the excited state with a disrotatory motion about the developing central bond of the bicyclobutane. This type of closure will place the 2-vinyl group exo when it occurs from II, but endo when it occurs from III. Since considerably more steric interaction is developed when the vinyl group is endo this may serve to rationalize the failure of III to undergo photolysis to this type of product. Many of the bands in the infrared spectrum of the photoproducts, which decrease in intensity after warm-up, are consistent with formation of *exo*-XI. For instance, bands at 3087 and 3056 cm^{-1} are reasonable[22] for cyclopropyl CH_2 stretches in a bicyclobutane, bands between 3000 and 2880 cm^{-1} are reasonable[22] for tertiary C–H stretches in this system and unreasonable[16] for olefinic C–H stretches. Also, bands at 1185, 1142, 975, 840, and 730 cm^{-1} could be assigned[16,18a] to vibrations associated with cyclopropyl rings of a bicyclobutane. A fairly strong band grows in at 916 cm^{-1}, which is in the region usually associated with the CH_2 way of a vinyl group.[16] The ultraviolet spectrum of methyl bicyclobutane-1-carboxylate has been found[23] to have an absorption maximum at 210 nm (ϵ 7000) and the ultraviolet spectra of some vinylcyclopropanes have been found[24] to have maxima around 200 nm. Therefore, it is not unreasonable to expect ultraviolet absorption around 200–210 mμ for *exo*-XI, as is observed in the photolysis products of II.

Thermolysis of alkyl-substituted bicyclobutanes has been found to be a concerted process, in which one ring opens conrotatory and one ring opens disrotatory, thus leading to two products from bicyclobutanes which do not have a C_2 symmetry axis.[25] The activation energy for this kind of process is about 40 kcal/mol and the reaction is rapid at 200°.[26] Introduction of a vinyl group at the 2 position of a bicyclobutane could well lower the activation energy sufficiently to make the thermolysis relatively facile at room temperature, either by conjugation with the transition state in a concerted process or by causing a changeover to a nonconcerted diradical process, which gains from allylic stabilization of the developing radical.[27] In either case, a mixture of II and III would be regenerated.

Thus, although far from rigorously established, it seems that 1,2,4-hexatriene (IV) and *exo*-2-vinylbicyclo[1.1.0]butane (*exo*-XI) are the most likely candidates for the thermally unstable photoproducts of II. Both may be formed only from II; both photoprocesses leading to them have analogies in other systems or under other conditions in the same system; both are compatible with the changes in the infrared and ultraviolet spectra; and both are consistent with the warm-up–redeposition behavior.

Experimental Section

The cryotip refrigerator and all the experimental procedures for performing the photolyses and recording the spectra have already been described.[11]

Samples of 1,3-cyclohexadiene (I) were purified by preparative vapor phase chromatography before use. A mixture of II and III (Chemical Procurement Co.) was purified by the known[28] procedure. Samples purified by preparative vapor phase chromatography were employed.

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Solvolysis of Trans-Fused Bicyclo[6.1.0]nonyl-2 Derivatives[1]

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Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received December 5, 1970*

Abstract: The rates and products of solvolysis of the trans-fused bicyclo[6.1.0]nonyl 2-(3,5-dinitrobenzoates) have been determined. The trans,trans isomer was found to be 1.8×10^4 times as reactive as the trans,cis isomer. This results from the unusual conformation of the latter in which the leaving group lies over the cyclopropane ring. Just as with the corresponding cis-fused derivatives, there is no crossover in products between the two epimers, and the rearrangement products were formed by stereospecific processes. The solvolysis of α-deuterium labeled derivatives also was studied, and only one of the four isomers (cis and trans fused) was found to give deuterium scrambling.

It now seems clear that the solvolysis of cyclopropylcarbinyl derivatives usually leads first to an unrearranged cyclopropylcarbinyl cation.[2] This, in turn, may rearrange to another cyclopropylcarbinyl cation *via* the stereospecific cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement.[3] The conformational effects

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(1) This investigation was supported by Public Health Service Grant No. 12800 from the National Institutes of General Medical Science. A preliminary report of part of this work has appeared: K. B. Wiberg and T. Nakahira, *Tetrahedron Lett.*, 3759 (1970).

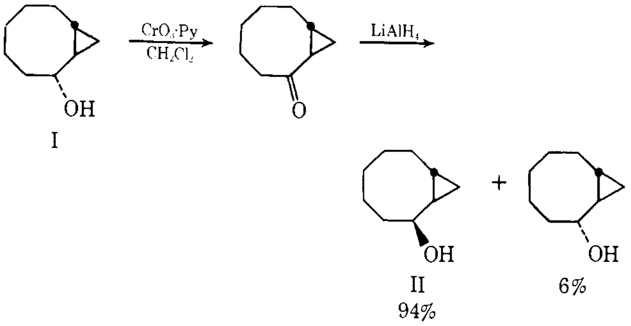
(2) *Cf.* K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1971.

(3) (a) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **90**, 4195

on the energy of the initially formed cation have been examined,[4] and as predicted, the more favorable geometry has been found to have the empty p-orbital positioned to give maximum overlap with the C–C bonds of the cyclopropane ring.[5] CNDO calculations have suggested that a small rotation of the carbinyl group away from the preferred geometry should produce a relatively small decrease in stabilization.[6]

Our earlier examination of compounds which on ionization give the bicyclo[5.1.0]octyl-2 cation led us to suggest that there may be two different ions, one formally derived from *endo*-bicyclo[5.1.0]octyl-2 derivatives and the other formally derived from the exo derivatives.[6] Friedrich and Wight[7] have provided elegant tracer and stereochemical evidence for two such ions. The stereochemical results of the solvolysis of bicyclo[6.1.0]-nonyl-2 and bicyclo[7.1.0]decyl-2 derivatives also indicate the presence of two isomeric cyclopropylcarbinyl cations which interconvert relatively slowly.[8]

