

Ring closures also appear to be a greater stabilizing factor than the conjugative effect of $\text{CH}=\text{CH}$ units. This is most directly seen in the spontaneous cyclizations of dienyl cations to cyclopentenyl cations,^{1,2,17} wherein the stabilizing effect of cyclization overcomes the loss of a conjugated $\text{CH}=\text{CH}$ unit, and also in the greater stability of I relative to IV or even V.

Past discussions of carbonium ion stabilities have usually centered on resonance energy effects. The data in this paper show that other effects overshadow the simple resonance energy effect with aliphatic allylic and polyenyl cations.

Experimental Section

Chemicals. The conjugative base of II is a mixture of 1,3,5,5-tetramethyl-1,3-cyclohexadiene and 1,5,5-trimethyl-3-methylene-cyclohexene. The mixture was prepared from methylolithium and isophorone.^{4,18} 2,4-Dimethyl-3-penten-2-ol, the precursor of III, was prepared from methylolithium and mesityl oxide.¹⁸ 2,6-Dimethyl-1,3,5-heptatriene, the conjugate base of IV, was prepared from LiAlH_4 and phorone.¹ 2,8-Dimethyl-1,3,5,7-nonatetraene was prepared from 5-methyl-2,4-heptadienal and 2-methyl-2-propenyltriphenylphosphonium chloride by the method of Sorensen.²

Equilibrium Measurements. A constant amount of polyene was introduced into varying strengths of aqueous H_2SO_4 . The absorptivity, A , was measured as a function of time at $25 \pm 1^\circ$ and at λ_{max} of the cation: II, 314 $\text{m}\mu$ (ϵ 11,900); III, 305 $\text{m}\mu$ (ϵ 19,000); IV, 396 $\text{m}\mu$ (ϵ 50,600); V, 473 $\text{m}\mu$ (ϵ 104,800). In 85–96% H_2SO_4 , the cations were stable at 25° , both at the 10^{-2} M concentrations used in nmr studies^{1–3} and at the 10^{-4} M concentrations used in the present study. As the acidity was reduced to levels at which

(17) T. S. Sorensen, *J. Amer. Chem. Soc.*, **89**, 3782, 3794 (1967); **91**, 6404 (1969).

(18) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, **85**, 2991 (1963).

cation and polyene coexisted in comparable amounts, the system rapidly decomposed. It was necessary to extrapolate the data to zero time. To improve the precision of this extrapolation, the rate laws for the decompositions were determined. This was done by varying the initial stoichiometric concentration and measuring initial rates.

Cations II and III decomposed by first-order rates and their data were extrapolated to zero time by plotting $\log A$ against time. Cations IV and V decomposed by second-order rates and their data were extrapolated to zero time using plots of A^{-1} against time. All four decomposition rates varied inversely with the h_0 acidity function⁵ in the ranges given in Table I. The complete rate eq for II and III is eq 3 and eq 4 for IV and V. The data are insufficient to interpret these rate laws. Also, these rates, found at $\sim 10^{-6}$ M concentration, may not obtain at higher concentration.

$$-d[\text{R}^+]/dt = k[\text{R}^+]/h_0 \quad (3)$$

$$-d[\text{R}^+]/dt = k[\text{R}^+]^2/h_0 \quad (4)$$

Reproducibility of the data is strongly dependent on the mode of introduction of the diene. The following procedure was adopted, not only because it gave reproducibility to within 5% but it also gave the highest A values and presumably the least decomposition and polymerization during the addition.

An acetic acid stock solution was prepared which contained about 10^{-2} mol l^{-1} of sodium acetate. An accurately measured 0.05 ml of this solution was injected through a calibrated microsyringe into 10.0 ml of the aqueous sulfuric acid. The latter was stirred vigorously by a magnetic stirrer during the injection. The syringe was wiped clean and a 0.05-ml increment added to each new concentration of aqueous sulfuric acid without dismantling the syringe. The purpose of the sodium acetate was to neutralize any trace of sulfuric acid that diffused back into the syringe.

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work.

Reactions of Trans-Fused Cyclopropanes. The Acid-Catalyzed Ring Cleavage of *trans*-Bicyclo[5.1.0]oct-3-ene¹

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Abstract: The acid-catalyzed addition of acetic acid to *trans*-bicyclo[5.1.0]oct-3-ene has been studied. It was found that product-determining protonation occurred exclusively at the bridgeheads. This acid-catalyzed opening of the cyclopropane ring gave a mixture of ten products. The detailed mechanistic aspects of the formation of these products are discussed. The reactivity of *trans*-fused cyclopropanes is considered in relation to the presence of "twist" bent σ bonds.

