pK_{CsCHA} values are summarized in Table I.

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Registry No. 1, 2071-20-7; I·Cs, 80359-57-5; 2, 7650-91-1; 2·Cs, 80359-58-6; 3, 80359-59-7; 3·Cs, 80359-60-0; 4, 1031-93-2; 4·Cs, 80359-61-1; 6, 2959-74-2; 6·Cs, 80359-62-2; 7, 80359-63-3; 7·Cs, 80359-64-4; 8, 6840-28-4; 8·Cs, 80359-65-5; benzyl chloride, 100-44-7; chlorodiphenylphosphine, 1079-66-9; lithium diphenylphosphide, 4541-02-0; *p*-phenylbenzyl bromide, 2567-29-5; 4-(phenylmethyl)-1,1-biphenyl, 613-42-3; 1-methyl-1,1′:4,1″-terphenyl, 28952-41-2; 4,4″-methylenebis[1,1′-biphenyl], 3901-32-4; 4-methyl-1,1′-biphenyl, 644-08-6.

Long-Range Corner Participation by Cyclopropane. 2. Synthesis and Study of 1-Substituted Tricyclo[3.2.2.$0^{2,4}$]nonanes[1]

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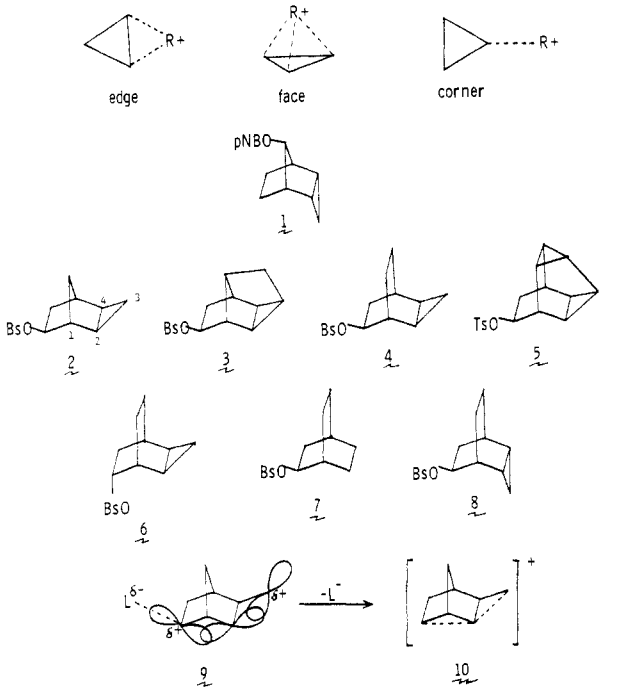
Acidity studies on tricyclo[3.2.2.$0^{2,4}$]nonane-1-carboxylic acid (**16**-COOH) vs. bicyclo[2.2.2]octane-1-carboxylic acid (**17**-COOH) show a slight inductive withdrawal by the cyclopropane ring. In spite of this, acetolysis of (tricyclo[3.2.2.$0^{2,4}$]non-1-yl)methyl tosylate (**16**-CH_2OTs) vs. (bicyclo[2.2.2]oct-1-yl)methyl tosylate (**17**-CH_2OTs) yields evidence of an anchimeric effect of 18.3 at 25 °C for cyclopropane assistance in this solvolysis. Product studies of the acetolysis of **16**-CH_2OTs demonstrate that *cyclopropano* ring expansion is preferred, and 83% of the product is acetate **21**, whereas *ethano* bridge migration is unimportant. These results, as well as studies undertaken in a previous paper, are discussed in terms of corner participation by the cyclopropane ring at the 1-carbinyl group via the back lobe at C-2 of the 2,4-bond.

Long-range effects of cyclopropane rings on carbonium ion processes have been of interest for some time. A review[2] extensively summarizes the work to 1973 and discusses in detail the anchimeric assistance associated with some homocyclopropylmethyl systems which include certain geometric requirements. When these constraints are absent, then no cyclopropyl participation occurs. Most examples of long-range participation by cyclopropane involve the "edge" of the cyclopropane ring interacting with the carbonium ion center, shown schematically in Chart I. When the geometry is ideal for edge participation, extremely large anchimeric effects can be observed, most notably in *endo,anti*-tricyclo[3.2.1.$0^{2,4}$]oct-8-yl *p*-nitrobenzoate (**1**), which solvolyzes 10^{12} times faster than the 7-norbornyl system.[3-7] Since most of the electron density of the bent bonds of cyclopropane is located outside the linear carbon–carbon line, it is not surprising that such participation is preferred.