In order to gain further information on the conformational requirements and structural characteristics of cyclopropylcarbinyl cations, we have examined the solvolysis of trans-fused bicyclo[6.1.0]nonyl derivatives. The trans,trans alcohol (I) was prepared by the reaction of *trans*-cycloocten-*trans*-3-ol[9] with the Simmons–Smith reagent.[10] This reaction is known to be stereospecific[11] and leads in this case to the cyclopropane ring trans to the hydroxy group. Oxidation with the chromium trioxide–pyridine complex in methylene chloride[12] gave the corresponding ketone and lithium aluminum hydride reduction gave the trans,cis alcohol (II) contaminated with only a small amount of I. In the case of the corresponding cis-fused ketone, reduction under the same conditions has been reported to give the corresponding alcohols in a 99:1 ratio.[11]



The rates of solvolysis were determined in 80% aqueous acetone giving the data in Table I. The cis-fused compounds were reexamined so that the rate constants would be directly comparable. The relative rates are summarized in Table II. The products of the solvolytic reactions were determined and are summarized in Scheme I along with the results reported by Poulter, Friedrich, and Winstein[8] for the cis-fused *p*-nitrobenzoates. No significant product difference was found when the dinitrobenzoates were investigated.

Table I. Rates of Solvolysis in 80% Aqueous Acetone

3,5-Dinitro-benzoate	T, °C	$k \times 10^5$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
trans,trans- (I)	80.0	45.0 ± 0.8	23.6	−7
	60.1	5.77 ± 0.15		
trans,cis- (II)	160.0	4.17 ± 0.12	29.2	−12
	140.0	0.77 ± 0.02		
cis,trans- (III)	140.0	35.4 ± 0.9	26.4	−11
	121.1	7.30 ± 0.18		
cis,cis- (IV)	100.0	22.3 ± 0.9	26.5	−5
	80.0	2.81 ± 0.11		

Table II. Relative Rates of Solvolysis at 100°

3,5-Dinitrobenzoate	k_{rel}
trans,trans- (I)	18,200
trans,cis- (II)	1
cis,trans- (III)	65
cis,cis- (IV)	1,410
Cyclooctyl	~0.04

The *cis*-bicyclo[5.1.0]octane-*trans*-8-methanol (V) was identified by comparison with an authentic sample prepared as shown in Scheme II. The cis,trans isomer would be expected to predominate in the addition to the olefin.[13] The *cis*-bicyclo[5.2.0]nonan-*trans*-8-ol (VI) was prepared as shown in Scheme III. The reduction with aluminum isopropoxide would be expected to give roughly the equilibrium mixture of the two alcohols. Since the cis,trans isomer (VI) would be expected to be the more stable, the isomer formed in a larger quantity was assigned this structure. This assignment was confirmed by a comparison of the nmr spectra with those for the corresponding bicyclo[4.2.0]-octane derivatives.[6]

An examination of the data in Table II and Scheme I leads to two significant observations. First, the cis/trans rate ratio for the trans-fused compounds is 18,200, whereas the ratio for the cis-fused derivatives is only 22. The more reactive of the trans-fused isomers is 13 times as reactive as the more reactive of the cis-fused derivatives whereas the less reactive of the trans-fused isomers is only $^1/_{65}$th as reactive as the less reactive of the cis-fused compounds. Second, the solvolyses of Ia and IIa lead to different product distributions just as had been found for IIIa and IVa. It may be noted that the formation of V and VI in the solvolysis of IIa probably results from further reaction of the initial products under the relatively severe reaction conditions. This has been observed in control experiments. Thus, the solvolysis of the tosylate derived from II gives only II and VII as products.

The change in rate ratios on going from the cis-fused to trans-fused series is easily understood. The conformations of both cis-fused derivatives are suited for giving a normal type interaction between the developing

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(11) C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 6892 (1969).

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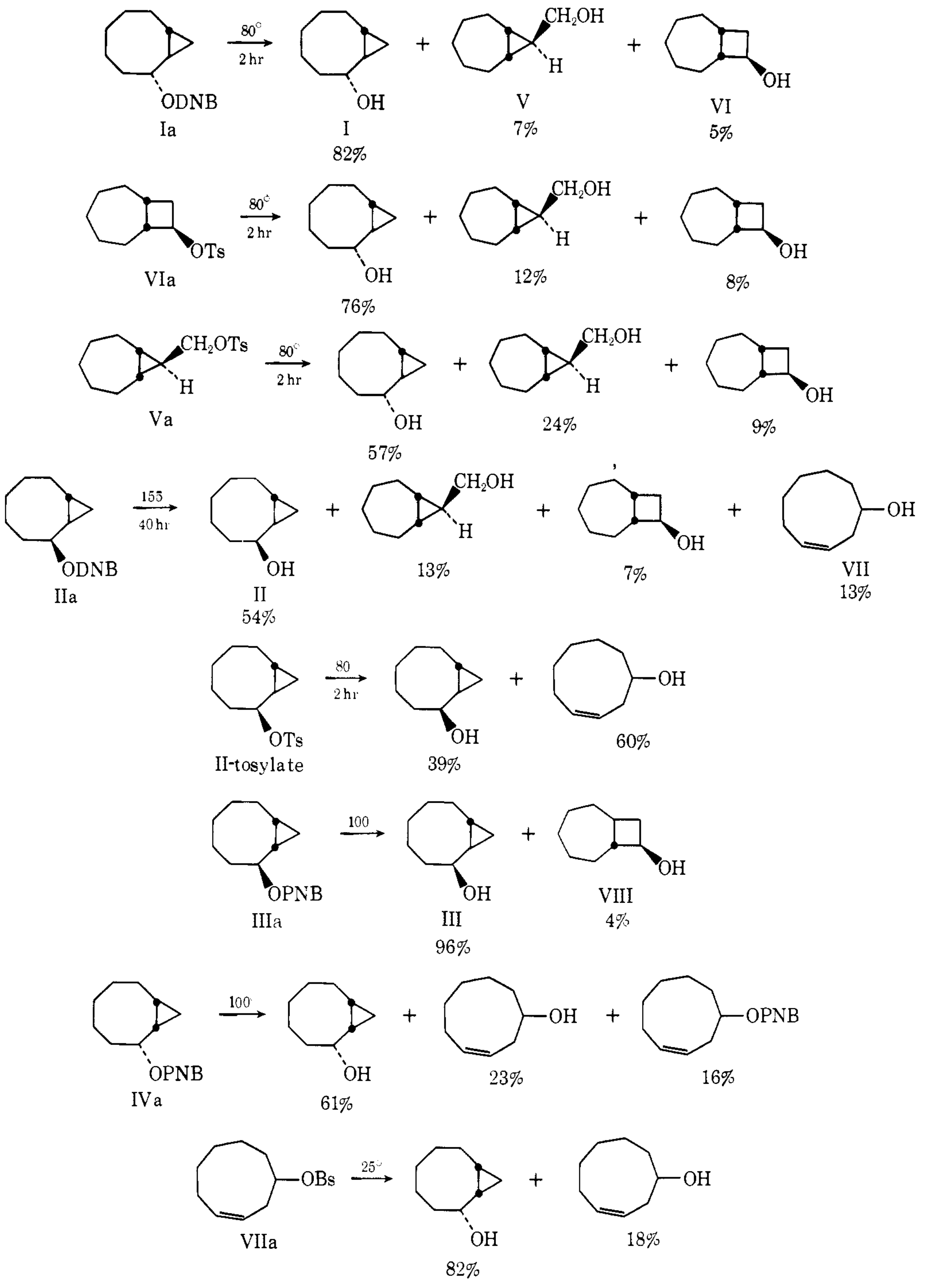
Scheme I. Products of Solvolysis[a]



