Reactions of Trans-Fused Cyclopropanes. The Synthesis and Solvolysis of 4-Hydroxy-*trans*-bicyclo[5.1.0]octane *p*-Bromobenzenesulfonate[1]

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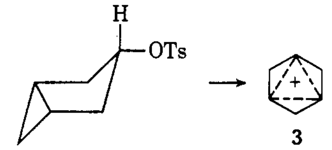
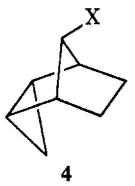
Abstract: 4-Hydroxy-*trans*-bicyclo[5.1.0]octane *p*-bromobenzenesulfonate (**1**) has been prepared *via* a 13-step synthesis starting with commercially available materials. The solvolysis of **1** was found to be pseudo first order in buffered acetic acid. Although the cyclopropyl moiety of **1** was held in close proximity to the developing carbonium ion site, no evidence for neighboring group participation of the cyclopropyl "bent" bonds was found. The acetolysis of **1** was approximately three times faster than cycloheptenyl 5-*p*-bromobenzenesulfonate and nine times slower than cycloheptyl *p*-bromobenzenesulfonate. Under buffered conditions **1** gave 75% *trans*-bicyclo[5.1.0]-oct-3-ene and 12% *trans*-bicyclo[5.1.0]octyl 4-acetate. These results, which indicate the critical stereochemical relationship necessary for cyclopropyl participation, are discussed in detail.

The last 5 years have witnessed an extensive exploration of cyclopropyl participation in solvolysis reactions. Of particular interest in relation to our studies were those investigations of cyclopropyl neighboring group participation where the incipient carbonium ion was not adjacent to the cyclopropyl ring. The first reported example of such participation was the solvolysis of **2** which was postulated to yield the trishomocyclopropenyl cation, **3**.[3] The controversial nature of this postulate[4] has spurred many groups, including ours, to study other forms of long-range cyclopropyl neighboring group participation.



2 **3**

One of the most impressive examples of cyclopropyl participation is that observed in the solvolysis of **4**, which was found to solvolyze 10^3 times faster than **5**, and 10^{14} times faster than **6**.[5,6] In the stereochemical relationship shown in **4** the cyclopropyl "bent" bond is such a powerful participating function that it provides an accelerating factor even in the solvolysis of **7** where the incipient cationic center is both tertiary and adjacent to a *p*-anisyl group.[7] Cyclopropyl participation in **7** is evident from the fact that **7** solvolyzed 10^3 times faster than **8** and that the major product from the solvolysis of **7** was **9**.[7] Very recently a case of cyclopropyl participation was described in which the cyclopropyl ring was four bonds removed from the developing carbonium ion.[8] In this example of long-range cyclopropyl participation, **10** was found to solvolyze almost 10^5 times faster than **11**.



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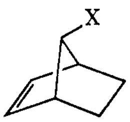

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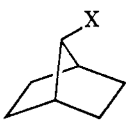

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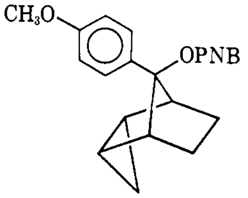

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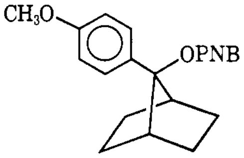

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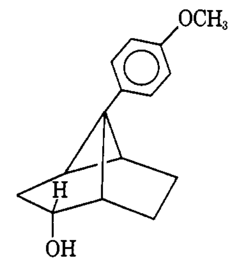

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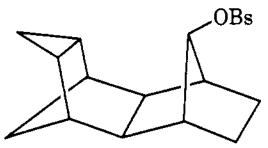

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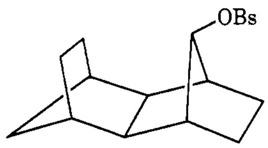

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All of the solvolyses discussed above bear one striking similarity; the developing p orbital of the carbonium ion is orthogonal to the participating bent

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(1) Paper XVI: "The Chemistry of Bent Bonds." For the previous paper in this series, see P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 1042 (1971).

(2) (a) Alfred P. Sloan Foundation Research Fellow, 1967–1969; (b) on leave from the Israel Ministry of Defense Scientific Department; (c) Goodyear Fellow, 1968–1969; Dow Chemical Fellow, 1969–1970.

(3) S. Winstein, J. Sonnenberg, and L. de Vries, *J. Amer. Chem. Soc.*, **81**, 6523 (1959); **83**, 3235, 3244 (1961); S. Winstein, E. C. Friedrick, R. Baker, and Y. Lin, *Tetrahedron, Suppl.*, **22** (8), 621 (1966).

(4) For other interpretations of the observation associated with the solvolysis of **2**, see E. J. Corey and H. Uda, *J. Amer. Chem. Soc.*, **85**, 1788 (1963); and E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963).

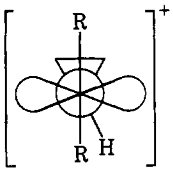
(5) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

(6) For a detailed discussion, see J. S. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

(7) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **92**, 2551 (1970).

(8) M. A. Battiste, J. Haywood-Farmer, H. Malkus, P. Seidl, and S. Winstein, *ibid.*, **92**, 2144 (1970). See also M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967).

bond of the cyclopropane in each case. This factor is particularly striking when one considers that the relatively stable cyclopropylcarbinyl cation prefers a conformation where the p orbital is parallel to the plane of the cyclopropane ring as shown in **12**.[9] For the cyclopropylcarbinyl cation the perpendicular conformation **13** is considered to be particularly poor.[9]



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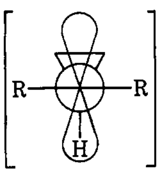

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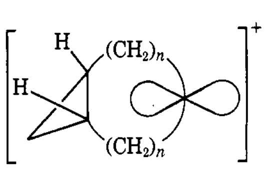

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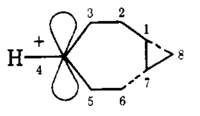
Thus, it seems somewhat surprising that the perpendicular conformation **14** should be the one which appears to be commonly involved in long-range neighboring group participation by the cyclopropyl moiety.

In view of the factors discussed above we decided to attempt to prepare a system in which the developing p orbital would be parallel or nearly parallel to the "bent" σ bond of a cyclopropane ring. In certain respects the cation **15** would appear to fulfill these requirements.



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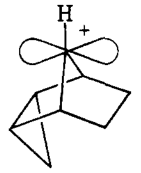

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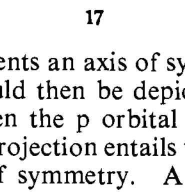
Models indicated that the distance from the incipient cationic center at C_4 to the center of the C_1–C_7 internuclear line would be about 2.4–2.5 Å for **15**, while a similar measurement for **16** gave an approximate distance of 2.3–2.4 Å. Thus it would appear that the cation to "bent" bond distance should be very similar for **15** and **16**.

In contrast to the similarity in distances are the orientations of the developing p orbitals. As previously discussed **16** is a very rigid molecule in which the developing p orbital must be perpendicular to the cyclopropane ring. However, **15** is also a very rigid molecule as a result of stretching the five-membered bridge from one side of the cyclopropyl ring to the other. The rigid structure of this trans-fused bicyclic system is best represented by **17** where the dotted line



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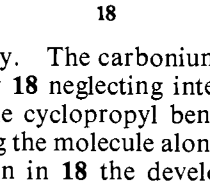
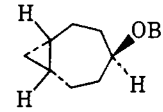


18

represents an axis of symmetry. The carbonium ion at C_4 could then be depicted by **18** neglecting interaction between the p orbital and the cyclopropyl bent bond. This projection entails viewing the molecule along the C_2 axis of symmetry. As shown in **18** the developing p orbital of the carbonium ion is close to being parallel to the cyclopropane ring. As a result this molecule should provide a new insight into the stereochemical factors which influence long-range neighboring group participation by the cyclopropyl ring. With these concepts in mind we set out to develop a synthetic route to **1** and to study its solvolytic behavior.