Highly strained polycyclic molecules, with their multifarious chemical idiosyncrasies, have provided an almost seductive attraction for organic chemists. Mute testimony to this premise has been provided by the approximately thousand papers dealing with the properties of strained carbocyclic compounds which have been published in the last dozen years. Bicyclo[1.1.0]-

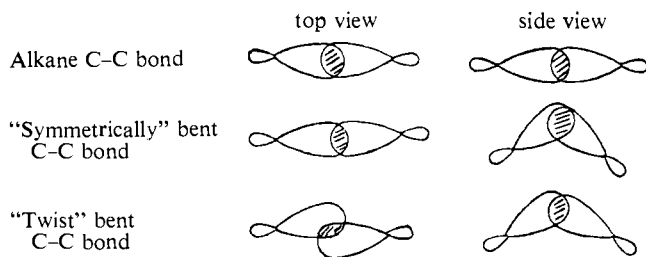
butane, bicyclo[2.1.0]pentane, bicyclo[1.1.1]pentane, and numerous tri- and tetracyclic small-ring compounds have been synthesized and studied. Of particular interest in relation to these compounds has been the nature of the carbon-carbon σ bond which is capable of bestowing such unusual chemical reactivity. Recently, we suggested that "bent" σ bonds should fall into two categories.⁴ As shown schematically below, these bent bonds have been classified as being either "symmetrically" bent or "twist" bent.

(1) Paper XVIII on "The Chemistry of Bent Bonds." For the previous paper in this series, see P. G. Gassman, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1812 (1971).

(2) Alfred P. Sloan Foundation Research Fellow, 1967–1969.

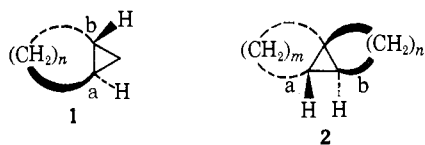
(3) Goodyear Fellow, 1968–1969; Dow Chemical Fellow, 1969–1970.

(4) P. G. Gassman, *Chem. Commun.*, 793 (1967).



In a "symmetrically" bent bond, the electron density associated with the overlapping orbitals which constitute the bond is not linearly aligned with the internuclear line as is the case in the normal alkane carbon-carbon σ bond. Instead, the electron density occurs symmetrically about a plane which passes through the two carbon atoms connected *via* the bent bond, with a one-dimensional displacement of the bonding orbitals from the internuclear line.⁵ Cyclopropane, cyclobutane, and the vast majority of the small bi-, tri-, and tetracyclic molecules which have been studied fall into this category of compounds having symmetrically bent carbon-carbon σ bonds.

In contrast to symmetrically bent carbon-carbon σ bonds, "twist" bent carbon-carbon σ bonds possess an additional parameter. As with symmetrically bent bonds, bond angle deformation in molecules containing "twist" bent bonds places significant electron density outside the internuclear line defined by the bonded carbons. However, when certain environmental restrictions are placed on the carbons joined by the bent bond a twisting or torquing apart of the bonding orbitals can occur. This opposing horizontal displacement of the bonding orbitals should result in decreased orbital overlap and increased chemical reactivity. Two classes of compounds which should contain "twist" bent bonds are represented by **1** and **2**. When m and n are sufficiently small the a-b bonds of both **1** and **2** should be extremely reactive due to the "twisting" of these bonds.



It seems likely that m and n will have to be four or less in order for this effect to be significant.

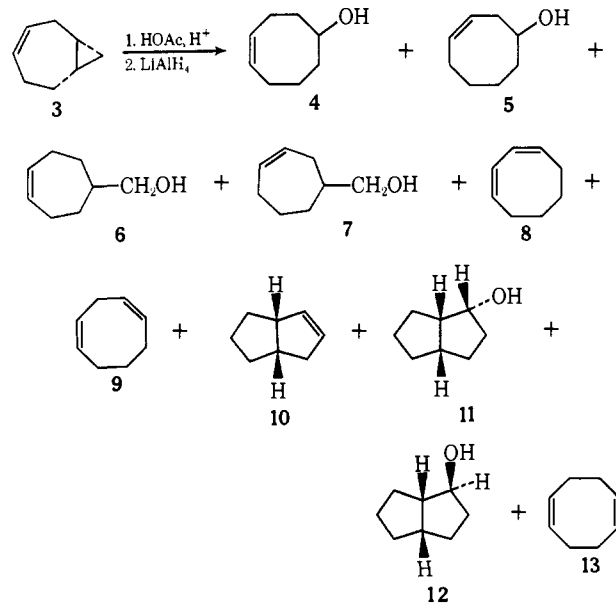
At this time *trans*-bicyclo[n .1.0]alkanes where n is four or less have yet to appear in the literature. It is only recently that the first synthesis of a derivative of *trans*-bicyclo[5.1.0]octane has been reported.⁶ In order to ascertain whether the cyclopropane would possess