(8)

(8)

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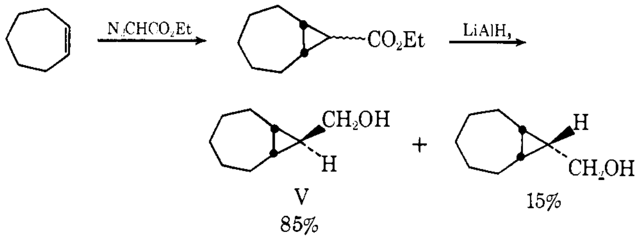
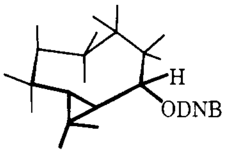
[a] All solvolyses were carried out in buffered solution using diisopropylethylamine.

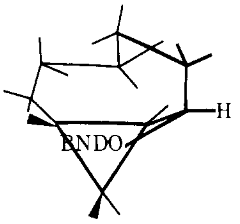
Scheme II



p-orbital and the cyclopropane ring. However, the situation is quite different with the trans-fused isomers. In IIa, the leaving group must lie over the cyclopropane ring whereas with Ia, the group lies away from the ring. Thus, IIa is constrained to accept an unusual conformation which renders it difficult for the cyclopropane ring to help stabilize the developing p-orbital. On the other hand, in Ia, the developing p-orbital will have its back lobe directly over the bridging C–C bond.

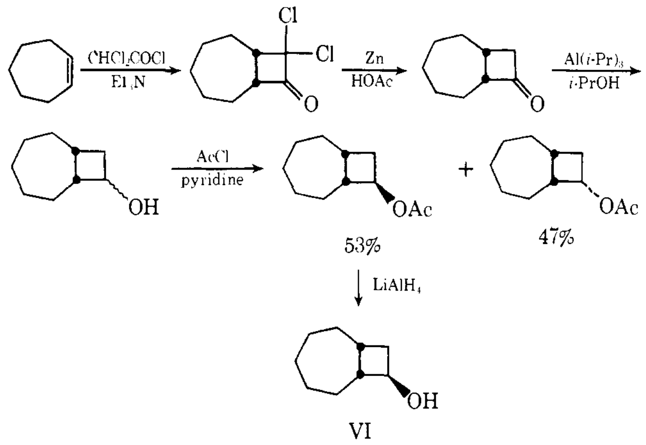


Ia



IIa

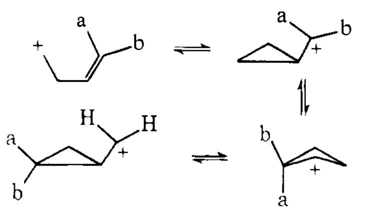
Scheme III



It seems not unreasonable to expect a poor interaction between the developing p-orbital and the cyclopropane ring when the leaving group lies over the ring. In this case, the backside of the p-orbital will not be stabilized by any interaction, whereas in the activated complex, the leaving group is still partially bonded to the frontside of the p-orbital.

The high reactivity of Ia is not as easily explained. One might at first think that the central bond of the trans-fused bicyclo[6.1.0]nonane ring system would be weakened by the trans fusion. However, the acetolysis of the cis- and trans-fused hydrocarbons led to similar proportions of external and central bond cleavage[14] suggesting that there are no unusual properties of the central bond. This is reinforced by the observation that the heats of combustion of *cis*- and *trans*-bicyclo[6.1.0]nonane are the same within experimental error (0.5 kcal/mol).[15] It seems likely that the reactivity is in part controlled by the angle between the axis of the p-orbital and the plane of the cyclopropane ring. This may lead to a particularly favorable interaction in the case of Ia. The geometries of these compounds are receiving further attention.