In contrast, participation by the face of the cyclopropane ring has, in the systems studied, been shown not to exist.[8-14] In between these two extremes is "corner" or

Chart I



"end-on" participation, which has been observed in only a few cases but which shows nowhere near the anchimeric effects of edge participation.[2] The best examples of corner participation may be the series of compounds **2**–**5**. The

(1) (a) Paper 1: Chenier, P. J.; Kiland, P. J.; Schmitt, G. D.; VanderWegen, P. G. *J. Org. Chem.* **1980**, *45*, 5413. (b) A portion of the present paper was presented at the Joint Central-Great Lakes Regional Meeting of the American Chemical Society, Dayton, OH, May 1981, Abstract No. ORGN-264, and at the 1981 Kilpatrick Symposium on Carbenes, Carbenoids, and Cyclopropanes in Organic Synthesis, Illinois Institute of Technology, Chicago, IL, June 1981.

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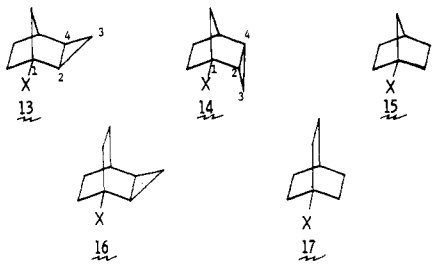
0022-3263/82/1947-0770$01.25/0

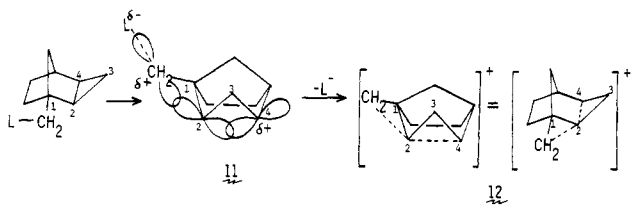
Chart II



exo-brosylate **2** solvolyzes 1130–1410 times faster in acetic acid at 25 °C than when the brosylate is endo.[15] *exo*-Brosylate **3** solvolyzes only 60 times faster than its endo analogue[16] because the cyclopropane ring in **3** is tilted back by the extra methylene bridge. *exo*-Cyclopropyl-*exo*-brosylate **4** solvolyzes 11 times faster than *exo*-cyclopropyl-*endo*-brosylate **6**,[17] 6.8 times faster than 2-bicyclo[2.2.2]octyl brosylate (**7**),[17,18] and 56 times faster than *endo*-cyclopropyl-*exo*-brosylate **8**.[17] Finally, tosylate **5** solvolyzes 20 times faster than 2-bicyclo[2.2.2]octyl tosylate.[19]

The developing p orbital in the solvolysis of compounds like **2** may not interact with the edge of the three-membered ring because of the distortion that would be required of these rigid polycyclic systems. Instead they may undergo assistance at the C-2 corner by the strategically placed back lobe of the 2,3-bond.[2,16] (This numbering of the bonds in **2** is used so that it will be analogous to later discussions of 1-substituted tricyclic systems.) Recalling that the carbon–carbon bonds of cyclopropane have much p character (most prefer to think of them as sp^5 hybridized), there is appreciable size to the back lobes of these overlapping orbitals. The back lobe of the 2,3-bond is in an excellent position to overlap with the developing p orbital as the leaving group departs. This is shown in structures **9** and **10**.

Models show that, in analogy to the back lobe of the 2,3-bond for brosylate **2**, the back lobe of the 2,4-bond in certain 1-carbinyl-substituted tricyclic systems is in an excellent position to overlap with the developing p orbital at the 1-carbinyl carbon, exemplified in structures **11** and **12**. Our first paper in this series[1] summarized our work



on the solvolysis of *exo*- and *endo*-(tricyclo[3.2.1.$0^{2,4}$]oct-1-yl)methyl tosylates (**13**-CH_2OTs and **14**-CH_2OTs, Chart II) and compared their reactivities to each other and to that of (norborn-1-yl)methyl tosylate (**15**-CH_2OTs). We now report the results of our synthesis and solvolysis of

Scheme I

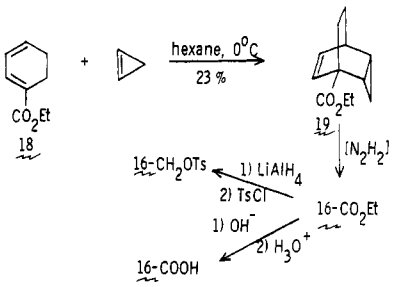


Table I. pK_a Studies at 28–29 °C

acid	pK_a ± 0.01	acid	pK_a ± 0.01
bicyclooctyl (17-COOH)	6.57[a]	*exo*-tricyclooctyl (13-COOH)	6.25[b]
tricyclononyl (16-COOH)	6.51	*endo*-tricyclooctyl (14-COOH)	6.15[b]
bicycloheptyl (15-COOH)	6.35[a,b]		

[a] Reference 28 reported 6.62 for 17-COOH and 6.37 for 15-COOH at 25 °C. [b] Reference 1.