(5) For detailed theoretical discussions of symmetrically bent bonds, see C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949); A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 1285 (1962); 3161 (1963); M. Randić and Z. Maksić, *Theor. Chim. Acta*, **3**, 59 (1965); Z. Maksić, L. Klasinc, and M. Randić, *ibid.*, **4**, 273 (1966); M. Randić, J. M. Jerkunica, and D. Stefanovic, *Croat. Chem. Acta*, **38**, 49 (1966); M. Pomerantz and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **88**, 3970 (1966); W. A. Burnett, *J. Chem. Educ.*, **44**, 17 (1967); N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 3966 (1967); K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(6) (a) P. G. Gassman, J. Seter, and F. J. Williams, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9-13, 1968, Abstracts, p O-98; P. G. Gassman, J. Seter, and F. J. Williams, *J. Amer. Chem. Soc.*, **90**, 6893 (1968). See also (b) W. Kirmse and Ch. Hase, *Angew. Chem., Int. Ed. Engl.*, **7**, 891 (1968); (c) A. J. Ashe, III, *Tetrahedron Lett.*, 523 (1969); and (d) K. B. Wiberg and A. de Meijere, *ibid.*, 519 (1969).

unusual reactivity when n was slightly larger than four we have investigated the acid-catalyzed addition of acetic acid to *trans*-bicyclo[5.1.0]oct-3-ene (**3**).

When a sample of **3** was heated in acetic acid with a catalytic amount of *p*-bromobenzenesulfonic acid a complex mixture of products was formed. As shown below **3** gave 19% **4**, 16% **5**, 14% **6**, 14% **7**, 13% **8**, 5% **9**, 5% **10**, 3% **11**, 3% **12**, and 3% **13**, accounting for 95% **3**. In order to facilitate separation and identifi-



cation, the crude mixture of acetates, which resulted from the acid-catalyzed addition of acetic acid to **3**, was reduced to the corresponding alcohols with lithium aluminum hydride.

The characterization of the various products was accomplished in the following manner. The four olefinic products were identified through comparison of their vpc retention times with those of authentic samples⁷ on three columns of widely differing polarities. Preparative vpc on a Carbowax 20M-KOH coated stationary phase permitted separation of the alcoholic products into three different mixtures which contained **4** and **5**, **6** and **7**, and **11** and **12**, respectively.

The mixture of **11** and **12** gave infrared and nmr spectra which indicated that the components of the mixture were saturated alcohols. Vpc on an XF-1150 coated stationary phase showed the presence of two components in equal amounts. These components had vpc retention times identical with those of authentic samples of **11** and **12**.¹⁰ In addition the infrared spectrum of the isolated mixture of **11** and **12** was identical with that of a 50:50 mixture of **11** and **12**. Finally, Jones oxidation¹¹ of the mixture of **11** and **12** gave *cis*-bicyclo[3.3.0]octan-2-one (**14**) which was identical in all respects with an authentic sample.

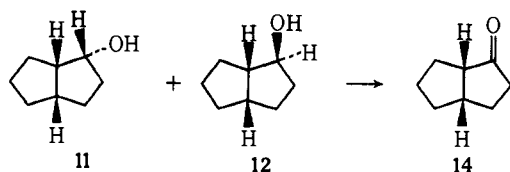
(7) Samples of 1,3-cyclooctadiene (**8**) and 1,5-cyclooctadiene (**13**) were commercially available. Samples of 1,4-cyclooctadiene (**9**) and *cis*-bicyclo[3.3.0]oct-2-ene (**10**) were prepared according to the method of Cope.^{8,9}

(8) A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **89**, 4024 (1967).

(9) A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

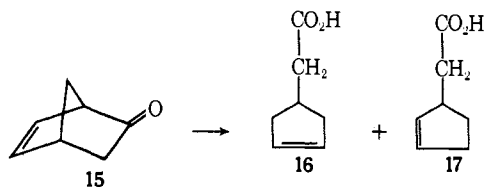
(10) A. C. Cope, H.-H. Lee, and H. E. Petree, *ibid.*, **90**, 2849 (1958).

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

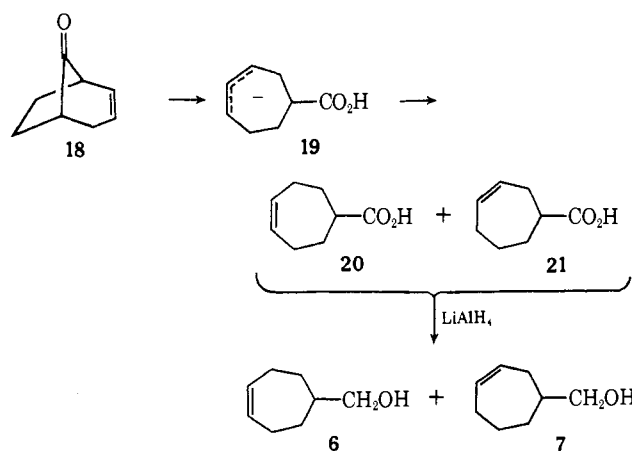


The mixture of **4** and **5** had infrared and nmr spectra consistent with the presence of unsaturated alcohols. A 50:50 mixture of authentic cycloocten-5-ol (**4**) and cycloocten-4-ol (**5**) had identical vpc retention times and spectra very similar to those of the isolated mixture. Hydrogenation of the mixture gave only cyclooctanol. Infrared analysis indicated that the isolated mixture consisted of 55% **4** and 45% **5**.