In our previous study of the rearrangements between allylcarbinyl, cyclopropylcarbinyl, and cyclobutyl cations, the stereochemistry was found to be[3a]

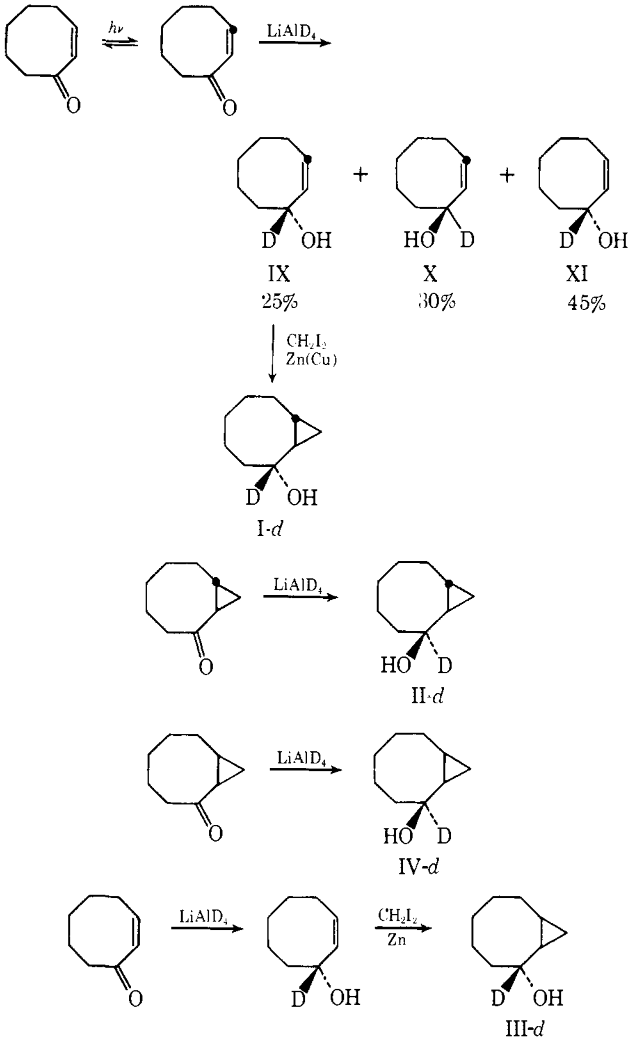


This course for the reaction has been confirmed by other work,[3,8] and is in accord with expectations based on orbital symmetry arguments.[3a]

The products derived from the trans-fused bicyclo[6.1.0]nonyl-2 derivatives fit the above pattern and provide a clear parallel with those derived from the corresponding cis-fused derivatives. In each case, there is no crossover in products between the two epimeric derivatives. The stereochemistry of the reactions is the same for the two cases. Thus, whereas IIIa gives the trans-fused bicyclo[5.2.0]nonan-8-ol, Ia gives the cis-fused alcohol. Similarly, whereas Ia gives V as a product, no corresponding product is formed from IIIa since this type of product would be required to be trans fused.

The work of Friedrich and Wight[7] on racemization and deuterium scrambling with the cis-fused bicyclo[5.1.0]octanols provides another method for examining differences among the ions formed in the solvolysis of both the cis- and trans-fused derivatives discussed above. Thus, the deuterium labeled alcohols were prepared as shown in Scheme IV. The photochemical equilibration of cyclooctenone has been shown by Eaton and Lin[16] to give largely the trans isomer. Reduction with lithium aluminum deuteride gave a mixture of three alcohols. The alcohol, IX, could be separated from the mixture by gas chromatography, and was converted to I-*d* by treatment with the Simmons–Smith reagent. The mixture of X and XI also was treated with the Simmons–Smith reagent to give the cyclopropane derivatives which could be partially separated to give II-*d* and III-*d*. The alcohols II-*d* and III-*d* were more satisfactorily prepared from the ketones as shown above.

Scheme IV



The more reactive alcohols, I-*d*, III-*d*, and IV-*d*, were converted to their 3,5-dinitrobenzoates. The less reactive trans,cis isomer (II-*d*) was converted to the tosylate in order to give a derivative which would undergo reac-

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(14) K. B. Wiberg and A. deMeijere, *Tetrahedron*, 519 (1969).

(15) K. B. Wiberg and E. C. Lupton, Jr., unpublished results.

(16) P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, **86**, 2087 (1964).

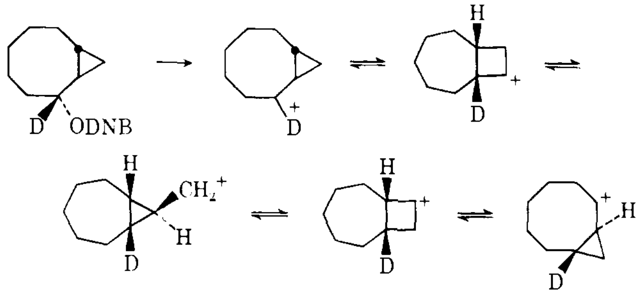
tion under relatively mild conditions. The solvolyses of the dinitrobenzoates were carried through 2.5 half-lives and the products were isolated. The tosylate from II-*d* was solvolyzed under similar conditions. The scrambling in the unrearranged products was determined by nmr spectroscopy by observation of the appearance of the α-proton signal. The data are summarized in Table III. Only the trans,trans isomer, Ia-*d*, gave any observable scrambling. In the case of IIa-*d* and IVa-*d*, the cyclononen-4-ol product also was examined, and no scrambling was observed.

Table III. Deuterium Scrambling in Solvolysis of 2-Deuteriobicyclo[6.1.0]nonyl-2 Derivatives

3,5-Dinitrobenzoate[a]	Temp, °C	% deuterium scrambling[b]
trans,trans- (I-*d*)	80	65 ± 3 (I)
trans,cis- (II-*d*)	80	0 ± 4 (II), 0 ± 3 (VII)
cis,trans- (III-*d*)	120	0 ± 3 (III)
cis,cis- (IV-*d*)	100	0 ± 3 (IV), 0 ± 2 (VII)

[a] Tosylate was used for the trans,cis isomer. [b] Deuterium scrambling was determined after 2.5 half-lives.

Several mechanisms are available for the deuterium scrambling observed with the trans,trans isomer, Ia-*d*. One of the more attractive of these involves the set of equilibria shown below in which the cation corresponding to V is a symmetrical species which will lead to the scrambling



Equilibration of these ions is indicated by the results of the solvolyses of VIa and Va (Scheme I) which give the same products in ratios similar to those found with Ia. The lack of scrambling with II-tosylate-*d* may simply result from the absence of a path such as that shown above.

The results obtained with the cis-fused isomers IIIa-*d* and IVa-*d* are in contrast to cis-fused bicyclo[5.1.0]octyl-2 derivatives in which the cis,trans isomer undergoes deuterium scrambling.[7] The difference between these cases can only be due to a change in conformation. Further, the lack of crossover in products between pairs of cis- and trans-fused epimers must also result from conformational effects. These factors are not clearly resolved from this work or that previously reported, and are currently under study.