1

Synthesis

The synthesis of any derivative of the *trans*-bicyclo[5.1.0]octyl system appeared to be a formidable task. No examples of this ring system had been reported in the literature. Only a few derivatives of the less strained *trans*-bicyclo[6.1.0]nonane had been prepared.[10] Our initial synthesis of **1**, which involved a 13-step procedure, is shown in Chart I.[11,12]

Starting with commercially available 1,4-dibromo-*trans*-2-butene (**19**) we prepared *trans*-4-octene-1,8-dioic acid (**20**) according to literature procedures[16] in 59% yield. Esterification with diazomethane or with methanol under acid catalyzed conditions converted **20** to **21** in better than 86% yield.[17] Simmons–Smith addition of methylene[18] to **21** gave **22** (70%), which on acyloin condensation using sodium in xylene gave a mixture of the two stereoisomeric acyloins **23**. Oxidation of the crude acyloin product with cupric acetate gave **24** in 51% overall yield from **22**. Reaction of **24** with tosylhydrazine gave the monotosylhydrazone, **25** (88% yield). Treatment of **25** at low temperature with aqueous sodium hydroxide gave 5-diazo-*trans*-bicyclo[6.1.0]nonan-4-one (**26**), which, without purification, was dissolved in dioxane–water solution and irradiated with a bank of eight 15-W Sylvania "Black-lite" fluorescent tubes. This photochemical ring contraction gave a 29% yield of the acid, **27**, based on **25**.

The structure assigned to the ring-contracted acid was based on its method of synthesis and on several pieces of spectroscopic and chemical data. The white, crystalline acid, **27**, showed an absorption in the near-infrared at 1.643 μ (ϵ 0.408) indicative of a 1,2-disubstituted cyclopropane.[19] In addition the nmr spectrum of **27** showed a two-hydrogen multiplet at

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(9) For recent discussions and leading references, see B. R. Ree and J. C. Martin, *J. Amer. Chem. Soc.*, **92**, 1660 (1970), and P. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969).

(10) These are the parent hydrocarbons in both optically inactive and optically active forms [A. C. Cope and J. K. Hecht, *ibid.*, **85**, 1780 (1963); E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655 (1968)], *trans*-bicyclo[6.1.0]nona-2,4,6-triene [G. Moshuk, G. Petrowski, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 2179 (1968)], and *trans*-bicyclo-[6.1.0]nonan-2-one [C. H. DePuy and J. L. Marshall, *J. Org. Chem.*, **33**, 3326 (1968)].

(11) Presented in part before the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9–13, 1968, Abstracts, p 0–98; for a detailed preliminary report, see P. G. Gassman, F. J. Williams, and J. Seter, *J. Amer. Chem. Soc.*, **90**, 6893 (1968).

(12) Subsequent to our initial report of the synthesis of **1**, three other laboratories reported their independent syntheses of the *trans*-bicyclo-[5.1.0]octyl ring system.[13-15]

(13) W. Kirmse and Ch. Hase, *Angew. Chem., Int. Ed. Engl.*, **7**, 891 (1968).

(14) A. J. Ashe, III, *Tetrahedron Lett.*, 523 (1969).

(15) K. B. Wiberg and A. de Meijere, *ibid.*, 519 (1969).

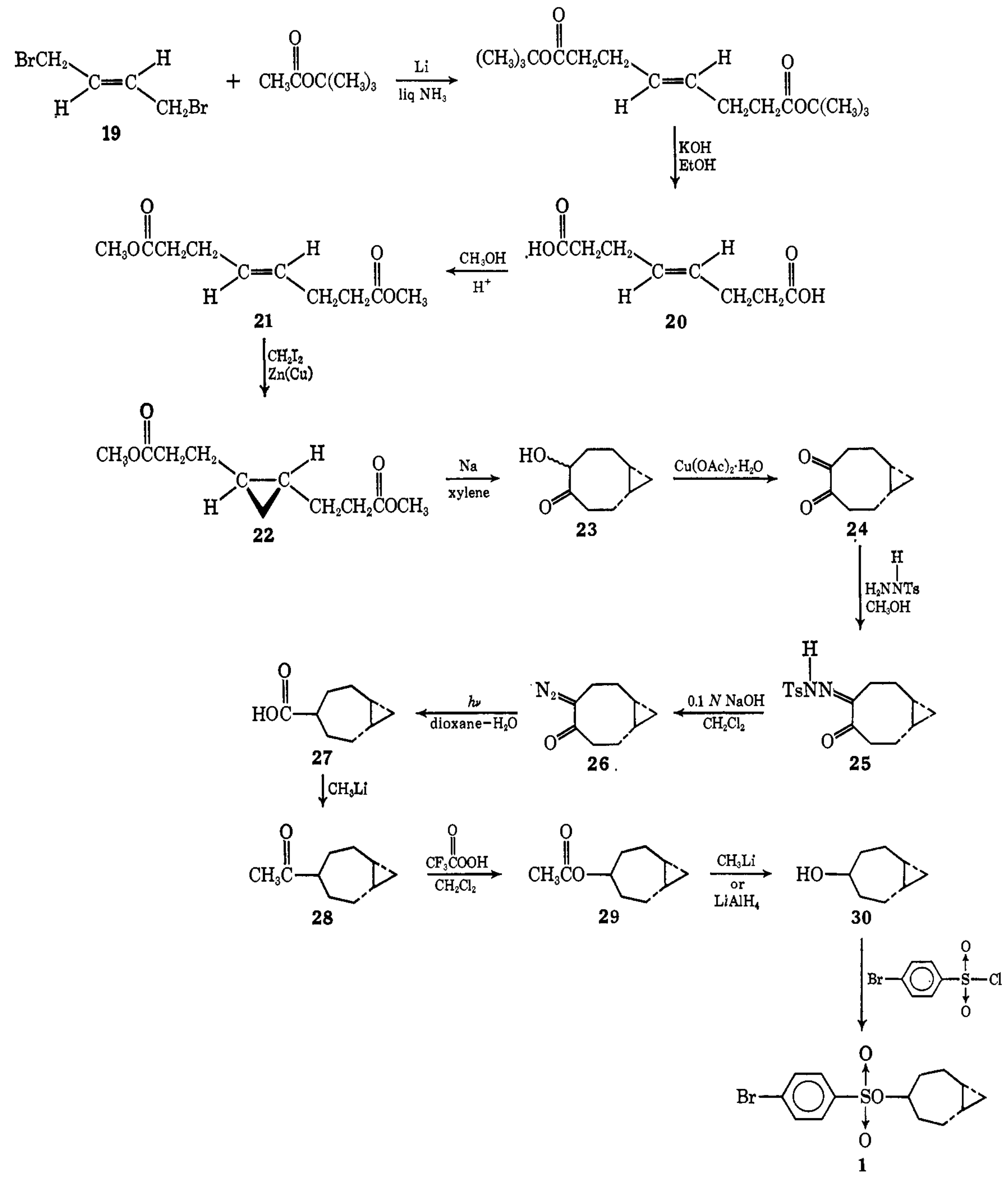
(16) K. Sisido, K. Sei, and H. Nozaki, *J. Org. Chem.*, **27**, 2681 (1962).

(17) The di-*tert*-butyl ester of **20** could be converted directly into **21** by refluxing with methanolic hydrochloric acid in 84% yield.

(18) For a leading reference to the method used, see E. LeGoff, *ibid.*, **29**, 2048 (1964).

(19) P. G. Gassman and F. V. Zalar [*ibid.*, **31**, 166 (1966)] have provided a detailed discussion of the use of near-infrared spectroscopy in the identification of substituted cyclopropanes.

Chart I



τ 9.93 characteristic of geminal cyclopropyl hydrogens.[20] In order to ensure that trans to cis isomerization of the substituents on the cyclopropane ring had not inadvertently occurred during one of the steps leading to **27**, it was desirable to compare a degradation product from **27** with the corresponding derivatives of *cis*-bicyclo[5.1.0]octane. In this regard **30** was compared with *cis*-bicyclo[5.1.0]octan-*exo*-4-ol and *cis*-bicyclo[5.1.0]octan-*endo*-4-ol. These three compounds had different ir and nmr spectra and different vpc retention times, but virtually identical mass spectral cracking patterns. The mass spectral data established the structural relationship between the three alcohols and completed the structure proof of **27**.