The mixture of **6** and **7** proved to be the most difficult to identify. The nmr spectrum of this mixture indicated the presence of unsaturated, primary alcoholic products. Spectra and vpc retention times of an authentic sample of **6**¹² were very similar to those of the mixture. Catalytic hydrogenation of the mixture gave a single product which was identical in all respects with a sample of cycloheptylmethanol prepared by catalytic hydrogenation of an authentic sample of **6**.¹² Unfortunately, we were unable to separate the mixture of **6** and **7** by vpc. Therefore we synthesized an authentic mixture. Utilizing the method of Gassman and co-workers,¹⁴ Paasivirta¹⁵ showed that norcamphor (**15**) could be cleaved to give an equimolar mixture of **16** and **17**. On the basis of this work, we subjected **18**¹⁶ to the efficient cleavage conditions of ether-potassium *tert*-



butoxide-water. Cleavage of **18** under these conditions should produce the allylic anion **19**, which on protonation should give comparable amounts of **20** and **21**.



Lithium aluminum hydride reduction of the cleavage

(12) An authentic sample of **6** was prepared *via* the lithium aluminum hydride reduction of 4-cycloheptene-1-carboxylic acid¹³ according to G. LeNy, *C. R. Acad. Sci., Paris*, **251**, 1526 (1960).

(13) G. Stork and H. K. Landesman, *J. Amer. Chem. Soc.*, **78**, 5129 (1956).

(14) P. G. Gassman, J. T. Lumb, and F. V. Zalar, *ibid.*, **89**, 946 (1967).

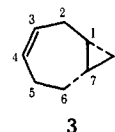
(15) J. Paasivirta, *Tetrahedron Lett.*, 2867 (1968).

(16) We wish to thank Professor J. Swenton for providing a generous sample of **18**.

mixture should then produce a mixture of **6** and **7**. The product of this reduction was spectroscopically identical in all respects with the mixture of **6** and **7** obtained from **3**. On the basis of the analogous work of Paasivirta¹⁵ it is felt that protonation should occur with comparable ease at either end of the allylic anion in **19** and that an approximately equimolar mixture of **20** and **21** (and therefore of **6** and **7**) should be formed. On this basis it was assumed that **3** gave approximately equal amounts of **6** and **7**.

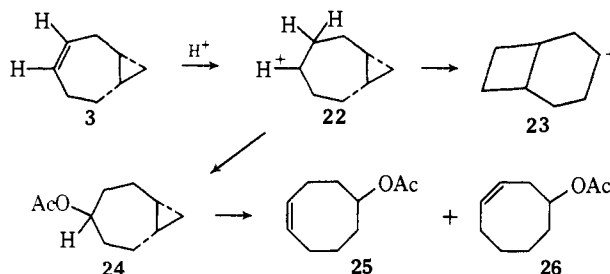
Discussion

In principle, **3** might be expected to undergo product determining¹⁷ protonation at positions 3, 4, 7, 8, or 1.



This study was designed to distinguish between the ease of product determining protonation of the double bond (positions 3 and 4) and product determining protonation of the trans-fused cyclopropane ring (positions 7, 8, and 1). In this regard we shall first consider the effects of protonation of the double bond. We will then demonstrate that all of the observed products can arise in a straightforward manner *via* initial protonation of the cyclopropane ring.¹⁸

Protonation at position 3 would produce the carbonium ion **22** which would be expected to either rearrange to the ion **23** or add acetic acid to produce **24**.

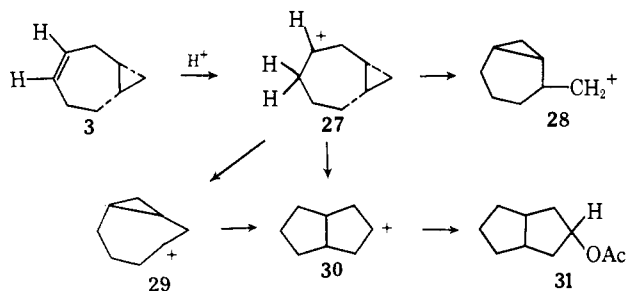


No products derived from the charged bicyclo[4.2.0]octane nucleus **23** were found. This would appear to rule out **23** as an intermediate. Similarly, the acetate **24**¹ was not present in the product mixture. However, since **24** would still contain a trans-fused cyclopropane, it seemed likely that if **24** were formed it might not survive the reaction conditions. This premise was verified by the finding that under the reaction conditions **24** gave a 50% yield of a mixture of **25** and **26**. In addition smaller amounts of four other products were formed. Since these four products were not observed in the acid-catalyzed addition of acetic acid to **3**, **24** could not have been an intermediate in the reactions of **3** with acid. The absence of products derived from both **23** and **24** indicates that product-determining protonation of **3** does not occur at the 3 position.