Experimental Section

***trans*-Bicyclo[6.1.0]nonan-*trans*-2-ol.** To a mixture of 20 g (0.32 mol) of zinc–copper couple[17] and 160 ml of dry ether was added 64 g (0.24 mol) of methylene iodide and 0.12 g of iodine. The mixture was heated to reflux for 30 min. A solution of 20 g (0.16 mol) of *trans*-cycloocten-*trans*-3-ol[9] in 20 ml of dry ether was then added dropwise over a 30-min period without external heating. After the addition, the mixture was heated to reflux for 20 hr and then cooled and filtered. The residue was washed with ether. The ether solution was washed with two 80-ml portions of 3% hydrochloric acid, two 80-ml portions of 10% sodium bicarbonate solution, and 80 ml of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After the ether was removed, distillation of the residue gave 13 g (58%) of *trans*-bicyclo[6.1.0]octan-*trans*-2-ol as the only product, bp 70° (1.1 mm).

The nmr spectrum showed bands at δ 0.25–0.83 (m, 4 H), 1.00–2.43 (m, 10 H), 2.54–3.15 (m, 1 H), and 3.40 (s, 1 H, moves on dilution).

Anal. Calcd for $C_9H_{16}O$: C, 77.1; H, 11.4. Found: C, 76.9; H, 11.4.

***trans*-Bicyclo[6.1.0]nonan-*cis*-2-ol.** To a stirred mixture of 150 ml of methylene chloride and 28 g (0.11 mol) of chromium trioxide-pyridine complex[12] in a 500-ml round-bottomed flask equipped with a stirrer and an addition funnel was added dropwise 5 g (36 mmol) of *trans*-bicyclo[6.1.0]nonan-*trans*-2-ol in 50 ml of methylene chloride at room temperature. The reaction mixture was stirred for an additional 20 hr, filtered, washed with 200 ml of water and 100 ml of saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. After the methylene chloride was removed, distillation of the residue gave 3 g (60%) of *trans*-bicyclo-[6.1.0]nonan-2-one, bp 100° (8 mm). The nmr spectrum showed bands at δ 0.4–1.1 (m, 3 H) and 1.1–2.9 (m, 11 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.3; H, 10.1. Found: C, 77.9; H, 10.1.

A solution of 5.5 g (40 mmol) of *trans*-bicyclo[6.1.0]nonan-2-one in 15 ml of dry ether was added dropwise to a stirred mixture of 1.6 g (42 mmol) of lithium aluminum hydride and 50 ml of dry ether. After heating to reflux for an additional 4 hr, the reaction mixture was cooled, and 20 g of ice water and 5 ml of 15% potassium hydroxide solution were carefully added to the reaction mixture. The precipitate was filtered and washed with two 25-ml portions of ether. The water layer was extracted with three 25-ml portions of ether. The combined ether extracts were washed with 100 ml of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After the ether was removed, 4.8 g of white solid material remained, which contained 94% *trans*-bicyclo[6.1.0]nonan-*cis*-2-ol as analyzed by vpc on a 20 ft × 3/8 in. 20% DEGS on 70–80 Anachrom column at 155°. Two recrystallizations from *n*-hexane afforded white crystals, mp 49–50°.

The nmr spectrum showed bands at δ 0.10–1.06 (m, 4 H), 1.06–2.42 (m, 10 H), 4.10–4.27 (m, 1 H), and 3.20 (s, 1 H, moves on dilution).

Anal. Calcd for $C_9H_{16}O$: C, 77.1; H, 11.4. Found: C, 77.0; H, 11.5.

3,5-Dinitrobenzoates. The dinitrobenzoates of the trans-fused alcohols and also of the previously reported cis-fused bicyclo-[6.1.0]nonan-2-ols[8] were prepared in the usual fashion. The trans,-trans isomer gave a derivative, mp 124–125° after recrystallization from *n*-hexane, and the trans,cis isomer gave a derivative, mp 96–98°. The cis,trans alcohol gave a derivative, mp 98–99°, and the cis,cis alcohol gave a derivative, mp 100.5–102°.

***cis*-Bicyclo[5.1.0]octane-*trans*-8-methanol.** To a stirred refluxing mixture of 30 g (0.31 mol) of cycloheptene and 1.5 g of copper–bronze in a 250-ml round-bottomed flask equipped with a stirrer, an addition funnel, and a water condenser fitted with a gas outlet was added dropwise over a 1-hr period 12 g (0.11 mol) of ethyl diazoacetate in 10 ml of dry ether. After additional refluxing and stirring for 1 hr the reaction mixture was cooled and filtered. Vacuum distillation yielded a fraction (9.3 g), bp 73–76° (1 mm), which contained some maleic ester.

The above crude product in 15 ml of dry ether was added dropwise to a stirred mixture of 2.5 g (66 mmol) of lithium aluminum hydride and 75 ml of dry ether. The reaction mixture was heated to reflux for an additional 4 hr with stirring and worked up as described above. After the ether was removed, distillation of the residue afforded 4.9 g (35 mmol) of alcoholic material, bp 68° (0.3 mm), which was found to be 85% *cis*-bicyclo[5.1.0]octane-*trans*-8-methanol and 15% *cis*-bicyclo[5.1.0]octane-*cis*-8-methanol by vpc analysis on a 20 ft × 3/8 in. 20% DEGS on 70–80 Anachrom column at 155°.

The nmr spectrum for *cis*-bicyclo[5.1.0]octane-*trans*-8-methanol had bands at δ 0.50–1.02 (m, 3 H), 1.02–2.46 (m, 10 H), 3.19–3.48 (broad d, 2 H), and 2.95 (s, 1 H, moves on dilution).

Anal. Calcd for $C_9H_{16}O$: C, 77.1; H, 11.4. Found: C, 76.9; H, 11.3.

