Impact of High-Lying σ Orbitals and Extensive Through-Bond Interaction on Chemical Reactivity. 3. Solvolysis of *syn*- and *anti*-Tricyclo[4.2.0.0^{2,5}]octa-3,5-diene Derivatives[1]

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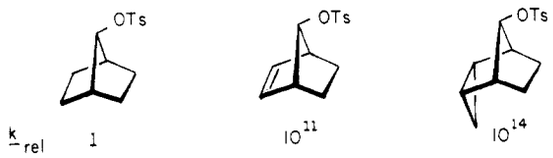
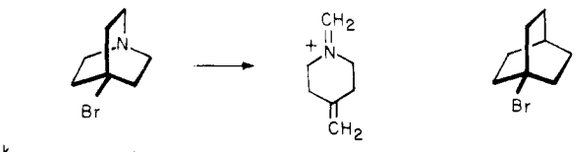
syn- and *anti*-Tricyclo[4.2.0.0^{2,5}]oct-7-en-*exo*-3-ol (**5a** and **9a**) were synthesized by selective hydroboration (9-BBN) of the appropriate cyclobutadiene dimer and converted through diimide reduction to their dihydro derivatives **6a** and **10a**. Kinetic analysis and product determinations for the acetolyses of the respective *p*-toluenesulfonates were carried out. All four compounds ionize some 50 times more slowly than cyclobutyl tosylate and at closely comparable rates. In **5b**, no through-space interaction between the π bond and the developing cationic center is seen to develop, as predictable from photoelectron spectroscopy data which reveal through-bond coupling to dominate. Somewhat unexpectedly, long range electronic transmission through the various σ frameworks, if present, does not demonstrate itself in enhanced solvolytic behavior. The possible product-determining steps are discussed. Finally, comparison of the present data with that available from other cyclobutane-containing sulfonate esters allows conclusions to be made concerning the geometric requirements for effective bicyclobutonium ion intervention.

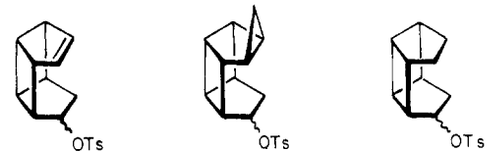
The transmission of electronic effects within molecules can take place "through bonds" or "through space". The level of these interactions is dictated chiefly by structure, geometry, and the types of orbitals involved. The extent and consequences of through-space interaction have received considerable attention and are now reasonably well understood in certain cases, but not others.[2] One classic example is the neutral norbornadiene molecule where the exceptionally favorable interaction of two degenerate π orbitals[3] leads to lowering of the ionization potential relative to norbornene[4] and facilitation of the photocyclization to quadricyclane.[5] A similar through-space orbital mixing can occur in certain carbocations such as the two-electron 7-norbornenyl system[3] where the net stabilization is reflected in an extremely large solvolytic rate enhancement relative to the comparable 7-norbornyl derivative.[6] That the interacting filled orbital need only be rich in p character is evidenced by the solvolytic reactivity of the *endo*-cyclopropyl congener.[7]



In contrast, through-bond coupling is operational in 1,4-diazabicyclo[2.2.2]octane (Dabco).[8,9] Its relationship to 4-bromoquinuclidine has provided a useful basis for analysis of the accelerated solvolytic behavior of the bromide relative to a bicyclo[2.2.2]octyl model and its conversion to products via a σ-bond (Grob) fragmentation.[10]



Unlike norbornadiene, the double bonds in hypostrophene[11,12] do not interact through space, but are instead effectively coupled through high-lying orbitals within the lateral σ bonds.[13] As a consequence, photoclosure to pentaprismane does not operate[11] and electrophilic additions to this diene proceed with extensive skeletal rearrangement.[14] Also, structurally derived *exo*-tosylates undergo acetolysis at significantly enhanced rates.[1]



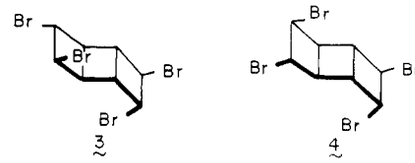
There are also molecules such as Dewar benzene where through-bond and through-space interactions are closely competitive.[15] Thus, extrusion of the CH_2 bridge in norbornadiene results in widening of the dihedral angle on the molecular underside and attenuation of direct π–π interaction such that transmission through the σ framework now gains considerable importance.