(17) The term product determining is used here to distinguish between completely reversible protonation which always gives back starting material and protonation which is followed by subsequent reactions of the resulting carbonium ion. The latter type of protonation could be partially reversible.

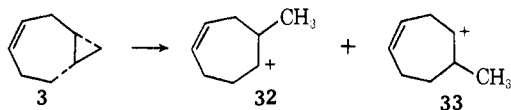
(18) The acid-catalyzed ring opening of *trans*-bicyclo[5.1.0]octane has been studied. For a discussion of the protonation of this saturated bicyclic see ref 6d.

Protonation of **3** at position 4 would produce the cation **27**. If this protonation were product determining, **27** might be expected to undergo a variety of

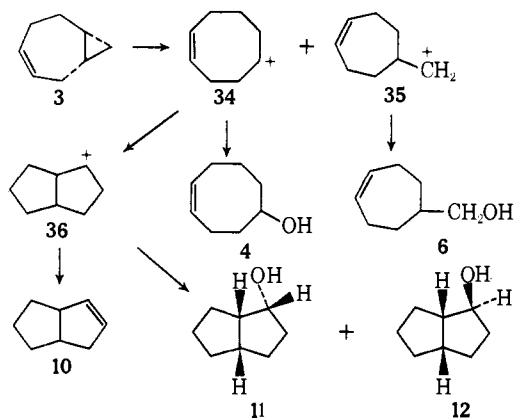


rearrangements. Migration of the C₁-C₃ bonding electron pair would result in the formation of the primary carbonium ion **28**. No products related to **28** were observed. A shift of the C₁-C₇ bonding electron pair could produce either **27** in a degenerate rearrangement if the ring fusion remained trans, or the cation **29**, if the ring fusion became cis. No products were observed which might have resulted from capture of nucleophilic solvent by **29**. An alternate mode of shifting the C₁-C₇ bonding electrons would yield the cation **30**. This ion could readily account for the formation of the olefin **10**. However, it seems likely that **30** should react with solvent to yield at least a small amount of **31**. The complete absence of 3-substituted bicyclo[3.3.0]octanes indicated that **30** was not an intermediate in the acid-catalyzed addition of acetic acid to **3**. Thus, it seems probable that protonation of **3** at position 4 was not product determining.

Protonation of **3** at position 8 would yield the methyl-substituted cycloheptenyl cations **32** and/or **33**. The absence of methyl-substituted products rules out this mode of protonation.

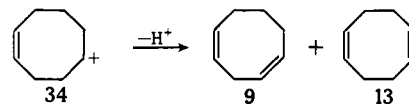


We are left with the possibilities of protonation at either C₁ or C₇. Careful analysis indicates that all of the products can be conveniently accounted for on the

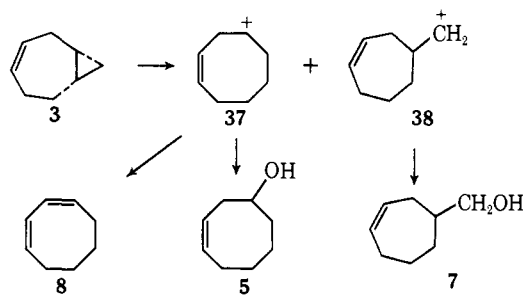


basis of protonation at these two positions. Protonation at C₁ would give the cations **34** and **35**. Direct capture of nucleophilic solvent by **34** would lead to **4**. A shift of the π electrons would give **36** which could lose a proton to give **10** or add solvent to account for **11** and

12. Solvent capture by **35** provides a simple explanation of the origin of **6**. In addition to explaining the origin of **4**, **6**, **10**, **11**, and **12**, the protonation of **3** at C₁ also readily explained the presence of **9** and **13**. Loss of a proton from **34** can occur in either direction to yield either of these dienes.

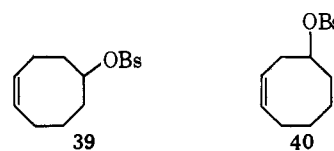


Protonation of **3** at the 7 position would produce the ions **37** and **38**. Solvent capture by **37** would lead to **5** while a similar reaction of **38** would account for **7**.

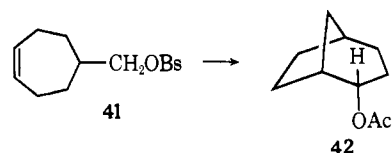


Proton expulsion by **37** would give **8** or **9**, depending on which proton was lost.