Reaction of **27** with methyllithium gave the methyl ketone, **28**, in 75% yield. In addition a small amount of the corresponding tertiary alcohol was formed. Baeyer–Villiger oxidation of **28** with trifluoroperacetic acid produced **29**, which on reaction with methyllithium gave **30** in 60% yield based on **28**. The use of lithium aluminum hydride instead of methyllithium gave an 82% yield of **30** based on **28**. The brosylate, **1**, was prepared in 93% yield from **30** for an overall yield of 3% from **19**.

In view of the costs of **19** and of *tert*-butyl acetate a more economical route to **22** was developed based on a modification of the procedure of Ashe.[14] As shown in Chart II, commercially available 1,5,9-cyclododecatriene (**31**, which consisted of 65% trans,trans,trans and 35% trans,trans,cis isomers) was treated with dichlorocarbene, generated from sodium trichloroacetate, to give a 53% yield of monodichlorocarbene adduct of the mixed isomers (**32**). Reductive dechlorination

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(20) For a recent discussion of cyclopropyl hydrogen absorptions of cis-fused bicyclo[*n*.1.0]alkanes, see J. G. Traynham, J. S. Dehn, and E. E. Green, *J. Org. Chem.*, **33**, 2587 (1968).

Table I. The Solvolysis of Seven-Membered Ring *p*-Bromobenzenesulfonates in Anhydrous Acetic Acid Buffered with Sodium Acetate

Compd	Temp, °C	Rate, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel} (60°)
37	60.00 ± 0.02	$(2.41 \pm 0.01) \times 10^{-5}$			
	80.00 ± 0.02	$(2.19 \pm 0.01) \times 10^{-4}$	25.5	−3.5	1.0
	90.00 ± 0.02	$(6.35 \pm 0.03) \times 10^{-4}$			
35	60.00 ± 0.02	$(5.06 \pm 0.18) \times 10^{-5}$			
	80.00 ± 0.02	$(4.91 \pm 0.15) \times 10^{-4}$	26.0	−0.4	2.1
	90.00 ± 0.02	$(1.42 \pm 0.01) \times 10^{-3}$			
1	60.00 ± 0.02	$(7.29 \pm 0.01) \times 10^{-5}$			
	70.00 ± 0.02	$(2.40 \pm 0.05) \times 10^{-4}$	25.6	−0.7	3.0
	80.00 ± 0.02	$(6.92 \pm 0.01) \times 10^{-4}$			
36	60.00 ± 0.02	$(8.06 \pm 0.33) \times 10^{-5}$			
	80.00 ± 0.02	$(7.93 \pm 0.00) \times 10^{-4}$	26.0	0.5	3.3
	90.00 ± 0.02	$(2.24 \pm 0.08) \times 10^{-3}$			
38	50.0	2.23×10^{-4}			
	60.0	6.70×10^{-4}	23.0	−4.2	27.8
	70.0	1.98×10^{-3}			

[a] See ref 23.

utilizing sodium–tetrahydrofuran–*tert*-butyl alcohol[21] gave the mixed isomers of **33** in 95% yield. Ozonolysis of **33** followed by oxidative work-up and esterification with methanolic hydrochloric acid gave a 62% yield of **22** and about 7% of the corresponding cis-disubstituted isomer. This material could be used in the acyloin condensation without complications.

Chart II

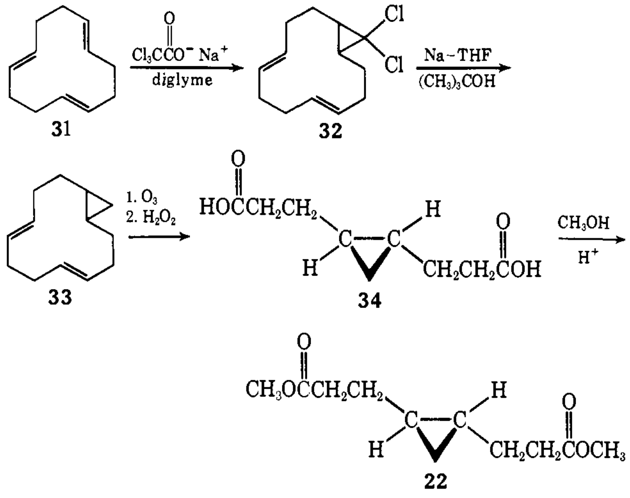
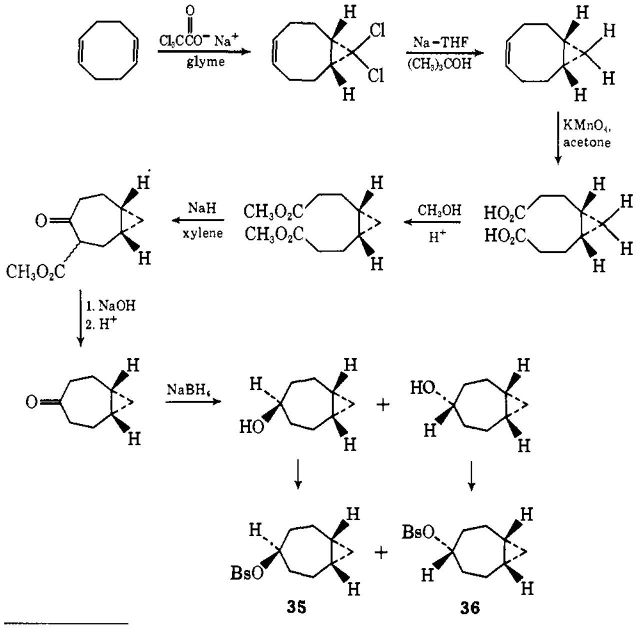


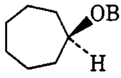
Chart III



For comparison purposes we desired the two epimeric cis-fused brosylates related to **1**. Thus, compounds **35** and **36** were prepared by a modification of the procedure of Cope and coworkers[22] as shown in Chart III. The major modification involved in this reaction scheme entailed the addition of dichlorocarbene to 1,5-cyclooctadiene, followed by reductive dechlorination of the intermediate dichlorocyclopropane according to the procedure of Gassman and Pape.[21]

Solvolysis Studies

Table I lists the pertinent kinetic data for **1**, **35**, **36**, cycloheptenyl 5-*p*-bromobenzenesulfonate (**37**), and cycloheptyl *p*-bromobenzenesulfonate (**38**).[23] As shown, the three bicyclic *p*-bromobenzenesulfonates all solvolyze about ten times slower than cycloheptyl *p*-bromobenzenesulfonate (**38**) in anhydrous acetic acid buffered with sodium acetate. Similarly, the three bicyclic *p*-bromobenzenesulfonates all solvolyze slightly faster than **37**.



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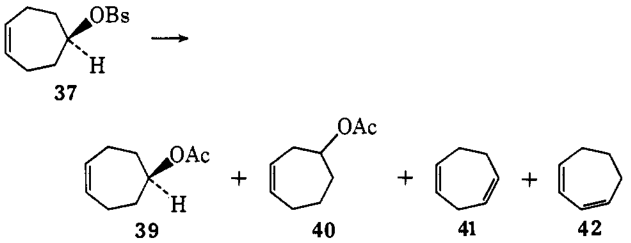
Cope and coworkers have identified the products obtained from **37**[24] and from the epimeric brosylates **35** and **36**.[25] These investigators found that **37** gave **39** (62%), **40** (10%), **41** (10%), and **42** (4%). The



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[21] P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

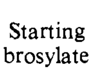
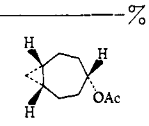
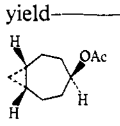
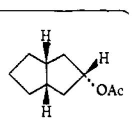
[22] A. C. Cope, S. Moon, and C. H. Park, *J. Amer. Chem. Soc.*, **84**, 4843 (1962).