Of particular interest at the present time are the *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes (**1** and **2**)[16] which

1 **2**

combine fascinating orbital topologies with widely divergent geometries. The electronic structures of these cyclobutadiene dimers have been of substantial theoretical interest and continue to be the subject of controversy.[17-19] Current interpretations of their photoelectron spectral features do not at all agree on precise orbital assignments. The analysis given by Gleiter, Heilbronner, and co-workers assumes a through-space interaction of 0.4 eV for the syn isomer.[17] But this conclusion has been challenged by Bodor et al.[19] Seemingly, conventional photoelectron spectroscopy may not be capable of resolving this dilemma and a different attack on this problem must be awaited.

Development of the chemistry of **1** and **2** has not kept pace with their theoretical scrutiny. The inability to convert a derivative of **1** photochemically to cubane was cited by Criegee in 1962.[20] At a later date, Nenitzescu and co-workers demonstrated that bromination of **2** proceeded *without skeletal rearrangement* to give a mixture of **3** and **4**.[21] Only by heating



3 **4**

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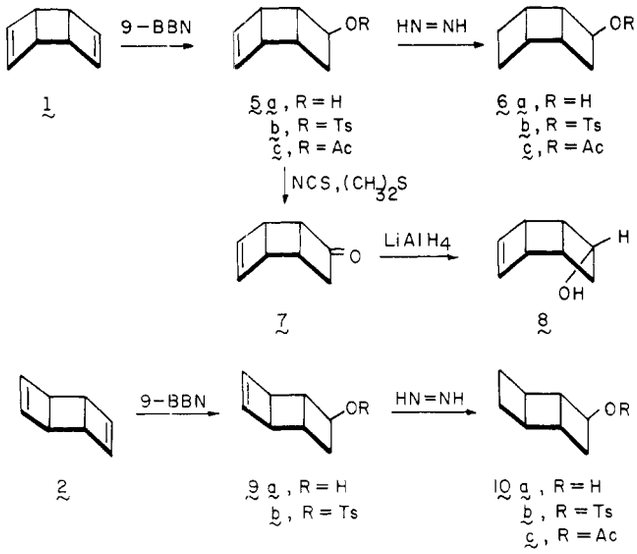
Scheme I



these tetrabromides with hydrogen bromide in dioxane or acetic acid could isomerization be induced.[21] Finally, when **1** and **2** are thermolyzed, both experience cleavage of the pair of central σ bonds to provide cyclooctatetraene.[22-24]

In the following, we present a detailed investigation into the solvolytic reactivity of four *exo*-tosylates derived from **1, 2,** and their dihydro derivatives and the course of the ensuing cationic rearrangements. It was anticipated that these derivatives might serve as chemical probes into the nature of those interactions operational in the vicinity of a cationic center and possibly their magnitude.

Results

The stereochemically pure alcohols **5a** and **9a** were prepared by selective hydroboration of **1** and **2** with 9-BBN in tetrahydrofuran[25] (Scheme I). Expectedly,[26] lithium aluminum hydride reduction of the derived *exo*-monoepoxides[23b] did not result in simple C–O bond cleavage. The assignment of exo stereochemistry follows from steric considerations and ^{1}H NMR data. Thus, the >C**H**OH protons appear as broadened triplets due to coupling to the adjacent methylene hydrogens and minimal interaction with the bridgehead proton ($\theta \approx 90°$). For verification purposes, **5a** was converted to labile ketone **7** by oxidation with *N*-chlorosuccinimide and dimethyl sulfide.[27] Its direct hydride reduction afforded *endo*-alcohol **8** whose α-hydroxyl proton was seen as a broadened multiplet because of added coupling to the bridgehead hydrogen. Additionally, that olefinic proton in **5a** which constitutes the finely spaced triplet at δ 6.50 is now downfield shifted (δ 6.62) as the result of deshielding by the nonbonded electrons on oxygen.

Saturated alcohols **6a** and **9a** could by obtained from their monounsaturated precursors by reduction with excess diimide generated in situ from dipotassium azodicarboxylate.[28] The corresponding tosylates[29] and 3,5-dinitrobenzoates[30] were prepared in classical fashion.

The solvolytic rate constants for these tosylates, as determined in sodium acetate buffered acetic acid, are given in Table I. The values are seen to fall within an exceptionally narrow range. In each case, slightly less than the theoretical amount of acid was liberated. The rate constants were determined using the "infinity titer" observed after 10 half-lives and represent the average of two independent runs. The solvolyses were followed through 1.5–2 half-lives and good first-order plots were obtained in each instance.