Owing to the key positions which the ions **34** and **37** have in our mechanistic scheme, it was of interest to compare the fate of these ions generated from protonation of **3** with the fate of similar ions generated from other precursors. Cope and coworkers^{9,19} have studied the solvolysis of **39** and **40** which would be expected to yield the ions **34** and **37**, respectively. Indeed, the products from **39** were the same as those postulated to arise



via **34**, although the ratios of products were different. These differences were probably due to the differences in the conformation and energetics of the initially generated cations. Cope and coworkers have found that the solvolysis of **40** gave *cis*-bicyclo[5.1.0]octan-2-ols (a mixture of *exo* and *endo*) in addition to **5** which we have postulated as arising from **37**. However, under our reaction conditions these *cis*-bicyclo[5.1.0]octan-2-ols were readily converted to **5**. In line with this discussion, it is interesting to note that LeNy¹² has studied the solvolysis of **41** and has found that solvolysis occurred with participation of the π electrons of the double bond to yield **42**. We observe no products with the



bicyclo[3.2.1]octane skeleton. This is reasonable since the *trans*-fused nature of **3** would not permit the initial

(19) A. C. Cope, S. Moon, and C. H. Park, *J. Amer. Chem. Soc.*, **84**, 4843 (1962); A. C. Cope, S. Moon, P. E. Peterson, *ibid.*, **84**, 1935 (1962).

formation of the ion **35** in a conformation suitable for participation of the π -electrons. Since the primary cation **35** should be highly reactive it is not surprising that it rapidly reacts with solvent to eventually yield **6**.

The products derived from the acid-catalyzed addition of acetic acid to **3** clearly demonstrate that product-determining protonation of the cyclopropane ring is preferred to similar protonation of the double bond. This is consistent with the expected reactive nature of the trans-fused cyclopropyl ring of **3**. The similarity in the ratios of **4** and **5**, and of **6** and **7**, indicates that the presence of the double bond exerts relatively little influence insofar as whether protonation occurs at C₁ or C₇. A curiosity in this respect is the relatively large amounts of the primary carbonium ions **35** and **38** which result from these protonations.²⁰

Summary

The product-determining protonation of **3** occurred exclusively at the 1 and 7 positions of the bicyclic nucleus to give a mixture of ten products. These protonations were consistent with expectations based on the predicted reactivity of the trans-fused cyclopropane ring in *trans*-bicyclo[*n*.1.0]alkanes where *n* is sufficiently small. In line with the concept that such ring fusions result in the formation of "twist" bent bonds, we are continuing our efforts to synthesize such systems with even more highly strained trans-fused cyclopropanes than that found in **3**.

Experimental Section

trans-Bicyclo[5.1.0]oct-3-ene (3). The preparation of **3** was carried out as previously described.¹

Acid-Catalyzed Addition of Acetic Acid to 3. A 356-mg sample of **3** was dissolved in 50 ml of 0.082 *N* *p*-bromobenzenesulfonic acid in acetic acid. The resulting solution was maintained at 80° for 3 hr. The reaction mixture was cooled and poured onto 100 ml of ice water, and the solution was extracted thoroughly with ether. The combined ether extracts were washed with water, saturated sodium bicarbonate solution, water, and saturated brine, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent was carefully removed by distillation. The residue was dissolved in 20 ml of anhydrous ether and this ethereal solution was slowly added to a stirred suspension of 0.40 g of lithium aluminum hydride in 30 ml of ether. After stirring for 2 hr the reaction mixture was hydrolyzed by the dropwise addition of 1.60 g of a 10% sodium hydroxide solution. After stirring for several hours the solution was filtered to remove the precipitated inorganic salts, and the ether was removed from the filtrate by careful distillation to give a mixture of ten products.

The olefinic products were identified by comparison of the vpc retention times with those of authentic samples on three vpc columns of widely differing polarities: 10% SE-30 on 80–100 Diatoport S at 55°, 10% Carbowax 20M-KOH (4:1) on 60–80 Chromosorb W at 70°, and 1% FS 1265 on 80–100 Chromosorb G at 40°. In this manner the presence of 1,3-cyclooctadiene (**8**), 1,4-cyclooctadiene (**9**), *cis*-bicyclo[3.3.0]oct-2-ene (**10**), and 1,5-cyclooctadiene (**13**) was established.

Part of the crude reaction mixture was subjected to preparative vpc on a 10% Carbowax 20M-KOH (4:1) on 60–80 Chromosorb W column at 130°. This separated the alcoholic components of the reaction mixture into three fractions.

