65 (t, J = 1.5 Hz, vinyl), 3.75 (s, 3 H, methyl), 3.69 (s, 3 H, methyl), 3.35 and 3.10 (AB q, J = 13.5 Hz, 2 H, benzyl), 2.40–1.80 (m, 4 H, aliphatic).

1-Benzylcyclopentane-1,2-dicarboxylic Acid (11). A mixture of 10.0 g (40.5 mmol) of **10** dissolved in 500 ml of ethyl acetate and 80 mg of Adams Pt catalyst was stirred under hydrogen atmosphere at room temperature. Slightly excess hydrogen (916 ml) of the theoretical amount (910 ml) was absorbed. The saturated dicarboxylic acid (**11**) was obtained almost quantitatively by recrystallization from carbon tetrachloride: mp 120–121 °C; ir (Nujol) 1685 (CO_2H), 930, 740, 700 cm^{-1}; NMR ($CDCl_3$) δ 11.35 (s, 2 H, carboxylic), 7.20 (s, 5 H, aromatic), 3.32 (m, 1 H, methine), 3.34 and 2.78 (AB q, J = 13.5 Hz, 2 H, benzyl), 2.20–1.70 (m, 6 H, aliphatic).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.57; H, 6.60.

3,4-Benzo-5-oxobicyclo[4.3.0]non-3-ene-1-carboxylic Acid (12). A solution of 10 g of **11** dissolved in 100 ml of concentrated sulfuric acid was stirred for 21 h at room temperature. After being poured onto 500 g of crushed ice, the mixture was extracted with ether. Recrystallization of an extract from benzene afforded 8.1 g of **12** (mp 129–130 °C) in 87% yield and 0.6 g (mp 140–145 °C) of a mixture of **12** and **13**. **12**: ir (Nujol) 1680 (CO_2H), 1670 (C=O), 775, 730, 710 cm^{-1}; NMR ($CDCl_3$) δ 11.08 (s, 1 H, carboxylic), 8.20–7.70 (m, 1 H, aromatic), 7.65–7.00 (m, 3 H, aromatic), 3.35 (m, 1 H, methine), 3.31 and 2.96 (AB q, J = 18.0 Hz, 2 H, benzyl), 2.50–1.50 (m, 6 H, aliphatic).

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.88; H, 6.08.

2,3-Benzo-6-carboxy-1-oxospiro[4.4]nonene (13). The acid anhydride (8.9 g), bp 180–185 °C (1.5 mm), was obtained in 84% yield by heating **11** (11.4 g) with acetic anhydride (63 ml) for 3 h. To a solution of the whole anhydride dissolved in 555 ml of 1,2-dichloroethane was added 13.2 g of $AlCl_3$ in one portion under cooling at 0 °C. Stirring was continued for 1 h in an ice–water bath and for 3 h at room temperature. The reaction mixture was poured onto a mixture of 50 ml of 6 M hydrochloric acid and crushed ice, followed by extraction with chloroform. Usual workup gave 6.1 g of the crude **13** in 69% yield. A pure sample was obtained by recrystallization from benzene (mp 177–178 °C): ir (Nujol) 1690 (C=O, CO_2H), 1600, 1300, 1240, 930, 750 cm^{-1}; NMR ($CDCl_3$) δ 14.35 (s, 1 H, carboxylic), 7.85–7.10 (m, 4 H, aromatic) 3.50 and 3.03 (AB q, J = 17.0 Hz, 2 H, benzyl), 3.02 (m, 1 H, methine), 2.50–1.50 (m, 6 H, aliphatic).

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.98; H, 6.20.

Reduction of the methyl ester of **13** with $NaBH_4$ gave rise to oxy ester in good yield. Its NMR spectrum in $CDCl_3$ showed a sharp singlet at δ 4.82 for α hydrogen to hydroxyl group and other signals.

3,4-Benzo-1-hydroxymethyl-5-hydroxybicyclo[4.3.0]non-3-ene (15). The crude keto ester (mp 78–80 °C) prepared from 5.4 g (0.024 mol) of **12** and diazomethane in ether was reduced with 4.0 g of $LiAlH_4$ in the usual way. The dihydroxy compounds thus produced were recrystallized from $CHCl_3$ to give 3.41 g (66% yield, mp 158–158.5 °C) of **15**, 1.02 g (20% yield, mp 100–113 °C) of another diol, and 0.68 g of a mixture of both. Further purification of the minor diol gave a pure sample which melted at 116–118 °C. Spectral data and chemical reactivity showed that these diols were the epimers.