Table II. Acetolysis Data

tosylate	temp,[a] °C	k,[b] s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
17-CH_2OTs	99.2 ± 0.1	(4.86 ± 0.25) × 10^{-6}	28.02	−8.07
	130.8 ± 0.1	(1.02 ± 0.062) × 10^{-4}		
16-CH_2OTs	98.9 ± 0.3	(44.2 ± 4.2) × 10^{-6}	26.05	−8.90
	130.8 ± 0.1	(7.74 ± 0.72) × 10^{-4}		

[a] Error expressed as a standard deviation. [b] Error expressed at the 95% confidence level. All correlation coefficients were >0.993.

(tricylco[3.2.2.$0^{2,4}$]non-1-yl)methyl tosylate (16-CH_2OTs) and its reactivity vs. (bicyclo[2.2.2]oct-1-yl)methyl tosylate (17-CH_2OTs). Acidity studies on the bridgehead acid 16-COOH vs. 17-COOH are also included in the present paper.

Results

Although some 1-substituted tricyclo[3.2.2.$0^{2,4}$]nonanes are known,[20,21] the desired 1-carbinyl tosylate 16-CH_2OTs and acid 16-COOH are not. Ester 16-CO_2Et has been made but by a laborious five-step synthesis from ethyl 1,3-cyclohexadiene-1-carboxylate (**18**).[22,23] We were able to synthesize this ester in only two steps as outlined in Scheme I. A convenient low-temperature Diels–Alder cycloaddition of **18** with cyclopropene gave a somewhat low yield of adduct **19**, but this could be easily separated from a higher boiling fraction. The cyclopropene was generated by the Closs method from allyl chloride and sodium amide.[24,25] Higher molecular weight adducts of **18** with oligomers of cyclopropene prevent the yield from being

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(17) Schueler, P. E.; Rhodes, Y. E. "Abstracts of Papers", 164th National Meeting of the American Chemical Society, New York, NY, Aug 1972; American Chemical Society: Washington, DC, 1972; No. ORGN-129. See also: Schueler, P. E. Ph.D. Dissertation, New York University, New York, NY, 1972. We thank Professor Rhodes for furnishing us with the details.
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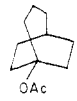
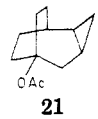
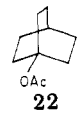
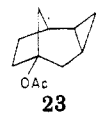
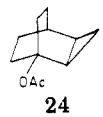
Table III. Acetolysis Rate Constants at 25 °C

tosylate	10^9k, s^{-1}	k_{rel}
17-CH_2OTs[a]	0.31	1.00
16-CH_2OTs[a]	5.68	18.3
15-CH_2OTs[b]	1.33	4.29
13-CH_2OTs[b]	8.80	28.4
14-CH_2OTs[b]	1.16	3.74

[a] This study. [b] Reference 1.

Table IV. Acetolysis Products

tosylate	major product	% yield	type of ring expansion
17-CH_2OTs[a,b]	 20	≥91	ethano
16-CH_2OTs[a]	 21	≥83	cyclopropano
15-CH_2OTs[c]	 22	≥98	methano
13-CH_2OTs[c]	 23	≥95	cyclopropano
14-CH_2OTs[c]	 24	≥99	methano

[a] This study. [b] References 26 and 27 reported the alcohol of **20** as the only product in the hydrolysis of 17-CH_2OTs. [c] Reference 1.

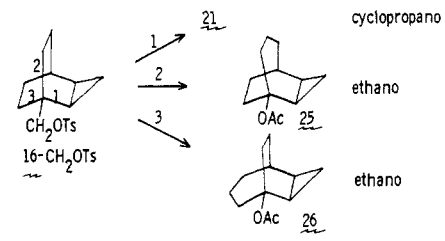
higher, as observed in other reactions of this type.[25]

Mild hydrogenation via diimide, generated from potassium azodicarboxylate, gave the saturated ester 16-CO_2Et. No exo/endo isomerism is possible here. Routine saponification gave the acid **16**-COOH, and hydride reduction followed by treatment with tosyl chloride made the tosylate 16-CH_2OTs readily available.

(Bicyclo[2.2.2]oct-1-yl)methyl tosylate (17-CH_2OTs) and the bridgehead acid (17-COOH) have been synthesized and studied, respectively, in solvolysis and acid dissociation.[23,26-28] These studies were repeated[29] under conditions identical with those used for systems **13**–**16**. Table I shows the results of pK_a studies done on acids **13**-COOH to **17**-COOH in 50% ethanol at 28–29 °C. Table II gives the acetolysis rate constants and activation parameters obtained for tosylates 16-CH_2OTs and 17-CH_2OTs. Table III shows the rate constants of tosylates 13-CH_2OTs to 17-CH_2OTs in acetolysis extrapolated to 25 °C. Table IV gives the major product formed in the acetolysis of these five tosylates.