The first fraction to elute was shown by vpc on a 2% XF 1150 on 80–100 Chromosorb G column at 100° to consist of an equimolar mixture of **11** and **12** through a comparison of retention times with those of authentic samples.¹⁰ Dropwise addition of Jones reagent to a solution of 10 mg of this fraction in 10 ml of acetone was carried out until a brown coloration persisted. The solution

was then stirred for 5 min, methanol was added to destroy any excess reagent, and water was added until all the salts were dissolved. The aqueous solution was extracted with ether and the ethereal extracts were combined and washed with water, saturated sodium bicarbonate, water, and saturated brine solution. The ethereal solution was dried over anhydrous magnesium sulfate and the drying agent was removed by filtration. The solvent was removed by careful fractional distillation to yield a single product which was shown to be identical with an authentic sample of *cis*-bicyclo[3.3.0]octan-2-one¹⁰ through a comparison of vpc retention times on three columns of greatly differing polarity.²¹

The second fraction gave an infrared spectrum with absorptions at 3.08 μ (OH stretch), 3.40 μ (vinylic CH stretch), 6.06 μ (C=C stretch), and characteristic peaks at 13.17, 13.70, and 14.12 μ . The nmr spectrum showed a two-proton multiplet centered at τ 4.30 (vinylic hydrogens) and a one-proton multiplet centered at τ 6.20 (HCOH). On the basis of these spectral data it was assumed that this fraction contained a mixture of unsaturated secondary alcohols. The infrared and nmr spectra were very similar to those of an equimolar mixture of authentic samples of cycloocten-5-ol (**4**) and cycloocten-4-ol (**5**). In addition vpc retention times of this synthetic mixture were identical with those of the reaction product on 10% Carbowax 20M-KOH (4:1) on 60–80 Chromosorb W at 150°, on 2% XF 1150 on 80–100 Chromosorb G at 100°, and on 3% FFAP on 45–60 Chromosorb G at 120°. A 15-mg sample of the isolated mixture was dissolved in 5 ml of ether and 5 mg of 5% palladium on carbon was added. The mixture was kept under a positive pressure of hydrogen for 8 hr and the catalyst was separated from the reaction mixture by centrifugation. The ethereal solution was shown to contain only one product which was identical with cyclooctanol in all respects. The relative amounts of **4** and **5** in the mixture were determined by infrared analysis on a Beckman IR-9 using a 5% solution in carbon disulfide. The characteristic absorptions of **4** at 726 cm⁻¹ and **5** at 758 cm⁻¹ were used in this determination. In this way the ratio of **4**:**5** was estimated to be 55:45.

The third fraction isolated by preparative vpc had infrared absorptions (neat) at 3.08 μ (OH stretch), 3.39 μ (vinylic CH stretch), 6.05 μ (C=C stretch), and characteristic peaks at 9.30, 9.60, and 9.80 μ . The nmr spectrum of this fraction showed a two-proton multiplet at τ 4.23 (vinylic hydrogens) and two doublets, the first centered at τ 6.56 (*J* = 6 cps) and the second centered at τ 6.54 (*J* = 6 cps). These spectral data were interpreted to mean that the fraction contained a mixture of two cycloheptylcarbinols. An authentic sample of **6** had infrared and nmr spectra similar to, but not identical with, the isolated fraction. A 15-mg sample of the isolated fraction was dissolved in 5 ml of ether and 5 mg of 5% palladium on carbon was added. The mixture was kept under a positive hydrogen pressure for 8 hr and then the catalyst was separated by centrifugation. Vpc of the ethereal solution showed that the only hydrogenation product present was cycloheptylmethanol. Removal of the ether under reduced pressure gave a residue which had an infrared spectrum identical with cycloheptylmethanol. Comparison of the infrared and nmr spectra of the isolated fraction with those of an authentic mixture of **6** and **7** indicated that the third fraction consisted of an approximately equimolar mixture of **6** and **7**.

The yields reported in the main body of this paper were determined by vpc and represent the average of three runs utilizing β -phenylethanol as an internal standard. The runs were exact duplicates of the preparative run described above. The yields were obtained *via* vpc on a 10% Carbowax 20M-KOH (4:1) on 60–80 Chromosorb W column with temperature programming. The olefins were determined at 70° and the alcohols were measured at 150°.

Cleavage of 18. In a 15-ml three-necked round bottomed flask equipped with a vent tube and rubber septum was placed 1.65 g of potassium *tert*-butoxide after the apparatus had been thoroughly flushed with dry nitrogen. The flask was cooled to 0° and 7 ml of anhydrous ether and 0.0886 g of water were added. The ice bath was removed and 0.200 g of **18** was added to the stirred solution. The reaction mixture was stirred at room temperature for 3 hr and cooled in an ice bath, and ice was added to the reaction mixture until two clear liquid phases were present. The aqueous phase was separated, diluted with 5 ml of water, and acidified with dilute

(20) Similar results have been noted for the acid-catalyzed ring opening of *trans*-bicyclo[5.1.0]octane by Wiberg and deMeijere.^{6d}

(21) The columns used were 2% XF 1150 on 60–80 Chromosorb G at 100°, 10% Carbowax 20M-KOH (4:1) on 60–80 Chromosorb W at 135°, and 10% SE 30 on 80–100 Diatoport S at 85°.

hydrochloric acid, and the acidified solution was thoroughly extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and filtered and the solvent was removed by careful distillation. The residue was dissolved in 5 ml of anhydrous ether and this ethereal solution was added slowly to a refluxing solution of 0.075 g of lithium aluminum hydride in 20 ml of ether. After the reaction mixture had been refluxed for 3 hr, the reaction vessel was cooled and 0.300 g of 10% sodium hydroxide solution was added dropwise. The solution was stirred for several hours and the precipitated inorganic salts were removed by filtration. The ether was removed by distillation and the residue was molecularly distilled to give 30 mg of a mixture of alcohols which had infrared and nmr spectra identical with those of the mixture obtained in the third fraction of products isolated from the acid-catalyzed addition of acetic acid to **3**.