Spectral data for **14**, mp 81–82 °C: ir (Nujol) 1730 (CO_2Me), 1670 (C=O), 1600, 1285, 835, 785, 740 cm^{-1}; NMR ($CDCl_3$) δ 8.00 (d, d, J = 8.0 and 1.5 Hz, 1 H, aromatic), 7.65–7.05 (m, 3 H, aromatic), 3.60 (s, 3 H, methyl), 3.40 (m, 1 H, methine), 3.37 and 2.97 (AB q, J = 16.0 Hz, 2 H, benzyl), 2.30–1.70 (m, 6 H, aliphatic).

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.54; H, 6.77.

Spectral data for **15**: ir (Nujol) 3300 (OH), 1035, 730 cm^{-1}; NMR (C_5D_5N) δ 8.10–7.85 (m, 1 H, aromatic), 7.5–7.0 (m, 3 H, aromatic), 5.19 (d, J = 5.3 Hz, 1 H, α-H), 3.69 (s, 2 H, oxymethyl), 3.03 and 2.65 (AB q, J = 13.5 Hz, 2 H, benzyl), 2.84 (m, 1 H, methine), 2.20–1.55 and 1.50–1.00 (m, 6 H, aliphatic), 1.30 (s, 2 H, hydroxyl).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.98; H, 8.41.

The minor diol was not oxidized with active MnO_2 in benzene under the same condition in which **15** was smoothly oxidized into **16**. Further investigation was not carried out. The minor diol: mp 116–118 °C; ir (Nujol) 3250 (OH), 1040, 730 cm^{-1}; NMR (C_5D_5N) δ 7.30–7.05 (m, 4 H, aromatic), 4.70 (d, J = 6.0 Hz, α-H), 3.47 (s, 2 H, oxymethyl), 3.39 and 2.45 (AB q, J = 13.5 Hz, benzyl), 2.83 (m, 1 H, methine), 2.20–1.50 and 1.14–1.00 (m, 6 H, aliphatic), 1.20 (s, 2 H, OH).

3,4-Benzotricyclo[4.3.1.0^{1,6}]dec-3-en-2-one (17). A suspension of 1.48 g (6.8 mmol) of **15** and 3.0 g of active MnO_2 in 150 ml of dry benzene was stirred at room temperature for 24 h. The residue obtained by filtration of the reagent and evaporaiion of the solvent was treated with 3.0 g of *p*-toluenesulforyl chloride in 50 ml of dry pyridine in an ice bath. The mixture was then stirred at room temperature for 15 h and finally under reflux for 3 h. After ordinary extraction of the product, its pentane solution was filtered through a small amount of neutral alumina, giving 830 mg (61% yield) of **17**: mp 64.5–65.5 °C; uv (EtOH) λ_{max} 244 nm (ϵ 11 600), 286 (1270); ir (Nujol) 1665 (C=O), 1600, 945, 740 cm^{-1}; NMR ($CDCl_3$) δ 8.00–7.60 (m, 1 H, aromatic), 7.55–6.96 (m, 3 H, aromatic), 3.39 and 3.02 (AB q, J = 18.9 Hz, 2 H, benzyl), 1.24 and 1.05 (AB q, J = 6.0 Hz, 2 H, cyclopropyl), 2.40–1.40 (m, 6 H, aliphatic).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.99; H, 7.25.

Oxidation of Ketone 17. Into a solution of 200 mg of chromium trioxide dissolved in 10 ml of 80% aqueous acetic acid was added 60 mg of **17**. The mixture was stirred for 5 min at room temperature and heated under reflux for 0.5 h. The mixture was poured onto 100 mg of ice after cooling, followed by filteration to give 31 mg of the crude diketone **18**. The product was recrystallized from cyclohexane to give a pure sample: mp 142–143 °C; ir (Nujol) 1668 (C=O), 1580, 1360, 1302, 1182, 990, 810, 730 cm^{-1}; NMR ($CDCl_3$) δ 7.60–8.06 (m, 4 H, aromatic), 2.16–2.40 (m, 6 H, aliphatic), 1.66 and 1.89 (AB q, J = 6.0 Hz, 2 H, cyclopropyl).

Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.12; H. 5.62.

Reduction with Na in Liquid NH_3 of Ketone 17. Into liquid ammonia was added, in small pieces, 0.23 g (10 mmol) of sodium metal followed by addition of a solution of 99 mg (0.5 mmol) of **17** dissolved in 10 ml of ether. The solution was stirred for 30 min and the ammonia was evaporated at room temperature. The white residue was treated with petroleum ether followed by addition of water carefully. The organic layer was washed with water and dried with anhydrous sodium sulfate. Evaporation of solvent gave rise to 88 mg (95%) of colorless oil. The product was assigned as 3,4-benzotricyclo[4.3.1.0^{1,6}]dec-3-ene (**19**) by comparison with VPC and NMR spectrum of an authentic sample.

Reduction of $LiAlH_4$ of Ketone 17. 3,4-Benzotricyclo[4.3.1.0^{1,6}]dec-3-en-2-ol (4-OH). The reduction of 985 mg of **17** with 500 mg of $LiAlH_4$ in 150 ml of dry ether was carried out by the ordinary procedure. Recrystallization from *n*-pentane gave a colorless solid, mp 89–90 °C, **4a**-OH (880 mg, 88%), and oily residue, 90 mg. It was found by its NMR spectrum that the oily residue consisted of two components, **4a**-OH and **4s**-OH, the ratio being about 1:2. The NMR spectrum of the mixture showed a singlet at δ 5.04 for α hydrogen, an AB quartet at δ 0.16 and 0.38 (J = 5.0 Hz) for cyclopropylmethylene hydrogens, and other signals assigned to **4s**-OH. For **4a**-OH: ir (Nujol) 3350 (OH), 1110, 1010, 735 cm^{-1}; NMR ($CDCl_3$) δ 7.70–7.40 (m, 1 H, aromatic), 7.30–6.90 (m, 3 H, aromatic), 4.83 (s, 1 H, α hydrogen), 3.15 and 2.79 (AB q, J = 16.0 Hz, 2 H, benzylic), 0.36 (s, 2 H, cyclopropyl), 2.50–1.30 (m, 7 h, aliphatic, hydroxyl).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.81; H, 8.14.

***p*-Nitrobenzoate (4a-OPNB) of 4a-OH.** The *p*-nitrobenzoate was prepared at 5 °C by allowing 207 mg of **4a**-OH to react with 386 mg of *p*-nitrobenzoyl chloride in 20 ml of dry pyridine. Workup gave a light yellow solid which was recrystallized from cyclohexane to give 314 mg (90%) of a solid: mp 135–136 °C; ir (Nujol) 1715, 1605, 1530, 1275, 1100, 745, 705 cm^{-1}; NMR ($CDCl_3$) δ 8.37 (s, 4 H, aromatic), 7.23 (s, 4 H, aromatic), 6.69 (s, 1 H, α hydrogen), 3.09 (s, 2 H, benzylic), 3.22 and 2.90 (AB q, J = 16.5 Hz, 2 H, benzylic), 2.30–1.10 (m, 6 H, aliphatic), 0.65 and 0.52 (AB q, J = 6.0 Hz, 2 H, cyclopropyl).

Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48; N, 4.01. Found: C, 72.10; H, 5.37; N, 3.94.

***p*-Nitrobenzoate (4s-OPNB) of 4s-OH.** Following the procedure described for **4a**-OPNB, 40 mg (0.2 mmol) of the mixture of **4s**-OH and **4a**-OH, ratio ca. 3:1, and 55 mg (0.3 mmol) of *p*-nitrobenzoyl chloride were allowed to react in 5 ml of dry pyridine. Workup and recrystallization from petroleum ether gave 45 mg of a white solid. Its NMR spectrum indicated that the product was **4s**-OPNB (95% pure). The ester was used for kinetics of solvolysis without further purification: NMR ($CDCl_3$) δ 8.35 (s, 4 H, aromatic), 7.20 (s, 4 H, aromatic), 6.62 (s, 1 H, α hydrogen), 3.38 and 3.10 (AB q, J = 16.0 Hz, 2 H, benzyl), 2.30–1.20 (m, 6 H, aliphatic), 0.60 and 0.42 (AB q, J = 6.0 Hz, 2 H, cyclopropyl).