[23] The kinetic data tabulated for **38** are those of H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

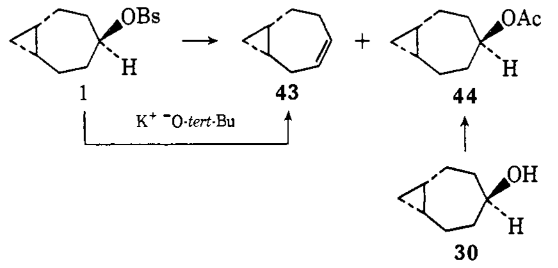
[24] A. C. Cope, C. H. Park, and P. Scheiner, *ibid.*, **84**, 4862 (1962).

[25] A. C. Cope, S. Moon, and C. H. Park, *ibid.*, **84**, 4850 (1962).

Table II. Products from **35** and **36** in Buffered Acetic Acid

	% yield			
Starting brosylate				
35	33	34	10	0
36	57	4	22	0.5

products from the acetolysis of **35** and **36** are listed in Table II. By comparison, the solvolysis of **1** was very clean. In buffered anhydrous acetic acid, **1** gave 76% **43** and 12% **44**. The structure of **44** was established by a comparison of the ir and nmr spectra of **44** with those of an authentic sample prepared from **30**. When **1** was



treated with potassium *tert*-butoxide in dimethyl sulfoxide at low temperature it was rapidly converted to **43**. The nmr spectrum of **43** had a two-proton multiplet at τ 4.35 for the vinylic hydrogens and a two-proton multiplet at τ 9.83 for the geminal cyclopropyl protons. This olefin was identical in all respects with that obtained from the solvolysis of **1**.

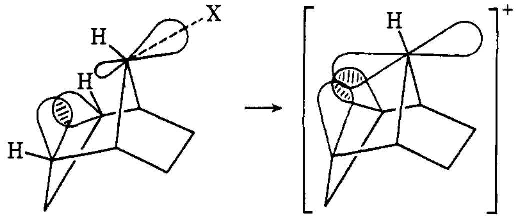
Discussion of Results

The kinetic data listed in Table I indicate that there is relatively little difference in the activation energies for the acetolyses of the five brosylates listed. The slightly faster rate of **38** can readily be interpreted as being a result of the inductive effect of the olefinic linkage in the case of **37** and of the cyclopropyl moiety in the solvolyses of **1**, **35**, and **36**. It is clear that the rates of solvolysis of **1**, **35**, and **36** provide kinetic evidence for a lack of cyclopropyl neighboring group participation in these solvolyses.

As previously demonstrated by Cope and coworkers, the products from **35** and **36** provide little, if any, evidence for neighboring cyclopropyl participation. In the acetolysis of **35** the cyclopropane remains intact and the products give no indication of any involvement of the cyclopropyl bent bonds. In the solvolysis of **36** greater than 99% of the product mixture appears to arise without involvement of the neighboring cyclopropyl ring.[26] In the cases of **35** and **36** the lack of cyclopropyl neighboring group participation is quite reasonable. Both of these molecules have considerable conformational freedom and the cis nature of the ring fusion places certain restrictions on the spatial relationship of the developing p orbital and the cyclopropyl ring. Bringing the developing p orbital into the vicinity of the cyclopropyl bent bonds in the solvolysis of either **35** or **36** would require the incorporation of additional strain in the transition state. Apparently the costs of the additional strain are greater than the benefits which might be derived through cyclopropyl stabilization of the incipient cation.

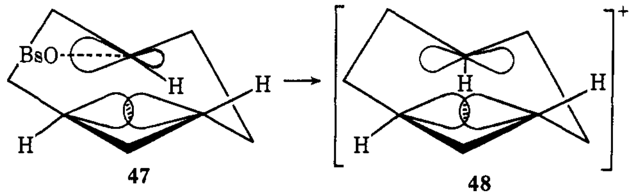
As discussed in the introduction, the trans fusion of the three-membered and seven-membered rings provides for the formation of a rigid structure in which the cyclopropane portion of the molecule is conformationally locked in close proximity to the developing cationic center. However, both the kinetics and products associated with the solvolysis of **1** provide strong evidence that there is no overlap between the p orbital of the cation and the bent σ bond of the nearby cyclopropyl ring. This indicates to us that the stereochemical orientation of electron-donating bonds of the cyclopropane moiety and of the electrophilic p orbital is extremely crucial.

It appears that two factors may be involved in the lack of cyclopropyl neighboring group participation in the solvolysis of **1**, in comparison to the dramatic effect of the cyclopropane bent bond in the solvolytic ionization of **4**. As shown, the back lobe of the developing p orbital in **45** is oriented directly toward the sphere of influence of the electron-donating bent bond of the cyclopropane. As **45** proceeds to **46** the p orbital continues to extend toward the bent bond and orbital overlap occurs. In this regard the orientation of the back lobe of the developing p orbital has effectively decreased the distance over which orbital interaction must occur.



45 **46**

In contrast, **47** depicts the similar crude orbital picture for **1**. In this case the orientation of the developing p orbital is almost parallel to the bent σ bond. Thus, as **47** proceeds toward **48** on the reaction path, the distance for effective orbital overlap is not decreased in a manner analogous to that involved in the conversion of **45** into **46**. Instead, the distance over which interaction of the orbitals must occur remains a near average of about 2.4 Å.



47 **48**

A factor which may be even more important than the distance effect discussed above is the problem of orbital density and overlap interactions. As shown in **48** the empty p orbital of the carbonium ion has a node where the bent bond of the cyclopropane has its maximum electron density. Similarly the cyclopropyl carbon–carbon σ bonds have minimum electron density in the vicinity of that portion of the p orbital normally

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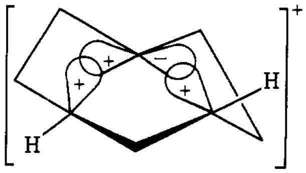
[26] It should be noted that the trace amount of bicyclo[3.3.0]octyl 3-acetate formed in the solvolysis of **36** has been attributed to a concerted process in which a hydride shift and cyclopropane cleavage are involved. It is questionable whether the formation involves a concerted or stepwise process since the carbonium ion which would result from a 1,2-hydride shift is known to yield the observed acetate as the major product.[25]

associated with bonding overlap. In this regard a simple stabilizing interaction would be difficult. Stabilization of the type shown in **49** which involves complete outward rupture of the cyclopropyl bond illustrates the limiting case for bent bond—p orbital interaction. From this example it can be readily recognized that any stabilizing influence provided to one end of the p orbital would probably be balanced against the nonbonding interaction at the other end of the p orbital.



49

In conclusion, the data obtained from the solvolysis of **1** indicate that participation of a single bent cyclopropyl bond can only occur in a stabilizing manner with one end of a developing p orbital. Thus, the stereochemical requirements for long-range participation by a neighboring cyclopropyl group should involve either the interaction of a single bent cyclopropyl bond with an orthogonal p orbital as in **46**, or the interaction of the orbitals of two different cyclopropyl carbon–carbon single bonds with the two ends of the p orbital. It appears that it is the latter situation which prevails in cyclopropyl participation of the type found in the formation of cyclopropylcarbinyl cations.

Experimental Section

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Melting points and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord as neat liquids, solutions, or powdered solids in potassium bromide disks. Near-infrared spectra were obtained on a Cary Model 14 recording spectrometer from 1 *M* solutions in AR carbon tetrachloride. Ultraviolet spectra were recorded on a Cary Model 15 recording ultraviolet spectrophotometer. Nuclear magnetic resonance spectra were obtained on Varian Associates A-60, A-60-A, and HA-100 spectrometers and reported τ units relative to tetramethylsilane (τ = 10.00) as the internal standard.

***trans*-4-Octene-1,8-dioic Acid (20).** Compound **20** was prepared by the method of Sisido, Sei, and Noyaki.[16] The 1,4-dibromo-*trans*-2-butene and *tert*-butyl acetate used in this preparation were purchased from Columbia Organic Chemicals and used without further purification.