Acetate **20** is the only possible ring-expanded bridgehead acetate from tosylate 17-CH_2OTs, and its structure is proved by its spectral properties. Previous hydrolysis studies of tosylate 17-CH_2OTs[26,27] showed that the bridgehead alcohol corresponding to acetate **20** is the only product formed in more polar solvents. Gas chromatographic analysis and spectral determination of a second trace product showed it to be unrearranged acetate 17-CH_2OAc. A trace third peak in the chromatogram was not determined because of insufficient amounts.

Scheme II



The structural assignment for the major product of the acetolysis of (tricyclo[3.2.2.$0^{2,4}$]non-1-yl)methyl tosylate (16-CH_2OTs) proved to be much more challenging. Only one major product (83% of the mixture) was formed. Three other trace products were not identified. GC was used to separate the major isomer. Proton NMR analysis at 60 MHz immediately identified this major isomer as a rearranged bridgehead acetate by the lack of any hydrogens α to the acetate group downfield at δ 3.5–4.0. ^{13}C NMR analysis[30] showed 12 carbons including the carbonyl carbon at 169.8 ppm and a quaternary bridgehead carbon deshielded by the acetate moiety at 82.7 ppm, but examination of the chemical shifts of the other 10 carbons did not prove the structure of this product conclusively. The three possible ring-expanded acetate products **21**, **25**, and **26** (Scheme II) are all unknown and would be predicted to have similar NMR and ^{13}C NMR spectra. Compound **21** would arise from cyclopropano bridge expansion, **25** from one ethano bridge expansion, and **26** from the other ethano bridge expansion. Acetates **25** and **26** are exo and endo isomers of each other.

Fortunately, high-resolution NMR spectoscopy at 500 MHz[31] allowed us to distinguish the actual product **21** from **25** and **26**, since **21** is the only isomer of the three with a methylene group adjacent to the cyclopropane ring. Table V gives the analysis of this methylene group as a and b and the neighboring cyclopropyl methine as c. In the undecoupled spectrum a appears as a doublet of doublets of doublets with a large geminal coupling of 14 Hz to b, a trans vicinal coupling of 10 Hz to c, and a small long-range coupling of 2 Hz. Although proton d is not resolved in the spectrum, it is a likely candidate for this third coupling through a W effect. Proton b is a doublet of doublets with a large geminal coupling of 14 Hz to a and a smaller cis vicinal coupling of 3 Hz to c. Proton c is a multiplet since it is coupled not only to a and b but also to the other three cyclopropyl hydrogens.

Irridation of c simplifies a to a doublet of doublets with J = 2 and 14 Hz, confirming that $J_{a,c}$ = 10 Hz. Proton b is also simplified to a doublet with J = 14 Hz, confirming that $J_{b,c}$ = 3 Hz. Irradiation of b simplifies a to a doublet

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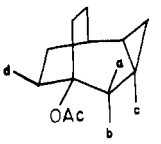
(29) We thank Professor J. W. Wilt, Loyola University, Chicago, IL, for samples of 17-COOH and 17-CH_2OH.
(30) We thank Professor J. M. Cook, University of Wisconsin—Milwaukee, for providing this spectrum.
(31) This instrument is available in the Department of Chemistry, University of Chicago.
(32) (a) Bly, R. S.; Cooke, Q. E. "Abstracts of Papers", 148th National Meeting of the American Chemical Society, Chicago, IL, Sept 1964; American Chemical Society: Washington, DC, 1972; No. 80-S. (b) Bly, R. S.; Quinn, E. K. "Abstracts of Papers", 153rd National Meeting of the American Chemical Society, Miami Beach, FL, Apr 1967; American Chemical Society: Washington, DC, 1972; No. 91-O.

Table V. 500-MHz NMR Analysis of Acetate 21



21

			multiplicity (J, Hz)			
proton[a]	J, Hz	δ	no decoupling	irradn of c	irradn of b	irradn of a
a	1323	2.65	ddd (2, 10, 14)	dd (2, 14)	dd (2, 10)	
b	1041	2.08	dd (3, 14)	d (14)		d (3)
c	406	0.81	m		m (changed)	m (changed)

[a] $J_{a,b}$ = 14, $J_{a,c}$ = 10, J_{bc} = 3, and $J_{a,d}$ = 2 Hz.