Reduction with $NaBH_4$ of Ketone 17. A mixture of 57 mg of **17** and 54 mg of $NaBH_4$ dissolved in 5 ml of 2-propanol was stirred under reflux for 20 h. Usual workup gave 50 mg (88%) of colorless solid, which was characterized as **4a**-OH by comparison of its NMR spectrum with that of the $LiAlH_4$ reduction product described above.

Acetylation of 4a-OH. A solution of 113 mg of **4a**-OH and 1 ml of acetic anhydride dissolved in 5 ml of pyridine was allowed to stand overnight. After the addition of 20 ml of ether, the solution was poured onto a mixture of 5 ml of concentrated hydrochloric acid and crushed ice. The usual workup gave 67 mg (50%) of an oily acetate (**4a**-OAc): ir (CCl_4) 1725 (OAc), 1220, 1050 cm^{-1}; NMR ($CDCl_3$) δ 7.20 (s, 4 H, aromatic), 6.43 (s, 1 H, α hydrogen), 3.26 and 2.90 (AB q, J = 16.0 Hz, 2 H, benzylic), 2.30 (s, 3 H, methyl), 2.20–1.00 (m, 6 H, aliphatic), 0.20 and 0.36 (AB q, J = 6.0 Hz, cyclopropyl).

Reduction of 4a-OPNB with $NaBH_4$. Into a solution of 400 mg of sodium borohydride in 10 ml of 60% aqueous diglyme 41 mg of **4a**-OPNB was added and the mixture was stirred at room temperature. The mixture was diluted with 50 ml of water, extracted with

n-pentane, and washed with water. Evaporation of the solvent gave rise to 20 mg of product. According to the NMR spectrum and VPC, it was identified as 3,4-benzotricyclo[4.3.1.0^{1,6}]dec-3-ene.

Reduction of 2,3-Trimethylenenaphthalene. The fine sodium sand was prepared from 750 mg (0.03 mol) of sodium in 50 ml of toluene. Into the above mixture was added a solution of 1.0 g (0.006 mol) of 2,3-trimethylenenaphthalene[15] dissolved in 20 ml of toluene. Heating the mixture under reflux for 1 h, sodium was carefully decomposed by the addition of 10 ml of anhydrous ethanol, followed by 40 ml of ice–water. A light yellow solid was obtained by the usual workup and recrystallized from methanol to yield 650 mg (mp 49–52 °C) (86%) of colorless solid. The VPC and NMR spectrum of product revealed that they consisted of two components, the ratio being about 10:3. The predominant product was 1,4-dihydro-2,3-trimethylenenaphthalene and minor product was the other dihydronaphthalene. The crude product was used for the following Simmons–Smith reaction without purification.

3,4-Benzotricyclo[4.3.1.0^{1,6}]dec-3-ene (19). A suspension of 18 g of zinc–copper couple, 40 ml of anhydrous ether, and several drops of CH_2I_2 was allowed to stir under reflux until the reaction began. Then a solution of 750 mg of dihydronaphthalene derivatives dissolved in 9 ml of methylene iodide was added over 1 h and the mixture was heated under reflux for 24 h. The usual workup gave 630 mg of oily product, which was a mixture of three components in the ratio of 8.0:2.0:1.5 by means of VPC analysis. The main product was isolated by preparative VPC, assigned as 3,4-benzotricyclo[4.3.1.0^{1,6}]dec-3-ene (**19**) by its NMR spectrum: ir (neat) 1600, 1450, 1300, 970, 740 cm^{-1}; NMR (CCl_4) δ 0.20 and 0.32 (AB q, J = 5.0 Hz, 2 H, cyclopropyl), 1.30–2.00 (m, 6 H, aliphatic), 2.78 and 3.11 (AB q, J = 15.0 Hz, 4 H, benzylic), 6.94 (s, 4 H, aromatic), mass m/e 184 ($C_{14}H_{16}$).