The nmr spectrum for *cis*-bicyclo[5.1.0]octane-*cis*-8-methanol

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[17] R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

had bands at δ 0.8–2.3 (m, 13 H), 3.55–3.83 (broad d, 2 H), and 2.80 (s, 1 H, moves on dilution).

***cis*-Bicyclo[5.2.0]nonan-8-one.** To a stirred mixture of 31 g (0.32 mol) of cycloheptene, 16 g (0.11 mol) of dichloroacetyl chloride, and 60 ml of *n*-hexane was added dropwise 12 g (0.12 mol) of triethylamine in 15 ml of *n*-hexane at 50° over a 45-min period. At the completion of the addition, the mixture was cooled and the precipitate was filtered off. Distillation gave 8.4 g (37%) of *cis*-9,9-dichlorobicyclo[5.2.0]nonan-8-one, bp 84° (0.12 mm). To 3 g (15 mmol) of this material in 35 ml of acetic acid was added 7.6 g of zinc with magnetic stirring over a 1-hr period. The reaction mixture was stirred for an additional 5 hr, 150 ml of water was then added, and the mixture was filtered. The organic material was extracted from the water solution with four 100-ml portions of ether. The ether extracts were washed with water and dried over anhydrous magnesium sulfate. After the ether was removed, distillation of the residue afforded 1.28 g (62%) of *cis*-bicyclo[5.2.0]nonan-8-one, bp 45° (0.3 mm). The nmr spectrum showed bands at δ 1.0–2.2 (m, 10 H), and 2.2–3.8 (m, 4 H).

***cis*-Bicyclo[5.2.0]nonan-*trans*-8-ol.** A solution of 2.5 g (18 mmol) of *cis*-bicyclo[5.2.0]nonan-8-one, 35 ml of dry isopropyl alcohol, and 7.4 g (36 mmol) of aluminum isopropoxide was heated under reflux. The acetone formed was distilled out along with some isopropyl alcohol. After 2 hr, the acetone test became negative in the distillate. The mixture was heated to reflux for 1 additional hr and then left overnight at room temperature. After most of the isopropyl alcohol was distilled off, 80 ml of cold 3% hydrochloric acid was added to hydrolyze the residue. The aqueous solution was extracted with three 50-ml portions of ether. The combined ether extracts were washed with 50 ml of 10% sodium bicarbonate solution and 50 ml of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After the ether was removed, 1.6 g (63%) of alcoholic material was obtained by distillation, bp 58° (1 mm). The nmr spectrum showed it was a mixture of two isomeric alcohols. Attempts to separate them by vpc were unsuccessful. In all cases the alcohols appeared as one peak. Treatment with acetyl chloride and pyridine gave a mixture of *cis*-bicyclo[5.2.0]nonyl *trans*- and *cis*-8-acetates, bp 65° (0.5 mm). Analysis of the mixture by vpc on a 20 ft × $^{3}/_{8}$ in. 20% Carbowax 20M on 60–70 Anachrom column at 185° showed two peaks, *cis*-bicyclo[5.2.0]nonyl *trans*-8-acetate (53%), retention time 79 min, and *cis*-bicyclo[5.2.0]nonyl *cis*-8-acetate (47%), retention time 85 min.

The nmr spectrum of the cis,trans isomer showed bands at δ 0.85–2.70 (m, 17 H) and 4.40–4.90 (m, 1 H). The nmr spectrum of the cis,cis isomer showed bands at δ 0.80–2.95 (m, 17 H) and 4.70–5.15 (q, 1 H).

A solution of 1.2 g (6.6 mmol) of *cis*-bicyclo[5.2.0]nonyl *trans*-8-acetate isolated *via* preparative gas chromatography in 6 ml of dry ether was added dropwise to the stirred slurry of 0.3 g (7.9 mmol) of lithium aluminum hydride and 20 ml of dry ether. The reaction mixture was worked up as described above. After the ether was removed, distillation of the residue gave 0.8 g (86%) of *cis*-bicyclo[5.2.0]nonan-*trans*-8-ol, bp 52° (0.8 mm).

The nmr spectrum showed bands at δ 0.95–2.55 (m, 14 H), 3.70–4.16 (m, 1 H), and 2.85 (s, 1 H, moves on dilution).

Anal. Calcd for $C_9H_{16}O$: C, 77.1; H, 11.4. Found: C, 76.9; H, 11.1.

3-Deuterio-*trans*-cycloocten-*trans*-3-ol. A solution of 5 g (40 mmol) of cycloocten-3-one in 250 ml of dry ether contained in a three-necked flask equipped with a quartz immersion well, a gas inlet, a gas outlet, and a magnetic stirring bar was irradiated through a Pyrex filter for 2 hr with a 450-W Hanovia high-pressure mercury arc lamp while maintaining a slight positive pressure of nitrogen on the system. Aqueous ethanol at −15° was made to flow between the lamp and the reaction solution. The reaction was followed by monitoring the disappearance of conjugated ketone absorption (5.97 μ) and the appearance of unconjugated ketone absorption (5.79 μ) in the infrared spectrum.[16] The reaction solution was then poured over a 15-min period into a stirred slurry of 0.85 g (20 mmol) of lithium aluminum deuteride in 200 ml of dry ether in a 1000-ml three-necked round-bottomed flask immersed in a Dry Ice–acetone bath. After the addition was completed, the mixture was stirred for an additional 2 hr at the Dry Ice temperature, then brought to room temperature and heated to reflux for 1 hr. Water (3 g) was then added and the mixture was stirred for 2 hr. The granular white precipitate was filtered off. The ether solution was dried over anhydrous potassium carbonate. After the ether was distilled off, 4.8 g of alcoholic material was obtained, which separated into two peaks on a 20 ft × $^{3}/_{8}$ in. 20% DEGS on 70–80 Anachrom column at 160°. The first peak (75%), retention time 34 min, contained two components, 3-deuterio-*cis*-cycloocten-3-ol and 3-deuterio-*trans*-cycloocten-*cis*-3-ol. The second peak (25%), retention time 39 min, was 3-deuterio-*trans*-cycloocten-*trans*-3-ol. Isomeric 3-deuteriocycloocten-3-ols were converted into acetates with acetyl chloride in dry pyridine, which separated into 3-deuterio-*cis*-cyclooctenyl 3-acetate (29%), retention time 33 min, 3-deuterio-*trans*-cyclooctenyl *cis*-3-acetate (20%), retention time 40 min, and 3-deuterio-*trans*-cyclooctenyl *trans*-3-acetate (15%), retention time 43 min, along with decomposition products (33%) on a 12 ft × $^{3}/_{8}$ in. 20% DOW 710 on 50–60 U Anaprep column at 140°. The identification of the trans,cis isomer was accomplished by converting it to 2-deuterio-*trans*-bicyclo[6.1.0]nonan-*cis*-2-ol using the Simmons–Smith reagent as described above. The trans,cis and the trans,trans acetates showed similar nmr spectra, with bands at δ 0.6–2.75 (m, 13 H) and 5.6–6.3 (m, 2 H), while the cis isomer showed bands at 1.0–2.7 (m, 13 H) and 5.6–6.1 (m, 2 H).