Dimethyl *trans*-4-Octene-1,8-dioate (21). A mixture of 31.60 g (0.18 mol) of **20** and 480 ml of absolute methanol was stirred magnetically while 40 ml of concentrated sulfuric acid was slowly added. The solution was refluxed for 19 hr and the methanol was removed under reduced pressure. The residue was poured into 500 ml of a saturated salt solution and extracted with three 300-ml portions of ether. The ether extracts were combined, washed with a 5% sodium bicarbonate solution, water, and a saturated salt solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution concentrated by distillation of the ether through a 10-in. column packed with glass helices at atmospheric pressure. The residue was distilled *in vacuo* to give 32.27 g (86%) of **21** as a colorless liquid, bp 90–91° (0.35 mm), which became semisolid on standing. Redistillation gave an analytical sample: $n^{26.6}\mathrm{D}$ 1.4445; infrared absorptions (neat) 5.72 (nonconjugated ester), 10.33 μ (*trans*-ethylenic hydrogen).

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.10; H, 8.13.

In order to demonstrate that isomerization of the double bond had not occurred during the Fischer esterification, a small amount of **20** was esterified with diazomethane which gave a product identical in boiling point, index of refraction, and infrared spectrum.

Transesterification of Di-*tert*-butyl *trans*-4-Octene-1,8-dioate. A mixture of 35 g of di-*tert*-butyl *trans*-4-octene-1,8-dioate in 700 ml of absolute methanol, and 15 ml of concentrated sulfuric acid was stirred magnetically at reflux for 24 hr. The methanol was removed under reduced pressure and the residue was poured into 500 ml of a saturated salt solution. The mixture was worked up as described above to give 20.81 g (84.5%) of the diester identical with an authentic sample of **21**.

***trans*-1,2-Cyclopropanedipropionic Acid Dimethyl Ester (22).** The diester **22** was prepared by the general procedure of LeGoff.[18] Into a three-necked, 1-l. round-bottomed flask fitted with a condenser, dropping funnel, and magnetic stirrer was placed *ca.* 1.2 mol of the zinc–copper couple (prepared from granular zinc) and 240 ml of anhydrous ether. A solution of diiodomethane (0.84 mol, total) and 120 g (0.60 mol) of **21** was slowly added over a period of about 2 hr. After 20 hr of continued reflux an additional 0.6 mol of couple and 0.42 mol of diiodomethane was added and refluxing continued for an additional 24 hr. The ethereal solution was decanted from the couple into a separatory funnel containing a mixture of *ca.* 500 ml of 1 *N* hydrochloric acid and ice. The ethereal layer was separated, washed with a second portion of ice–hydrochloric acid, washed three times with water and once with saturated sodium chloride, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution concentrated by distillation of the ether through a 10-in. helice-packed column at atmospheric pressure. The crude product showed *ca.* 50% unchanged starting material and 50% **22**, as estimated by gas chromatography through a 0.6% PDEAS on Chrom G column at 115°. Two subsequent recyclizations, followed by distillation *in vacuo*, yielded 13.48 g of a fraction, bp 75–98° (0.3 mm), containing *ca.* 19% starting material and 81% **22** and 77.06 g of a second fraction, bp 98–105° (0.3 mm), containing *ca.* 10.5% starting material and 89.5% **22**.[27] An analytical sample of **22** was prepared by preparative gas chromatography (5 ft 20% butanediol succinate on firebrick column at 140°).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.74; H, 8.44.

***trans*-Bicyclo[6.1.0]nonan-4-on-5-ol (23).** The acyloin **23** was prepared by a conventional acyloin condensation[28] of **22**. In a 2-l. three-necked, round-bottomed flask was placed 650 ml of dry xylene and, after the system was flushed with nitrogen for several minutes, 36.6 g of sodium. The sodium was dispersed by vigorous stirring at reflux for 10 min. With continued heating and somewhat slower stirring, 77.06 g of a mixture containing 10% *cis*-1,2-cyclopropanedipropionic acid dimethyl ester and 90% **22** in 360 ml of xylene was added dropwise over a period of 24 hr. The reaction was slowly cooled to ice bath temperature and a solution of 200 ml of glacial acetic acid in 200 ml of xylene was added dropwise with continued stirring and cooling. After the addition of 500 ml of water, the two-phase mixture was filtered to remove a small amount of gum. The aqueous phase was separated and back-extracted with 150 ml of xylene. The combined xylene phases were washed with water and saturated sodium chloride and dried over anhydrous magnesium sulfate. The drying agent was filtered and the solution concentrated by distillation of the xylene at reduced pressure to give 41.6 g of crude reaction product. An analytical sample was obtained by distilling *in vacuo* a small amount of the crude product and subjecting the fraction, bp 68–88° (0.25 mm), to chromatography on silica gel. Elution with 30% ether in benzene gave a white solid **23**, which was recrystallized from Skelly B to give an analytical sample, mp 79–80°.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.26; H, 8.94.

***trans*-Bicyclo[6.1.0]nonane-4,5-dione (24).** The diketone **24** was obtained by standard cupric acetate–acetic acid oxidation[29] of the crude acyloin reaction product. Into a 1-l. round-bottomed flask fitted with an efficient mechanical stirrer and reflux condenser was placed 40.0 g of the crude acyloin product **23** in 25 ml of methanol, 120 g of cupric acetate monohydrate, and 300 ml of 50% aqueous acetic acid. The mixture was heated over a free flame until refluxing occurred for 1 min and then allowed to cool to room temperature. The cooled mixture was filtered and the filtrate poured into a solution of saturated sodium chloride. The solution was

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[27] The first fraction was recycled and the second fraction was used for the acyloin condensation.

[28] "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 840.

[29] "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 838.

extracted thoroughly with ether and the combined ether extracts were washed with successive, portions of saturated sodium chloride, sodium bicarbonate solution and saturated sodium chloride, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration, and the solution was concentrated by distillation of the ether through a 10-in. helice-packed column at atmospheric pressure. The residue was distilled *in vacuo* to give 18.2 g (38% based on **22** used),[30] bp 70–72° (0.25 mm), of the diketone **24**, which was shown to be homogeneous by vpc on an F & M HI-PAK 6-ft column packed with 10% silicone gum rubber SE-30 on Diatoport S at 100°. Redistillation gave an analytical sample of **24**, bp 71° (0.25 mm), $n^{31}\text{D}$ 1.4755.

Anal. Calcd for $C_9H_{12}O$: C, 71.02; H, 7.95. Found: C, 70.90; H, 7.98.

Monotosylhydrazone of *trans*-Bicyclo[6.1.0]nonane-4,5-dione (25). The derivative **25** was first prepared by the following procedure. A mixture of 2.19 g (0.01 mol) of **24** and 2.78 g (0.01 mol) of tosylhydrazine in 50 ml of dry methanol[31] was stirred for 5 min in a 100-ml round-bottomed flask fitted with a magnetic stirrer and drying tube. The resulting white precipitate was collected by filtration and dried to give 2.50 g (54%) of **25**, mp 175–176° dec. Two recrystallizations of **25** from methanol gave an analytical sample, mp 179–180° dec.

Anal. Calcd for $C_{16}H_{20}O_3N_2S$: C, 59.97; H, 6.29; N, 8.75. Found: C, 59.77; H, 6.26; N, 8.85.

The filtrate from the above reaction was stirred for an additional 15 min and the new precipitate was collected by filtration and dried to give 0.74 g of the ditosylhydrazone of **24**, mp 183–184° dec, which was recrystallized twice from methanol to give an analytical sample,[32] mp 184–185° dec.

Anal. Calcd for $C_{24}H_{32}O_5N_4S_2$: C, 55.8; H, 6.1; N, 10.6. Found: C, 55.4; H, 6.2; N, 10.8.