Acid-Catalyzed Reaction of 4-Acetoxy-*trans*-bicyclo[5.1.0]octane (24) with Acetic Acid. A sample of **24** was dissolved in acetic acid which was 0.082 *N* in *p*-bromobenzenesulfonic acid. The solution was heated to 80° for 3 hr, cooled, and worked up in a manner similar to that described in the acid-catalyzed addition of acetic acid to **3** (*vide supra*). Vpc analysis showed the presence of a 50% yield of an equimolar mixture of **4** and **5**. In addition the presence of four other components was demonstrated. These components were not present in the reaction mixture obtained from the acid-catalyzed addition of acetic acid to **3**. As a result they were not characterized.

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Stable Free Radicals. V. The Reaction between 1-Ethyl-4-carbomethoxypyridinyl and Benzyl Halides¹

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Abstract: The rates of reaction of the stable free radical, Py·, 1-ethyl-4-carbomethoxypyridinyl, with benzyl bromide and a number of benzyl chlorides (4-CH₃O, 4-CH₃, H, 4-Cl, 4-NO₂) have been measured in several solvents and, for the unsubstituted chloride and bromide, at several temperatures. The rate constant for the reaction of Py· with C₆H₅CH₂Cl is little affected by substitution except for the 4-NO₂ derivative, and the solvent effect on the rate is modest for C₆H₅CH₂Cl and C₆H₅CH₂Br. Criteria for decisions about the mechanisms of radical reactions are discussed and it is concluded that Py· reacts with benzyl chlorides and bromides (except for the 4-NO₂ compound) in an *atom-transfer* reaction.

Free radicals which are unreactive enough to be transferred and utilized under conditions different from those under which the radical was generated may be termed "stable."^{1a,4} Stable radicals offer the opportunity for direct kinetic measurements under different conditions, permitting the use of such mechanistic criteria as solvent sensitivity. In addition, stable radicals discriminate among possible reactants to a far greater extent than reactive radicals and thus offer one of the most sensitive probes into reactivity toward radicals.

We have now examined the rates of reaction of the stable pyridinyl radical, 1-ethyl-4-carbomethoxypyridinyl (**1**), with a number of benzyl halides. The term *atom-transfer reaction* fits the characteristics of most of the reactions examined. One striking exception is the very rapid reaction of **1** with 4-nitrobenzyl halides, which we believe to be an *electron-transfer reaction*. The latter cases are treated in the following article.⁵

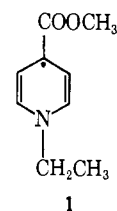
(1) Previous articles in this series are: (a) E. M. Kosower and E. J. Poziomek, *J. Amer. Chem. Soc.*, **86**, 5515 (1964); (b) E. M. Kosower and J. L. Cotter, *ibid.*, **86**, 5524 (1964); (c) E. M. Kosower and I. Schwager, *ibid.*, **86**, 5528 (1964); (d) M. Itoh and E. M. Kosower, *ibid.*, **90**, 1843 (1968).

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(4) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 405.

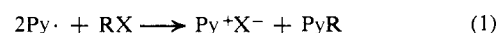
(5) M. Mohammad and E. M. Kosower, *J. Amer. Chem. Soc.*, **93**, 2713 (1971).



1

Results

The reaction of pyridinyl radicals with alkyl halides consumes two radicals for each halide (eq 1). The



ultimate products of the reaction are the pyridinium halide and a mixture of 1,2- and 1,4-dihydropyridines.^{1a,c,6}

The rates of reaction are easily measured by following the disappearance of Py· at λ_{max} 6325 (ϵ_{max} 83) or 3950 Å (ϵ_{max} 4700) in the apparatus shown in Figure 1. The rate constants for the reaction of Py· with benzyl halides were calculated from eq 2, corresponding to a mechanism in which a bimolecular reaction between a radical and halide is succeeded by a fast reaction which consumes a second radical (eq 3 and 4).

$$k = \frac{1}{t} \frac{1}{(2A_0 - B_0)} \ln \frac{B_0[(2A_0 - B_0) + B]}{2A_0B} \quad (2)$$

(6) E. M. Kosower and H. P. Waits, Abstracts of the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 109S, and manuscript in preparation.