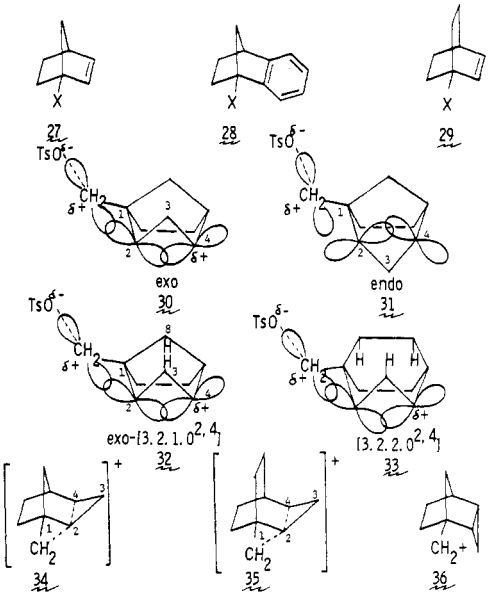
of doublets with J = 2 and 10 Hz, proving that $J_{a,b}$ = 14 Hz. Proton c is changed by this irradiation but is still a multiplet. Finally, irradiation of a makes b a doublet with J = 3 Hz, showing that $J_{a,b}$ = 14 Hz. Proton c is also changed by this irradiation but is still a multiplet. These assignments could not be possible if structure **25** or **26** was the product, since the methylene group is not next to the cyclopropane ring in these structures.

Discussion

The acidity study of tricyclo[3.2.2.0^{2,4}]nonane-1-carboxylic acid (16-COOH) was performed to confirm our suspicion that, as with analogous cyclopropyl acids in this series, there is slight inductive withdrawal by the cyclopropane ring, causing a small increase in acidity and decrease in pK_a vs. the reference acid bicyclo[2.2.2]octane-1-carboxylic acid (17-COOH), 6.51 vs. 6.57. This was shown to be the case in our previous work[1] with the *exo*-tricyclooctyl acid **13**-COOH and the *endo*-tricyclooctyl acid **14**-COOH, both of which have lower pK_a's than the bicycloheptyl acid **15**-COOH. We would certainly expect then that no inductive effect of cyclopropane could stabilize a carbonium ion generated at the 1-carbinyl position. In fact, a pure inductive effect of cyclopropane might be expected to slightly hinder solvolysis at the 1-carbinyl group. It is also interesting to note that a double bond and aromatic ring placed similarly in this series show similar but larger depressions of pK_a values.[28] Acids **27**-COOH and **28**-COOH (Chart III) have pK_a's of 5.98 and 5.88 vs. that of the bicycloheptyl acid **15**-COOH at 6.35. Similarly, acid **29**-COOH has a lower pK_a (6.20) vs. that of the bicyclooctyl acid **17**-COOH (6.57).

In the acetolysis studies we have previously explained[1] the anchimeric effect of the *exo*-cyclopropane ring in **13**-CH_2OTs and the propensity for this *exo*-cyclopropano bridge to ring expand in the product to be due to long-range corner participation of the back lobe of the 2,4-bond. When the cyclopropane ring is endo, as in tosylate **14**-CH_2OTs, the rate of solvolysis and the type of ring expansion, i.e., methano bridge migration, is similar to having no cyclopropane ring present. This is most readily seen in a side view of the exo (**30**) vs. the endo (**31**) case. As the tosylate leaves in *exo*-tosylate **13**-CH_2OTs, the incipient ion **30** can be stabilized by overlap with the back lobe of this strategically placed 2,4-bond. When the *endo*-tosylate **14**-CH_2OTs reacts via **31**, no such stabilization can take place. So k_{exo}/k_{endo} is 7.6 at 25 °C and only the *exo*-cyclopropano bridge migrates. This cannot be explained by inductive difference. Both are shown to be withdrawing in the acidity studies, whereas in acetolysis the *exo*-tosylate **13**-CH_2OTs is faster than even the bicycloheptyl tosylate **15**-CH_2OTs by a factor of 6.6, but by inductive withdrawal the *endo*-tosylate is slower than **15**-CH_2OTs.

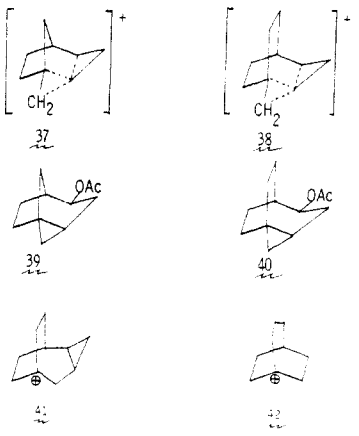
Chart III



An alternate interpretation for this kinetic and product difference between *exo*- and *endo*-cyclopropanes was presented by a referee to the original paper in this series,[1] involving relief of interaction between hydrogens at C-3 and C-8 in *exo*-tosylate **13**-CH_2OTs due to the boatlike shape of this ring system, causing **13**-CH_2OTs to solvolyze faster than **14**-CH_2OTs, where this interaction is not present. It is for this reason that the present study was initiated. In the tricyclononyl tosylate **16**-CH_2OTs no such interacting flagpole hydrogens exist. Also, the addition of an extra methylene group to this bridge would be expected to tilt the 1-carbinyl tosylate moiety down slightly and in a better position to overlap with the back lobe at C-2 if corner participation were operating. This can be seen in a comparison of structures **32** and **33**. Thus if relief of interaction of the hydrogens were important, we would expect no such anchimeric effect for tosylate **16**-CH_2OTs, but if corner participation were important, we would see the same (or possibly an increased) anchimeric assistance in the solvolysis of **16**-CH_2OTs via structure **33**.