***trans*-Bicyclo[6.1.0]nonyl *cis*-2-Tosylate.** To a stirred ice-cold solution of 0.82 g (4.3 mmol) of *p*-toluenesulfonyl chloride in 5 ml of dry pyridine was added 0.4 g (2.9 mmol) of *trans*-bicyclo[6.1.0]nonan-*cis*-2-ol. The solution was stored for 2 days at −1°. The reaction mixture was then poured into 25 ml of ether, washed with three 15-ml portions of ice-cold 10% hydrochloric acid, two 15-ml portions of 10% sodium bicarbonate solution, and 15 ml of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The ether was removed to give 0.6 g of solid material which was recrystallized from *n*-hexane, mp 72.5–75.0°.

***cis*-Bicyclo[5.2.0]nonyl *trans*-8-Tosylate.** The above tosylate was prepared from 0.2 g (1.4 mmol) of *cis*-bicyclo[5.2.0]nonan-*trans*-ol and 0.41 g (2.1 mmol) of toluenesulfonyl chloride in 3 ml of pyridine as described above. The tosylate (0.28 g) was recrystallized from *n*-hexane, mp 53–55.5°.

***cis*-Bicyclo[5.1.0]octane *trans*-8-Methyl Tosylate.** To a stirred ice-cold mixture of 0.31 g (2.2 mmol) of *cis*-bicyclo[5.1.0]octane-*trans*-8-methanol and 0.42 g (2.2 mmol) of toluenesulfonyl chloride in 15 ml of dry ether was added over a 20-min period, 0.6 g of powdered potassium hydroxide. Stirring at 0° was continued for 12 hr. The reaction mixture was then washed with 10 ml of ice-cold water and dried over potassium carbonate. The ether was removed to give a yellow liquid. A small amount of pentane was added and the pentane solution was stored at −1° for 1 hr. Approximately 0.2 g of solid material crystallized from pentane, mp 38–40°.

Solvolysis of *trans*-Bicyclo[6.1.0]nonyl *trans*-2-(3,5-Dinitrobenzoate) in 80% Aqueous Acetate. A solution of 2 g (6 mmol) of *trans*-bicyclo[6.1.0]nonyl *trans*-2-(3,5-dinitrobenzoate), 1.55 g (12 mmol) of *N*,*N*-diisopropylethylamine, and 180 ml of 80% aqueous acetone was prepared, sealed in a tube, and placed in an oil bath at 80°. After 2 hr, the tube was removed from the bath, cooled, and opened. Most of the acetone was removed by distillation and the remaining aqueous solution was saturated with sodium chloride and extracted with three 50-ml portions of ether. The combined ether extracts were washed with 75 ml of ice-cold 10% hydrochloric acid, 75 ml of ice-cold 10% sodium bicarbonate solution, and 50 ml of saturated sodium chloride solution and dried over potassium carbonate. The ether was distilled off and the residue was separated into its components by vpc on a 20 ft × $^{3}/_{8}$ in. 20% Carbowax 20M on 60–70 Anachrom column at 150°. The products were *trans*-bicyclo[6.1.0]nonan-*trans*-2-ol (82%), retention time 107 min, *cis*-bicyclo[5.1.0]octane-*trans*-8-methanol (7%), retention time 112 min, and *cis*-bicyclo[5.2.0]nonan-*trans*-8-ol (5%), retention time 122 min.

Solvolysis of *trans*-Bicyclo[6.1.0]nonyl *cis*-2-(3,5-Dinitrobenzoate) in 80% Aqueous Acetone. A solution of 2 g (6 mmol) of *trans*-bicyclo[6.1.0]nonyl *cis*-2-(3,5-dinitrobenzoate), 1.55 g (12 mmol) of *N*,*N*-diisopropylethylamine, and 180 ml of 80% aqueous acetone was prepared, and 3.3-ml portions were sealed in ampoules which were immersed in an oil bath at 155°. After 40 hr, the ampoules were removed from the oil bath, cooled, and opened. After the same treatment as described above, the products were separated by vpc on a 20 ft × $^{3}/_{8}$ in. 20% Carbowax 20M on 60–70 Anachrom column at 165°. The products were *trans*-bicyclo[6.1.0]nonan-*cis*-2-ol (54%), retention time 93 min, *cis*-bicyclo[5.1.0]octane-trans-8-methanol (13%), retention time 99 min, *cis*-bicyclo[5.2.0]nonan-*trans*-8-ol (7%), retention time 105 min, and cyclononen-4-ol (13%), retention time 121 min.

The nmr spectrum of cyclononen-4-ol obtained above showed bands at δ 1.25–1.87 (m, 8 H), 1.87–2.60 (m, 4 H), 3.50–3.92 (m, 1 H), 5.37–5.70 (m, 2 H), and 2.95 (s, 1 H, moves on dilution).