3,4-Benzo-1-methoxycarbonyl-5-hydroxybicyclo[4.3.0]non-3-ene (20). Into a solution of 4.2 g (0.017 mol) of **14** dissolved in 70 ml of methanol were added 1.0 g of $NaBH_4$ and 100 mg of $NaHCO_3$ under cooling with ice bath. After stirring the mixture at 0–5 °C for 18 h, ordinary procedure for extraction with ether was applied to give a colorless oil (3.8 g) along with the minor product, a colorless solid (0.6 g, mp 157–161 °C): ir (Nujol) 3450 (OH), 1710 (C=O), 1240, 1150, 1040 cm^{-1}.

3,4-Benzo-1-methoxycarbonylbicyclo[4.3.0]nona-3,5-diene (21). A solution of 4.2 g of **20** and 200 mg of *p*-toluenesulfonic acid dissolved in 200 ml of dry benzene was heated under reflux for 1.5 h. Recrystallization of the crude product from petroleum ether gave a colorless solid, 3.3 g, mp 71–73 °C, in 85% yield: ir (Nujol) 1720 (CO_2Me), 1480, 1190, 750 cm^{-1}; NMR ($CDCl_3$) δ 7.10 (s, 4 H, aromatic), 6.39 (t, J = 2.1 Hz, 1 H, vinyl), 3.52 (s, 3 H, methyl), 3.42 and 2.71 (AB q, J = 15.0 Hz, 2 H, benzylic), 2.80–1.50 (m, 6 H, aliphatic).

3,4-Benzo-1-hydroxymethylbicyclo[4.3.0]nona-3,5-diene (5-OH). To a stirred suspension of 0.6 g (0.016 mol) of $LiAlH_4$ in 50 ml of dry diethyl ether was added the solution of 1.24 g (0.005 mol) of **21** dissolved in 50 ml of ether. The mixture was allowed to stir for 1 day at room temperature before excess hydride was carefully decomposed with 1 ml of water. Extraction of the product with chloroform gave rise to 0.8 g (80%) of a solid. Recrystallization from cyclohexane gave a colorless crystal: mp 96–98 °C; ir (Nujol) 3400 (OH), 1450, 1115, 1040, 745 cm^{-1}; NMR ($CDCl_3$) δ 7.12 (s, 4 H, aromatic), 6.35 (t, J = 2.2 Hz, 1 H, vinyl), 3.28 (s, 2 H, oxymethyl), 3.10 and 2.65 (AB q, J = 15.0 Hz, 2 H, benzylic), 2.70–1.50 (m, 6 H, aliphatic), 1.58 (s, 1 H, OH).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.86; H, 8.00.

Brosylate 5-OBs of Primary Alcohol 5-OH. A solution of 200 mg (1.0 mmol) of **5-OH** and 251 mg (1.1 mmol) of *p*-bromobenzenesulfonyl chloride in 2 ml of dry pyridine was allowed to stand at 5 °C for 52 h. After addition of 25 ml of cold, dry ether to the mixture and filtration of a solid, all the solvents were thoroughly removed under reduced pressure without warming the flask. The product was recrystallized from a mixture of benzene and cyclohexane to give 260 mg (62%) of a colorless solid: mp 75–76 °C; ir (Nujol) 1380 (SO_2), 1180 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.53 (s, 4 H, aromatic), 7.20–6.60 (m, 4 H, aromatic), 6.21 (t, J = 2.2 Hz, 1 H, vinyl), 3.70 and 3.42 (AB q, J = 9.0 Hz, 2 H, oxymethyl), 3.30 and 2.64 (AB q, J = 15.0 Hz, 2 H, benzylic), 2.80–1.10 (m, 6 H, aliphatic).

Anal. Calcd for $C_{20}H_{19}O_3BrS$: C, 57.29; H, 4.57; Br, 19.06. Found: C, 56.69; H, 4.75; Br, 18.72.