Tosylate **16**-CH_2OTs *does* solvolyze 18.3 times faster than bicyclooctyl tosylate **17**-CH_2OTs, and its product study does show that once again the cyclopropano bridge ring expands. This can be explained by corner participation, and the present study rules out relief of interaction between the flagpole hydrogens in **13**-CH_2OTs. Participation by the 2,4-bond must be occurring in the rate-determining step for the solvolysis of both **13**-CH_2OTs and **16**-CH_2OTs and the ions are best represented as **34** and **35**. When the ring is endo there is no delocalization such

Chart IV



as in **36**. Whether or not the 1,2-bond is also delocalized in the rate-determining step is questionable, although the 1,2-bond certainly must break eventually since cyclopropano bridge expansion occurs and C-2 eventually becomes bonded to the CH_2 group in the product. The ions could be represented, though by this study need not be represented, with additional delocalization of the type shown in **37** and **38** (Chart IV). One may ask why breakage of the 2,4-bond does not become complete, yielding products derived from ring opening of the cyclopropane, as in **39** and **40**. This, of course, would require that a bridgehead spirocyclopropane be formed which is much too strained to be a viable product. But the lack of any ring opening does not preclude the 2,4-bond partially breaking and, through its back lobe, stabilizing the ion being generated.

Although we believe that corner participation by cyclopropane is the best and most complete way of explaining the kinetic and product studies, referees to this paper have pointed out alternative arguments in view of the lack of a large amount of assistance. There may be differential solvent participation in stabilizing the ground and transition states in the solvolysis of 16-CH_2OTs and 17-CH_2OTs. This is certainly possible, though we cannot develop a general theory explaining the solvolysis and products of 13-CH_2OTs–17-CH_2OTs on this basis. Also, the stabilities of the rearranged ions **41** (from 16-CH_2OTs) and **42** (from 17-CH_2OTs) may certainly be different, but we find difficulty with justifying **41** being more stable than **42**. It is even more challenging to explain the completely different pathways taken by *exo*-tosylate 13-CH_2OTs and *endo*-tosylate 14-CH_2OTs in terms of their rearranged ion stabilities. Finally, we do not deny that the solvolyses of these primary tosylates may be partially bimolecular, but this does not explain the data either. Adding a cyclopropane ring, especially an exo ring, would be expected to sterically slow down the bimolecular reaction if it has an effect at all. Our results do not show this to be the case.

Further work is being done on these and related cyclopropyl systems to delineate the extent of corner participation.

Experimental Section

Melting and boiling points are uncorrected. The melting points were taken on a Thomas-Hoover apparatus. The following instruments were used: a Varian T-60 NMR spectrometer, Perkin-Elmer 727 and 283 infrared spectrophotometers, and Varian Aerograph A-90-P and 700 Autoprep gas chromatographs. NMR data are given in parts per million (δ) relative to internal Me_4Si unless specified otherwise. Only significant IR absorptions (reciprocal centimeters) are listed. Gas chromatography was performed on SE-30 and QF-1 columns with helium as the carrier gas. Microanalyses were performed by Micro-Tech Laboratories.

Ethyl *endo*-Tricyclo[3.2.2.0^{2,4}]non-6-ene-1-carboxylate (19). A cyclopropene generator was set up, with a scale of 212 g of sodium amide and 425 mL of allyl chloride.[25] Ethyl 1,3-cyclohexadiene-1-carboxylate (**18**, 31.0 g, 204 mmol), made by the literature method,[22,23] was magnetically stirred in hexane (200 mL) at 0 °C. The cyclopropene was generated and bubbled through the hexane solution for 5 h during the addition of allyl chloride to sodium amide. The hexane solution was stirred overnight at 0 °C. The mixture was dried with anhydrous potassium carbonate and filtered, and the filtrate was evaporated and vacuum distilled. The product was contaminated with some starting material and a higher molecular weight byproduct. Redistillation gave **19** as a colorless oil: 9.00 g (46.9 mmol, 23%); bp 66–74 °C (0.3 mm); IR (neat) 3080 (cyclopropyl CH), 3055 (vinyl CH), 1760 (C=O), 1618 (very weak, C=C), 1258 (asymmetric CO), 1079 (symmetric CO) cm^{-1}; NMR (CCl_4, external Me_4Si) δ 5.6–6.2 (m, 2, vinyl), 4.23 (q, 2, CH_2O), 2.6–2.9 (m, 1, bridgehead), 1.35 (t, 3, CH_3), 0.8–2.0 (m, 4, CH_2), 0.1–0.7 (m, 4, cyclopropyl). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.04; H, 8.33.