An alternate procedure was used to prevent formation of the ditosylhydrazone. In a 2-l. round-bottomed flask fitted with a mechanical stirrer, a pressure-equalizing dropping funnel, and a drying tube was placed 88 g (0.58 mol) of **24** in 150 ml of dry methanol. To this stirred solution was slowly added 53.9 g (0.29 mol) of tosylhydrazine in 750 ml of dry methanol. A white precipitate began to form even before the addition was complete. The solution was stirred for 0.5 hr after completion of addition, and the precipitate was collected by filtration, washed with cold methanol, and dried to give 85.85 g of **25**, mp 179–180°. The filtrate was concentrated to *ca.* 150 ml under reduced pressure, poured into 500 ml of water, and extracted with three 200-ml portions of ether. The ether extracts were combined, washed with water and a saturated salt solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution was concentrated by distillation of the ether through a column packed with glass helices at atmospheric pressure. The residue was distilled *in vacuo* to give 41.6 g of the starting material, **24**. The yield of **25** based on 46.4 g of **24** (88 g − 41.6 g) was 88%.

5-Diazo-*trans*-bicyclo[6.1.0]nonan-4-one (26). A 100-ml round-bottomed flask was covered with aluminum foil and equipped with a magnetic stirrer and drying tube. The flask was immersed in an ice–water bath and 1.717 g (0.005 mol) of **25** in 25 ml of methylene chloride was stirred with 55 ml of 0.1 *N* aqueous sodium hydroxide for 24 hr. The bright yellow organic layer was separated from the aqueous layer, washed with 15 ml of 0.1 *N* aqueous sodium hydroxide and 15 ml of a saturated salt solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the methylene chloride was removed at reduced pressure to give 0.264 g of a bright yellow oil which showed infrared absorption (neat) at 4.85 and 6.15 μ. The spectrum also showed the presence of small amounts of **25**. The basic washings from above were combined with the aqueous layer and with 25 ml of methylene chloride. This solution was stirred for an additional 24 hr in the ice bath. Following work-up and an additional 24-hr stirring period, a total of 0.906 g of a mixture of diazo compound, **26**, and starting material, **25**, was obtained.

***trans*-Bicyclo[5.1.0]octane-4-carboxylic Acid (27).** The acid **27** was prepared using the procedure of Meinwald and Gassman.[33] A solution of 4.42 g of crude **26** in 300 ml of spectrograde *p*-dioxane and 90 ml of water was irradiated in a Pyrex tube, using a bank of eight 15-W Sylvania "Blacklite" fluorescent tubes. After nitrogen evolution had ceased the solvent was distilled off under reduced pressure and the residue was dissolved in sodium carbonate solution. The solution was extracted with ether, cooled in an ice–water bath, and made very slightly acidic with a 10% hydrochloric acid solution. The white precipitate which formed was collected by filtration and air dried to give 1.18 g of **27** (29% based on **25**), mp 84–85°, which showed an absorption in the near-infrared at 1.643 μ (ϵ 0.408), and had an nmr spectrum which showed a multiplet at τ 9.93 (2 H). Two sublimations gave an analytical sample, mp 85–87°.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.90; H, 9.11.

Methyl *trans*-Bicyclo[5.1.0]oct-4-yl Ketone (28). The methyl ketone **28** was prepared from **27** following the general procedure of DePuy and coworkers.[34] A solution of 10.0 g (0.065 mol) of **27** in 420 ml of anhydrous ether was stirred under nitrogen while 90 ml of methyllithium (Foote Mineral Co., 5.02%) was added at such a rate as to maintain steady refluxing of the ether. After stirring for 5 min, the mixture was hydrolyzed by the addition of 300 ml of saturated ammonium chloride solution. The ether layer was separated, washed with a saturated ammonium chloride solution, water, and a saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution was concentrated by distillation of the ether through a column packed with glass helices. The residue was distilled *in vacuo* to give 7.56 g (75%) of **28**, bp 56–60° (0.22 mm) (of >95% purity as estimated by vpc on 19% Carbowax 20M on Chrom W column at 150°) and 1.09 g, bp 67–70° (0.22 mm), of a mixture estimated to consist of 40% **28** and 60% alcohol derived from the addition of methyllithium to **28** by vpc on the same column.

An analytical sample of **28** was collected by preparative gas chromatography on a 19% Carbowax 20M on Chrom W column at 150°, $n^{26}\text{D}$ 1.4805.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.01; H, 10.61.

The 2,4-dinitrophenylhydrazone of **28** recrystallized twice from 95% ethanol as bright orange needles, mp 120.0–121.5°.

Anal. Calcd for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.67; H, 5.83; N, 16.68.

An analytical sample of the tertiary alcohol, mp 51–52°, was also collected by preparative vpc on a 19% Carbowax 20M on Chrom W column at 150°. The white solid showed characteristic infrared absorptions (KBr) at 2.90 μ (OH str) and a doublet at 7.33 μ (gem dimethyl). The nmr spectrum showed a six-proton singlet at τ 8.88. The near-infrared spectrum of this alcohol showed an absorption at 1.644 μ (ϵ 0.290).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.34; H, 11.75.

***trans*-Bicyclo[5.1.0]oct-4-yl Acetate (29).** Peroxytrifluoroacetic acid[35] prepared from 1.84 g (0.008 mol) of trifluoroacetic anhydride and 0.228 ml of 90% hydrogen peroxide (0.0088 mol) in 10 ml of methylene chloride was added dropwise over a 2-hr period to a stirred slurry of 0.536 g (0.0035 mol) of **28**, 3 g (0.02 mol) of disodium hydrogen phosphate, and 10 ml of methylene chloride. The solution was stirred at room temperature for 1 hr, refluxed gently for 0.5 hr, and stirred at room temperature for an additional 0.5 hr. The solids were removed by filtration and washed well with methylene chloride. The combined organic layers were washed with 20 ml of water, two 20-ml portions of a saturated sodium bicarbonate solution, and 20 ml of water, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the methylene chloride was removed by distillation at atmospheric pressure to give a crude sample of **29** which contained a small amount of the trifluoroacetate as indicated by infrared absorptions (neat) at 5.57 and 5.74 μ. Vpc at 100° on an F & M Hi-Pak 6-ft 10% silicone gum rubber SE-30 on Diatoport S column showed the complete absence of **28**.

An analytical sample of **29** was prepared from the alcohol **30**. Acetic anhydride (0.815 g) was slowly added dropwise to a stirred solution of 0.450 g (0.0036 mol) of **30** in 6 ml of anhydrous pyridine at room temperature. The solution was stirred for 1 hr and al-

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[30] Yields of up to 51% **24** have been found when **22**, obtained from an alternate route (*vide post*), was used in the acyloin reaction and the reaction set-up was equipped with a high dilution head.

[31] The methanol was dried by refluxing over magnesium turnings. See Louis F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass. p 289.

[32] The compound contained 1 mol of methanol of crystallization.

[33] J. Meinwald and P. G. Gassman, *J. Amer. Chem. Soc.*, 82, 2857 (1960).

[34] C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, **29**, 2813 (1964).

[35] W. D. Emmon and G. B. Lucas, *J. Amer. Chem. Soc.*, 77, 2287 (1955).

lowed to set at 0° for 24 hr. The cooled solution was poured into a mixture of 1 *N* hydrochloric acid and Skelly F, and, after separation of the organic layer, the aqueous phase was extracted with Skelly F. The combined organic phases were washed with dilute hydrochloric acid, water, sodium bicarbonate solution, water, and saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution concentrated by distillation of the ether at atmospheric pressure. The residue was distilled *in vacuo* to give 0.375 g (62%) of **29**, bp 83° (3.2 mm). A middle cut, $n^{28}\text{D}$ 1.4671, was submitted for analysis.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.42; H, 9.84.