General Kinetic Procedures. For each run approximately 50 mg (ca. 0.14 mmol) of ester was weighed into a 50-ml volumetric flask and dissolved in 80% aqueous acetone (ca. 3×10^{-3} M); 80% aqueous acetone mixtures were prepared by mixing 40 ml of dry acetone with 10 ml of distilled water. Rates at each temperature (25.0, 30.0, 40.0 °C in accuracy, ±0.03 °C) were measured by quenching 5.00-ml aliquots in 20 ml of dry acetone and immediately titrating with a standard aqueous sodium hydroxide solution (ca. 0.01 M) to a blue end point, using 2 drops of a 1% methanol solution of bromothymol blue as an indicator, and the kinetic plots were linear to 75% conversion; reported values are the average of two runs (Table II). In all cases infinite titers were measured after ca. 10 half-lives and 96.7–98.5% of theoretical *p*-nitrobenzoic acid or *p*-bromobenzenesulfonic acid was removed.

A solution of 107 mg (0.28 mmol) of **4a-OPNB** in 100 ml of 80% aqueous acetone was allowed to stand at 25 °C for 1 h (ca. ½ half-life). The solution was poured into a mixture of ether (300 ml) and water (100 ml). The ether layer was washed with water and dried over anhydrous sodium sulfate. Solvent was removed at reduced pressure and 90 mg of a colorless solid remained. A comparison of the NMR spectrum before and after the reaction showed that **4a-OPNB** was not isomerized into **4s-OPNB**, **5-OPNB**, and **6-OPNB** under the solvolysis conditions.

Treatment of 4a-OH with *p*-Nitrobenzoic Acid. A solution of 400 mg of **4a-OH** and 300 mg of *p*-nitrobenzoic acid dissolved in 100 ml of 80% aqueous acetone was warmed at 40 °C for 2 days. Into the solution was added 350 mg of $NaHCO_3$ and most of the acetone was removed under reduced pressure followed by extraction with ether, washing with water, and drying over anhydrous K_2CO_3. Solvent was removed at reduced pressure to give 250 mg (63%) of a colorless solid. Recrystallization from cyclohexane gave rise to a pure sample, tertiary alcohol **6-OH**: mp 92–93 °C; uv (EtOH) λ_{max} 225 nm (ϵ 12 000); ir (Nujol) 3300 (OH), 1055, 910, 820, 735 cm^{-1}; NMR ($CDCl_3$) δ 7.17 (s, 4 H, aromatic), 6.17 (s, 1 H, vinyl), 3.05 and 2.40 (AB q, J = 15.0 Hz, 2 H, benzyl), 2.50–1.50 (m, 8 H, aliphatic), 1.84 (s, 1 H, OH).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.17; H, 8.16.

Preparative Solvolysis of 4a-OPNB. A solution of 200 mg (0.57 mmol) of **4a-OPNB** and 0.5 ml (ca. 2.5 mmol) of 2,6-lutidine in 100 ml of 80% aqueous acetone was heated at 40 °C for 20 h (ca. 40 half-lives). The solution was concentrated under reduced pressure, 50 ml of water was added, and the resulting suspension was extracted with ether. The combined ether extracts were washed with water and dried with anhydrous K_2CO_3. Removing the solvent at reduced pressure gave 110 mg of a light yellow oil. Each compound was identified by comparison of its NMR spectra with those of an authentic sample. Product distribution was determined by the average ratio of NMR integral values in the vinyl proton signal for **6-OH** and α-proton signals for **4a-OH** and **4s-OH** in five runs. Thus, it was determined that the product consisted of a mixture of **4a-OH** (13%), **4s-OH** (42%), and **6-OH** (45%).

A mixture containing 100 mg (0.5 mmol) of **4a-OH**, 0.5 ml (2.5 mmol) of 2,6-lutidine, and 84 mg (0.5 mmol) of *p*-nitrobenzoic acid in 100 ml of 80% aqueous acetone was heated at 40 °C for 20 h (ca. 20 half-lives). After usual workup, 95 mg of colorless solid was obtained. A comparison of the NMR spectrum before and after heating showed that **4a-OH** was stable to the reaction conditions. Similar treatment of **5-OH** and **6-OH** gave the same results.

Preparative Solvolysis of 5-OBs. A solution of 154 mg (0.37 mmol) of **5-OBs** and 77 mg (0.72 mmol) of 2,6-lutidine in 50 ml of 80% aqueous acetone was stirred at room temperature for 72 h. The sample was worked up as described for **4a-OPNB** to give 68.2 mg (86%) of a light yellow liquid. Each alcohol was assigned by comparison of its NMR spectrum with those of an authentic sample. The product consisted of a mixture of **4a-OH** (13%), **4s-OH** (41%), and **6-OH** (46%), but a primary alcohol (**5-OH**) could not be detected by way of an extraneous peak due to its singlet signal at δ 3.28 for hydroxymethyl hydrogen of primary alcohol.