Solvolysis of *trans*-Bicyclo[6.1.0]nonyl *cis*-2-Tosylate in 80% Aqueous Acetone. An ice-cold solution of 0.13 g (1 mmol) of *N*,*N*-diisopropylethylamine and 17 ml of 80% aqueous acetone was poured into a tube containing 0.15 g (0.51 mmol) of *trans*-bicyclo[6.1.0]nonyl *cis*-2-tosylate. The tube was sealed and immersed in an oil bath at 80°. After 2 hr the tube was removed from the bath, cooled, and opened. After the same treatment as described above, the products were separated by vpc on the Carbowax column. The products were *trans*-bicyclo[6.1.0]nonan-*cis*-2-ol (39%) and cyclononen-4-ol (60%).

Solvolysis of *cis*-Bicyclo[5.2.0]nonyl *trans*-8-Tosylate in 80% Aqueous Acetone. The solvolysis was carried out as described above. The products were *trans*-bicyclo[6.1.0]nonan-*trans*-2-ol (76%), *cis*-bicyclo[5.1.0]octane-*trans*-8-methanol (12%), and *cis*-bicyclo[5.2.0]nonan-*trans*-8-ol (8%).

Solvolysis of *cis*-Bicyclo[5.1.0]octane *trans*-8-Methyl Tosylate in 80% Aqueous Acetone. The solvolysis was carried out as described above. The products were *trans*-bicyclo[6.1.0]nonan-*trans*-2-ol (57%), *cis*-bicyclo[5.1.0]octane-*trans*-8-methanol (24%), and *cis*-bicyclo[5.2.0]nonan-*trans*-8-ol (9%).

Solvolyses of 2-Deuteriobicyclo[6.1.0]nonyl-2 Derivatives. The solvolyses were carried out under the same conditions as before. The reactions were stopped after 2.5 half-lives and treated as described above after the removal of unreacted or rearranged 3,5-dinitrobenzoates. Products were analyzed on a 20 ft × $^3/_8$ in. 20% Carbowax 20M on 60–70 Anachrom column at 170°. The *trans*,*trans*-3,5-dinitrobenzoate (Ia-*d*) solvolyzed at 80° gave three products. The main product (80%), the trans,trans alcohol, showed 65 ± 3% scrambling of deuterium by nmr. The *trans*,*cis*-tosylate, solvolyzed at 80° for the same length of time as the *trans*,-*trans*-3,5-dinitrobenzoate (Ia-*d*), afforded two products (the trans,-cis alcohol, 36%, and cyclononen-4-ol, 62%), whose nmr spectra showed no appreciable deuterium scrambling (0 ± 4%. 0 ± 3%). The *cis*,*trans*-3,5-dinitrobenzoate (IIIa-*d*) solvolyzed at 120° gave two products. The main product (96%), the cis,trans alcohol, showed no appreciable deuterium scrambling (0 ± 3%). The *cis*,*cis*-3,5-dinitrobenzoate (IVa-*d*) solvolyzed at 100° afforded two products (the cis,cis alcohol, 75%, and cyclononen-4-ol, 25%), whose nmr spectra showed no appreciable deuterium scrambling (0 ± 3%, 0 ± 2%).

Kinetic Method. Acetone was purified by distillation from potassium permanganate and degassed by boiling for several minutes. Distilled water was degassed in the same manner. The solvents and solutions were kept under a nitrogen atmosphere to minimize oxidation of the solvent at higher temperature. In all cases, the solvent was 80% acetone by volume.

In each case, 60 ml of a 0.006 *M* solution of the 3,5-dinitrobenzoate was prepared and 3.3-ml portions were sealed in ampoules. A set of ampoules was immersed in an oil bath at the appropriate temperature. Allowing 10 min for temperature equilibration, the zero point was taken. The ampoules were removed from the bath and plunged into ice–water to stop the solvolysis. After warming to room temperature, a 3.00-ml portion of the solution was removed and titrated with 0.0050 *M* sodium hydroxide solution to a bromothymol blue end point. Infinity titers were determined after 10 half-lives.

Reactions of Trans-Fused Cyclopropanes. The Synthesis and Solvolysis of the Epimeric 2-Hydrovy-*trans*-bicyclo[6.1.0]nonane *p*-Nitrobenzoates[1]

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Abstract: The epimeric 2-hydroxy-*trans*-bicyclo[6.1.0]nonanes have been synthesized and their respective *p*-nitrobenzoates have been solvolyzed in 30:70 water–dioxane. At 100° the trans,trans isomer solvolyzed 1.2×10^4 times faster than the cis,trans isomer. In addition, the epimeric *p*-nitrobenzoates produced different product mixtures on solvolysis, indicating that the solvolyses of the epimeric *p*-nitrobenzoates followed different mechanistic paths. The rate differences and the divergence of products are discussed in terms of the conformations of the epimeric *p*-nitrobenzoates. These, in turn, are related to the steric requirements for cyclopropyl participation in the formation of cyclopropylcarbinyl cations. Our results would appear to provide strong evidence for the necessity of backside participation by the cyclopropyl group in the formation of cyclopropylcarbinyl cations.

Various groups have investigated the generation of carbonium ion centers adjacent to cyclopropyl rings when the cyclopropyl moiety was part of a cis-fused bicyclo[*n*.1.0]alkane derivative.[5] The objective of these studies was to determine the mode of interaction of the cyclopropyl ring with the incipient carbonium ion. When *n* was small, such as in the bicyclo[3.1.0]-hexyl system, prevailing evidence indicated that a single carbonium ion intermediate was formed.[5a–c] When *n* was somewhat larger, as in the *cis*-bicyclo[5.1.0]octyl and *cis*-bicyclo[6.1.0]nonyl systems, it would appear that two distinct cationic intermediates were formed when the epimeric 2-substituted derivatives of these systems were solvolyzed.[5d,e,6] In view of the conformational mobility of the eight-membered ring of the *cis*-bicyclo[6.1.0]nonane skeleton, the exact stereochemical relationship between the leaving group at C-2 and the neighboring cyclopropyl ring was undefined. In this regard we felt it would be of interest to study the corresponding solvolytic processes in the much more rigid *trans*-bicyclo[6.1.0]nonanes, where the trans ring

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[1] Paper XXV on "The Chemistry of Bent Bonds." For the previous paper in this series, see P. G. Gassman and J. S. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971).

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