***trans*-Bicyclo[5.1.0]octan-4-ol (30). Method A.**[34] A solution of the crude acetate **29** (prepared from 0.536 g of **28**) in 10 ml of anhydrous ether was stirred under nitrogen in a three-necked, 25-ml round-bottomed flask. A 4.20-ml portion of methyllithium solution (Foote Mineral Co., 5.02%) was slowly added over a period of 1.5 hr. The mixture was stirred an additional 0.5 hr and then poured onto ice. After vigorous stirring the layers were separated and the aqueous layer was extracted with two 10-ml portions of ether. The combined ether extracts were washed with 10 ml of water and 10 ml of saturated sodium chloride, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent was removed by distillation at atmospheric pressure to give 0.447 g of crude reaction product. The crude product was subjected to molecular distillation (0.1 mm, bath at 60°) to give 0.276 g (64% based on **28**) of **30** estimated to be >95% pure by vpc on 10% Carbowax 20M-KOH (4:1) on 60-80 Chrom W column at 150°. An analytical sample of **30** was collected by preparative vpc on a 10% Carbowax 20M-KOH (4:1) on 60-80 Chrom G column at 150°, $n^{26.0}\text{D}$ 1.4950.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.53; H, 11.32.

The impurity was collected by chromatography on the same column and shown to be identical with the tertiary alcohol obtained from the addition of methyllithium to **28**.

Method B. The crude acetate **29** (prepared from 10.3 g of **28**) dissolved in 150 ml of anhydrous ether was added to 2.0 g of finely pulverized lithium aluminum hydride in 200 ml of anhydrous ether. The addition rate was controlled so as to maintain a steady reflux of the ethereal solution. The reaction mixture was stirred for 1 hr and was then hydrolyzed by the dropwise addition of 8.0 g of a 10% solution of sodium hydroxide. After stirring overnight, the fluffy white precipitate was removed by filtration and washed thoroughly with ether, and the combined ethereal filtrates were concentrated by distillation of the ether through a 10-in. column packed with glass helices at atmospheric pressure. The residue was distilled *in vacuo* to give 6.36 g of **30** (74% based on **28**), bp 83-86° (2.6 mm), and 1.10 g, bp 89-100° (2.6 mm), of a mixture estimated to consist of *ca.* 65% **30** and 35% tertiary alcohol by vpc on 10% Carbowax 20M-KOH (4:1) on 60-80 Chrom W column at 150°. The total yield of **30** produced, based on **28**, was 82%. The near-infrared spectrum of **30** showed an absorption at 1.643 μ (ϵ 0.276) and the nmr spectrum had a two-proton multiplet at τ 9.88, both consistent with the presence of a cyclopropyl group.

***trans*-Bicyclo[5.1.0]oct-4-yl *p*-Nitrobenzoate.** To a cooled solution of 0.267 g (0.002 mol) of **30** in 10 ml of dry pyridine was slowly added 0.466 g (0.0025 mol) of *p*-nitrobenzoyl chloride. The solution was stirred for 1 hr and then allowed to set at 0° for 24 hr. The solution was poured into 20 ml of an ice-water mixture and after vigorous stirring 0.321 g (55%) of the *p*-nitrobenzoate of **30**, mp 64-68°, was collected by filtration. Low-temperature recrystallization from hexane yielded 0.230 g, mp 68-70°.

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.43; H, 6.31; N, 4.85.

***trans*-Bicyclo[5.1.0]oct-4-yl Brosylate (1).** The brosylate **1** was prepared from **30** in 93% yield following the procedure of Brown.[23] To a cooled solution of 4.85 g of *p*-bromobenzenesulfonyl chloride in 15 ml of anhydrous pyridine was added 2.0 g (0.016 mol) of **30**. After 24 hr at 0° the solution was cautiously diluted to 2.5 times its volume with water. The aqueous pyridine solution was extracted thoroughly with ether and the combined ether extracts were washed exhaustively with 1 *N* hydrochloric acid, followed by washing with water and saturated brine, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution was concentrated on the rotary evaporator to yield 5.1 g of crude **1**. Three recrystallizations from ether gave an analytical sample, mp 99-100°. The continued presence of the cyclopropyl group was indicated by a two-proton multiplet at τ 9.95 in the nmr spectrum.

Anal. Calcd for $C_{14}H_{17}O_3SBr$: C, 48.70; H, 4.96; S, 9.29. Found: C, 48.86; H, 5.12; S, 9.09.

***trans*-Bicyclo[5.1.0]octan-4-one.** A solution of 6.99 g (0.055 mol) of **30** was dissolved in 600 ml of reagent grade acetone and cooled to 10-20°. Jones reagent[36] was added dropwise until the color of the solution changed from green to brown, then a few extra drops were added. The solution was stirred for 5 min and than enough methanol was added to destroy excess reagent. Water was added until all the salts were dissolved and the aqueous solution was then extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution, water, and saturated salt solution followed by drying over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution was concentrated by distillation of the ether through a column packed with helices. The residue was distilled *in vacuo* to give 5.97 g (86%) of *trans*-bicyclo[5.1.0]octan-4-one, bp 74° (13 mm). The product showed $\lambda_{\max}^{\text{EtOH}}$ 215 nm (ϵ 190) and $\lambda_{\max}^{\text{EtOH}}$ 286 nm (ϵ 16) and had an nmr spectrum which showed a two-proton multiplet centered at τ 9.75 (CCl_4). An analytical sample of this ketone was collected by preparative vpc on a 25% XF1150 on 60-80 Chrom W column at 130°, $n^{27}\text{D}$ 1.4793.

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.20; H, 9.78.

The 2,4-dinitrophenylhydrazone was prepared and recrystallized three times from 95% ethanol to give an analytical sample, mp 167-168°.

Anal. Calcd for $C_{14}H_{16}O_4N_4$: C, 55.25; H, 5.30; N, 18.41. Found: C, 55.18; H, 5.38; N, 18.24.

***trans*-Bicyclo[5.1.0]oct-3-ene (43).** To a stirred solution of 0.244 g of potassium *tert*-butoxide in 2 ml of dry dimethyl sulfoxide was added 0.345 g (0.001 mol) of **1** in 2 ml of dry dimethyl sulfoxide. The solution was stirred at 20-25° for 30 min, followed by the addition of 5 ml of pentane. The mixture was stirred for 1 min and then poured onto an ice-water mixture. The layers were separated and the aqueous phase extracted with pentane. The combined pentane extracts were washed with a saturated salt solution and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution was concentrated by careful distillation of the pentane at atmospheric pressure. The crude residue was shown to be homogenous by vpc on an F & M Hi-Pak 6-ft 10% silicone gum rubber SE-30 on Diatoport S column at 65°. The crude product was purified by preparative vpc on a 20 ft × 3/8 in. 30% SE-30 on 45-60 Chrom W column at 110°. The nmr spectrum of **43** had a two-proton multiplet at τ 4.35 (vinylic hydrogens) and a two-proton multiplet at τ 9.83 consistent with presence of a cyclopropyl group. A small amount of the autoprepared material was submitted for an analytical sample.

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.80; H, 11.20.

13,13-Dichlorobicyclo[10.1.0]trideca-4,8-dienes (32). A mixture of 200 g of commercial 1,5,9-cyclododecatrienes (Columbian Carbon Co.), 113 g of sodium trichloroacetate, and 100 ml of dry diglyme was heated at 105° for 2 hr with vigorous stirring.[37] After the carbon dioxide evolution had ceased the reaction mixture was cooled and the precipitate filtered. The precipitate was washed well with diglyme and the solution was then concentrated by removal of the diglyme, bp 52° (10 mm). Distillation *in vacuo* yielded 87 g of starting material, bp 50-55° (0.13 mm), and 92.90 g (53% based on reacted triene) of the mixed isomers of **32**, bp 110-113° (0.17 mm). Yields for several runs ranged from 45 to 60%.

Bicyclo[10.1.0]trideca-4,8-dienes (33). A mixture of 139 g of finely cut (*ca.* 1/8 in. squares) sodium metal in 1300 ml of tetrahydrofuran was heated at reflux while 100 ml of *tert*-butyl alcohol was added dropwise. The heat was reduced and a solution of 92 g of the mixed isomers of **32** in 90 ml of *tert*-butyl alcohol was added at such a rate so as to maintain vigorous reflux. The solution was stirred at reflux until the sodium clumped and the reaction turned a bright purple color. The solution was cooled to room temperature and poured through a wire strainer into a 3-l. erlenmeyer flask. The sodium in the strainer was washed with Skelly F and the Skelly F washings were added to the erlenmeyer. Ice was slowly added to the solution with vigorous swirling, followed by the addition of

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(36) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(37) J. M. Locke and E. W. Duck, *Chem. Ind.* (*London*), **41**, 1727 (1965).

sufficient water to dissolve the sodium *tert*-butoxide. The layers were separated and the aqueous layer was extracted with several portions of Skelly F. The combined organic layers were washed successively with two 700-ml portions of water and one 500-ml portion of saturated sodium chloride, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution was concentrated by distillation of the ether through a column packed with helices at atmospheric pressure. The residue was distilled *in vacuo* to give 62.60 g (95%) of isomers of **33**, bp 73–80° (0.4 mm).