Acetolysis of 4a-OPNB. A solution of 127 mg (0.36 mmol) of **4a-OPNB** in 10 ml of anhydrous acetic acid containing 58.8 mg (0.72 mmol) of potassium acetate was heated at 50 °C for 4 days, cooled, and poured into the mixture of 80 ml of petroleum ether and 100 ml of ice–water. The organic layer was separated and the aqueous solution was extracted with 10 ml of petroleum ether in several portions. The combined extracts were washed with 5% aqueous sodium hydrogen carbonate solution and with water and dried over anhydrous sodium sulfate. Removal of solvent gave 75.8 mg (94.5%) of a white-yellow oil. The NMR and ir spectrum showed that the product consisted of some acetates. Reduction of the acetates with $LiAlH_4$ in dry ether gave 44 mg of yellow oil. Each compound was identified by comparison of its NMR spectrum with those of an authentic sample. The oily product consisted of primary alcohol **5-OH** and tertiary alcohol **6-OH**, the ratio being about 4:1, and a trace of secondary alcohol. The secondary acetate **4a-OAc** was converted into tertiary acetate **6-OAc** under the same conditions.

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Registry No.—**4s**-OH, 58692-29-8; **4s**-OPNB, 58692-30-1; **4a**-OH, 58717-76-3; **4a**-OPNB, 58717-77-4; **4a**-OAc, 58692-31-2; **5**-OH, 58692-32-3; **5**-OBs, 58692-33-4; **6**-OH, 58692-34-5; **7**, 10386-81-9; **8**, 58692-35-6; **9**, 58692-36-7; **10**, 58692-37-8; **11**, 58692-38-9; **12**, 58692-39-0; **13**, 58692-40-3; **14**, 58692-41-4; **15**, 58692-42-5; **17**, 58692-43-6; **18**, 58692-44-7; **19**, 58692-45-8; **20**, 58692-46-9; **21**, 58692-47-0.

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Mechanism and Stereochemistry in Addition of Acetic Acid to Quadricyclane

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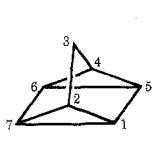
Addition reactions of carboxylic acids (**5a–d**) to tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**1**, quadricyclane) at 20 °C gave corresponding esters (**6** and **7**) of *exo*-2-norbornenyl alcohol and nortricyclyl alcohol. Solvent effect on the product distribution and the rate of the addition reaction excluded the mechanism involving norbornenyl cation (**4**) as a sole intermediate. A six-centered addition mechanism is presented by the authors to account for both the solvent effects and deuterium distribution in labeled **6** obtained from addition of acetic acid-*O*-d_1 or dichloroacetic acid-*O*-d_1.

Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**1**, quadricyclane) allowed several physical organic approaches to a possible conjugation between two cyclopropane rings arranged nearly parallel and in close proximity. Regiospecificity and stereospecificity shown in [$2\sigma + 2\sigma + 2\pi$] cycloaddition reaction[1] of **1** strongly suggest concerted fissions of C_1–C_7 and C_5–C_6 cyclopropane bonds and, therefore, an existence of a kind of "conjugation" in **1**.[2] The conjugation contributed to at least one-fourth (ca. 3.5 kcal/mol) of the stabilization of 1-quadricyclylcarbinyl cation **2**,[2] which exhibited 1.2×10^8 times rate enhancement (14.0 kcal stabilization) compared with cyclopropylcarbinyl cation.

Protonation of quadricyclane with a cleavage of the C_1–C_7 or C_5–C_6 bond could be assumed to give an incipient nortricyclyl cation **3** which is known to be prone to rearrange to norbornenyl cation **4**[3] from solvolysis studies.



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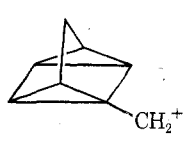

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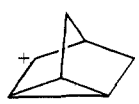

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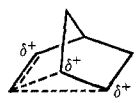

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