Ethyl Tricyclo[3.2.2.0^{2,4}]nonane-1-carboxylate (16-CO_2Et). Potassium azodicarboxylate was prepared fresh by Thiele's method.[33] By use of the general procedure of Baird, Franzus, and Surridge,[34] ester **19** (15.0 g, 78.0 mmol) and potassium azodicarboxylate (50.5 g, 263 mmol, 3.4 equiv) in anhydrous methanol (180 mL) were reacted with acetic acid (33 mL) in methanol (150 mL) over 1.5 h. Stirring was continued an additional 1 h. Water (500 mL) was added, and the mixture was extracted four times with ether (150 mL). The ether layers were combined, dried with anhydrous magnesium sulfate, and filtered, and the filtrate was evaporated and vacuum distilled to give 16-CO_2Et as a colorless oil: 8.8 g (45.4 mmol, 58%); bp 69–74 °C (0.3 mm); IR (neat) 3079 (cyclopropyl CH), 1755 (C=O), 1242 (asymmetric CO), 1067 (symmetric CO) cm^{-1}; NMR (CCl_4, external Me_4Si) δ 4.08 (q, 2, CH_2O), 1.8–2.1 (m, 1, bridgehead), 1.27 (t, 3, CH_3), 0.8–1.8 (m, 8, CH_2), 0–0.7 (m, 4, cyclopropyl). The product contains some **19**, but a pure sample can be collected by GC (QF-1, 150 °C). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.02; H, 9.50.

(Tricyclo[3.2.2.0^{2,4}]non-1-yl)methyl Tosylate (16-CH_2OTs). Alcohol 16-CH_2OH was made by lithium aluminum hydride reduction of ester 16-CO_2Et in the normal fashion.[35] Vacuum distillation gave a 64% yield of a colorless oil: bp 73–81 °C (0.4 mm); IR (neat) 3342 (OH), 3079 (cyclopropyl CH), 1038 (CO) cm^{-1}; NMR (CCl_4) δ 3.55 (variable with concentration, s, 1, OH), 3.22 (s, 2, CH_2O), 1.1–2.1 (m, 9), 0.1–0.9 (m, 4, cyclopropyl). The crude alcohol was treated with tosyl chloride and pyridine in the usual manner,[36] and tosylate 16-CH_2OTs was formed in 62% yield. Six recrystallizations from petroleum ether (bp 30–60 °C) gave a pure sample: mp 50.5–52.5 °C; IR (KBr) 1343 and 1170 (S=O) cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.9 (AA'XX', 4, Ar H), 3.72 (s, 2, CH_2O), 2.41 (s, 3, CH_3), 1.7–2.0 (m, 1, bridgehead), 1.1–1.7 (m, 8, CH_2), 0.1–1.0 (m, 4, cyclopropyl). Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.64; H, 7.24. Found: C, 66.70; H, 7.37.

Tricyclo[3.2.2.0^{2,4}]nonane-1-carboxylic Acid (16-COOH). Ester 16-CO_2Et was saponified with 10% sodium hydroxide under reflux for 3 h. Acid 16-COOH (mp 130–132 °C) was formed in 57% yield after one recrystallization from petroleum ether (bp 60–110 °C). Three recrystallizations gave a pure sample: mp 130.5–132 °C; IR (KBr) 2400–3600 (OH), 1689 (C=O), 1278 (CO) cm^{-1}; NMR ($CDCl_3$) δ 11.1 (s, 1, COOH), 0.1–2.2 (m, 13). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.26; H, 8.60.

Bicyclo[2.2.2]octane-1-carboxylic Acid (17-COOH). A sample of this acid was obtained[29] and used for the pK_a studies; lit. mp 134–137 °C,[27] 140–142 °C.[23]

(Bicyclo[2.2.2]oct-1-yl)methyl Tosylate (17-CH_2OTs). Acid 17-COOH[29] was reduced to alcohol 17-CH_2OH with lithium aluminum hydride and then treated with tosyl chloride to yield tosylate 17-CH_2OTs by the literature method;[23,27] mp 72–76 °C (lit. mp 68–69 °C,[27] 73 °C[23]).

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pK_a Studies. The pK_a of acids **16**-COOH and **17**-COOH was taken by dissolving 0.30 mmol of acid in 50% ethanol (50 mL, 1:1 absolute ethanol–distilled water, v/v) and titrating with 0.05 N aqeuous sodium hydroxide at 29 °C while the pH was measured vs. increments of base added. The pK_a was obtained from the pH at the half-neutralization point. Results are given in Table I.