***trans*-1,2-Cyclopropanedipropionic Acid (34).** A mixture of acids consisting primarily of **34** was prepared from the ozonolysis of the mixed isomers of **33** following the general procedure of Henne and Hill.[38] A mixture of isomers of **33** was dissolved in 280 ml of absolute methanol and a small amount of pentane. The solution was cooled to −78° and a stream of ozone was bubbled through the mixture until the reaction was complete. The solution was allowed to warm to room temperature and the methanol was removed under reduced pressure. The viscous oil was dissolved in 300 ml of glacial acetic acid and divided into two equal portions. Each portion was slowly added dropwise to a stirred mixture of 130 g of 30% H_2O_2, 5.7 ml of concentrated sulfuric acid, and 230 ml of water. During the addition the temperature was slowly raised to *ca.* 60°. After the addition was complete the solution was slowly and cautiously brought to reflux (vigorous refluxing begins at *ca.* 90°) and stirred at reflux for 2 hr. The solutions were cooled and the combined reactions extracted thoroughly with ether. The ethereal solution was extracted with 10% sodium hydroxide until the washings were basic. The combined base extracts were neutralized with 6 *N* hydrochloric acid. The aqueous solution was saturated with salt and extracted thoroughly with ether. The ether extracts were combined and washed with water and saturated salt solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution concentrated by distillation of the ether through a 10-in. column packed with glass helices at atmospheric pressure to give a crude mixture of acids which were esterified.

The crude mixture of acids (consisting mainly of **34**) from the ozonolysis of a 200-g mixture of the isomers of **33** was dissolved in 1 l. of absolute methanol, 700 g of 2,2-dimethoxypropane, and 5 ml of 6 *N* hydrochloric acid. The solution was refluxed for 24 hr, cooled to room temperature, and concentrated on a rotary evaporator. The residue was dissolved in 500 ml of ether and washed with successive 300-ml portions of water, saturated sodium bicarbonate, water, and saturated sodium chloride, followed by drying over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution was concentrated by distillation of the ether through a 10-in. column packed with helices. The residue was distilled *in vacuo* to give 145.6 g (60% based on **33**) of liquid, bp 100–105° (0.4 mm), estimated by gas chromatography on 0.6% PDEAS on Chrom G column at 120° to consist of *ca.* 90% **22** and 10% *cis*-1,2-cyclopropanedipropionic acid dimethyl ester. A small amount of each product was collected by preparative vpc (15% butanediol succinate on 45–60 Chrom G column at 150°) and shown to be identical with authentic samples.

Preparation of 35 and 36. The epimeric brosylates, **35** and **36**, were prepared according to a modification of the published procedure.[22] The modifications are given in detail below.

9,9-Dichloro-*cis*-bicyclo[6.1.0]non-4-ene. *cis,cis*-1,5-Cyclooctadiene was treated with sodium trichloroacetate in glyme at 105° according to the procedure of Fray[39] to give the monodichlorocarbene adduct in 61% yield.

***cis*-Bicyclo[6.1.0]non-4-ene.** A mixture of 48.25 g (2.1 mol) of finely cut (*ca.* 1/8 in. squares) sodium metal in 1125 ml of tetrahydrofuran was heated at reflux while 90 ml of *tert*-butyl alcohol was added dropwise. The heat was reduced and 25 g (0.13 mol) of 9,9-dichlorobicyclo[6.1.0]non-4-ene in 85 ml of *tert*-butyl alcohol was added at such a rate so as to maintain vigorous reflux. The solution was stirred at reflux until the sodium clumped and the solution turned a bright purple color (*ca.* 4 hr). The solution was cooled to room temperature and poured through a wire strainer into a 3-l. erlenmeyer flask. The sodium in the strainer was washed well with Skelly F and the Skelly F washings were added to the erlenmeyer. Ice was slowly added to the solution with vigorous swirling, followed by the addition of sufficient water to dissolve the sodium *tert*-butoxide. The layers were separated and the aqueous layer was extracted with two 500-ml portions of Skelly F. The combined organic layers were washed successively with two 700-ml portions of water, and one 700-ml portion of saturated salt solution followed by drying over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution concentrated by distillation at atmospheric pressure of the solvent through a 10-in. column packed with helices. The residue was distilled *in vacuo* to give 14.6 g (91.5%) of *cis*-bicyclo[6.1.0]non-4-ene, bp 82–83° (40 mm), $n^{26}\mathrm{D}$ 1.4805, shown to be *ca.* 98% pure by vpc on an F & M Hi-Pak 6-ft 10% silicone gum rubber SE-30 on Diatoport S column at 100°. The near-infrared spectrum of this olefin showed an absorption at 1.644 μ (ϵ 0.264) characteristic of a disubstituted cyclopropane.

4-Cycloheptenyl *p*-Bromobenzenesulfonate (37). This brosylate was prepared according to the procedure of Cope and coworkers.[24]

Kinetics. Reagents. Anhydrous acetic acid was prepared by refluxing a solution of acetic anhydride and sodium acetate in glacial acetic anhydride for 24 hr and subsequent fractional distillation in a dry atmosphere. Standard sodium acetate in acetic acid (*ca.* 0.1 *M*) was prepared by the careful addition of anhydrous acetic acid to a solution of anhydrous sodium carbonate in acetic anhydride, such that *ca.* 1% acetic anhydride remained after the water was removed, followed by refluxing in a dry atmosphere for 5 hr[40] (calculated to be 2.650 g of anhydrous sodium carbonate and 7.56 g of acetic anhydride diluted to 500 ml with anhydrous acetic acid). Standard perchloric acid in acetic acid (*ca.* 0.02 *M*) used in titrating acetolysis aliquots was prepared by the careful addition of 70% perchloric acid to a solution of anhydrous acetic acid and acetic anhydride, such that 1% acetic anhydride remained after the water was removed, followed by standing at room temperature for 12 hr. The molarity of the standard perchloric acid in acetic acid was determined by titrating an aliquot *vs.* potassium acid phthalate (primary standard) in anhydrous acetic acid using bromophenol blue as the indicator.

Procedure. The kinetic procedure followed was essentially that of Winstein and coworkers.[41] All rates were determined using an infinity titer which agreed within 1% of the calculated value, except for 4-cycloheptenyl brosylate in which case it was necessary to use calculated values. All solvolytic runs in buffered anhydrous acetic acid gave linear pseudo-first-order plots through greater than 75% reaction.

Acetolysis Products from 1. A solution of 1.0 g of **1** in 50 ml of 0.1 *M* sodium acetate in acetic acid was heated at 80.0° for 3 hr. The solution was cooled, poured onto an ice–water mixture, and the aqueous solution extracted with ether. The combined ether extracts were washed with a saturated sodium bicarbonate solution, water, and a saturated salt solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the ether removed by careful distillation at atmospheric pressure. The resulting mixture was separated by preparative vpc on a 5% SE-30 on 42–60 firebrick column. The column was temperature programmed so that **43** was collected at 68° and **44** was collected at 135°. Each compound was identified by comparison of its ir and nmr spectra with those of an authentic sample. The yields listed in the discussion section were the average of three runs using 1-octanol as an internal standard.

An acetolysis of **1** at 80° for 1000 sec showed only two products, **43** and **44**, and permitted the isolation of unreacted brosylate, mp 100–101°, mmp with **1**, 100–101°, whose infrared spectrum was identical with **1**.

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