Kinetic Studies. Standard procedures were followed for the acetolysis studies. Standardized 0.05 M sodium acetate in glacial acetic acid containing 0.3% acetic anhydride was the solvent, with a tosylate concentration of 0.025 M. Aliquots (2 mL) were sealed in ampules and heated to the reaction temperature. The excess sodium acetate was back-titrated in the ampule with standard 0.014 *p*-toluenesulfonic acid in acetic acid with bromophenol blue indicator (yellow to colorless end point). The first-order plots were linear to at least 66% completion. All correlation coefficients were at least 0.993. Results are given in Tables II and III.

Acetolysis Products. Tosylates **16**-CH_2OTs and **17**-CH_2OTs were studied by dissolution in acetic acid with 2 equiv of anhydrous sodium acetate and refluxing for a number of half-lives. Water was added, and the products were extracted with ether. The combined ether layer were washed with 10% sodium bicarbonate, water, and brine. The resulting solution was dried with anhydrous magnesium sulfate and filtered, and the filtrate was rotary evaporated. The products are shown in Table IV.

For the products of bicyclooctyl tosylate **17**-CH_2OTs, gas chromatography (SE-30, 170 °C) showed three possible product peaks in a 6.5:91.4:2.1 ratio. These were collected together (SE-30, 220 °C) and analyzed by NMR, which showed that all major absorptions were in the range δ 1.2–2.4, including the acetate sharp singlet at δ 1.80, indicating that bridgehead acetate **20** was the major product. A very small trace absorption as a singlet at δ 3.80 was interpreted as the carbinyl methylene of unrearranged acetate **17**-CH_2OAc. The trace third product, if indeed an acetate, was not determined. Although the alcohol corresponding to rearranged acetate **20** has been reported[26,27] as the hydrolysis product of **17**-CH_2OTs, acetate **20** itself is unknown and was therefore analyzed. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.73; H, 10.02.

For the products of tricyclononyl tosylate **16**-CH_2OTs, gas chromatography (QF-1, 124 °C) showed four possible product peaks in a 4.0:4.7:8.3:83.0 ratio. The major product was collected and analyzed by NMR as acetate **21**. For a discussion of the 500-MHz NMR spectrum of **21** see the Results and Table V. The 60-MHz ^1H NMR and ^{13}C NMR data of **21** follow: ^1H NMR ($CDCl_3$) δ 1.2–2.9 (m, 11, bridgehead and CH_2), 1.85 (s, 3, CH_3), 0.2–1.0 (m, 4, cyclopropyl); ^{13}C NMR[30] ($CDCl_3$) 169.8 (C=O), 82.7 (CO), 39.5, 30.7, 30.6, 26.9, 26.5, 22.4, 22.2, 19.1, 9.2, 5.7 ppm. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.26; H, 9.13.

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Registry No. 16 (X = CO_2Et), 65115-95-9; **16** (X = CH_2OTs), 80360-28-7; **16** (X = CH_2OH), 80360-29-8; **16** (X = CO_2H), 65115-96-0; **17** (X = CO_2H), 699-55-8; **17** (X = CH_2OTs), 2346-03-4; **17** (X = CH_2OH), 2574-42-7; **18**, 3725-40-4; **19**, 80360-30-1; **20**, 80360-31-2; **21**, 80360-32-3; cyclopropene, 2781-85-3.

Substituent Effects on the Acid Hydration of Acetylenes

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The rates of hydration in aqueous sulfuric acid of 1-butyne, 2-butyne, 1-hexyne, 1-cyclopropylacetylene, and 1-butene are reported, together with rates in D_2SO_4 for the alkynes plus 3-hexyne. All of the compounds are proposed to react through the Ad_E2 mechanism of rate-limiting protonation on carbon. A general correlation of log k_{H^+}(alkyne)/log k_{H^+}(alkene) is observed, whose slope of 1.25 is a quantitative measure of the greater sensitivity to substituent effects of alkynes compared to alkenes in protonation.

The reaction of alkynes with electrophilic reagents, especially protons, has been the subject of continuing interest as described in a number of reviews[1,2] and reports of recent research.[3] A topic of particular interest has been the comparison of the reactivity of particular alkene/alkyne pairs with different electrophiles.[2,4-6]

We have devoted considerable attention to the electrophilic reactions of alkenes, especially to the effect of substituents on reactivity in acid-catalyzed hydrations,[7] including a recent comparative study of the isomers allene and propyne.[8] Therefore, an understanding of the general factors governing the reactivity of alkynes is of interest to us.

The systematic comparison of the effect of substituents on the electrophilic reactivity of alkenes substituted on only one carbon[7] as well as 1,2-disubstituted alkenes[9a] has been quite rewarding as a guide to understanding the details of these processes. It has been particularly en-

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