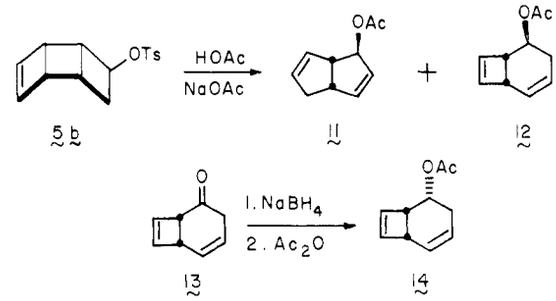
The acetolysis of **5b** proceeded efficiently (95% yield) to give acetates **11** (85%) and **12** (6%) and two unknown compounds (3 and 6%) which could not be adequately separated from **11**

Table I. Rates of Acetolysis in Acetic Acid 0.0510 M in Sodium Acetate

Registry no.	Compd	T, °C	$k(\times 10^5)$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel} (85.2 °C)
65085-72-5	**5b**	68.2	0.91 ± 0.02	27.2	−2	3.6[a]
		79.0	3.75 ± 0.10			
		90.0	10.75 ± 0.27			
65085-73-6	**6b**	79.0	0.95 ± 0.04	26.1	−7	1[a]
		90.0	3.05 ± 0.14			
		100.6	8.97 ± 0.23			
65137-66-8	**9b**	68.2	0.47 ± 0.02	26.2	−6	1.6
		85.2	3.04 ± 0.09			
		100.6	14.82 ± 0.47			
65137-67-9	**10b**	85.2	3.23 ± 0.30			1.7

[a] Interpolated values.

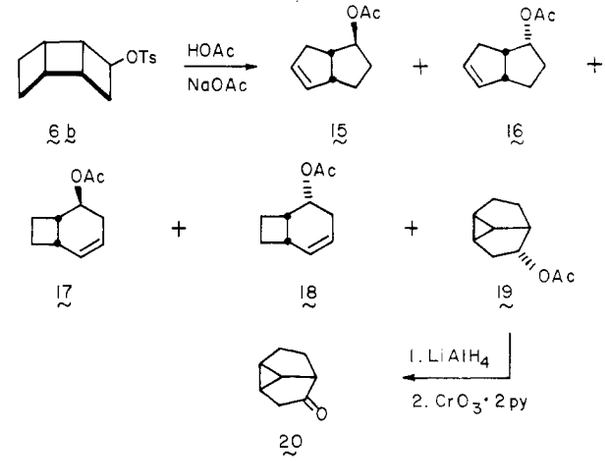
to permit identification. The major component has previously been obtained as the product of acid-catalyzed HOAc addition to semibullvalene and shown to be stable to the solvolysis conditions employed.[31] The ^{1}H NMR spectra of the two samples were identical. The structural assignment to **12** is based solely upon its proton magnetic resonance spectrum and particularly direct comparison with that of **14** formed by sequential sodium borohydride reduction and acetylation of bicyclo[4.2.0]octa-4,7-dien-2-one (**13**).[32] The *endo*-acetate



exhibits a spectrum very similar to that of **12** except for the signal attributable to >C**H**OAc. The dihedral angle relationships in **14** provides for a high level of spin interaction with proximate hydrogens such that a doublet of triplets (J = 10 and 7 Hz) is clearly visible. In **12,** this signal occurs as a narrow multiplet.

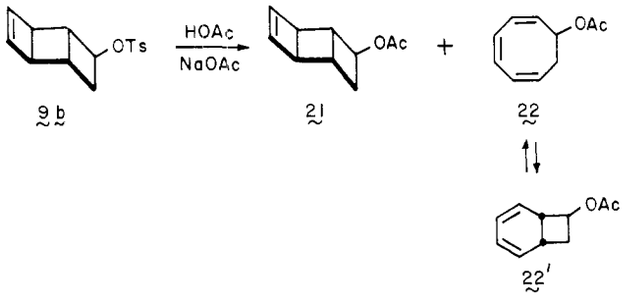
Comparable buffered acetolysis of **6b** gave rise to a five-component mixture consisting of **15** (21%), **16** (11%), **17** (11%), **18** (5%), and **19** (52%) (Scheme II). Subsequent reexposure of each acetate to the reaction conditions resulted in no further structural change. The four less dominant components had been previously prepared in these laboratories[33] and were individually identified by their VPC retention times and ^{1}H

Scheme II



NMR spectra. The spectral features obtained for major product **19** corresponded closely to those reported by Haywood-Farmer and Pincock for the indicated structure.[34] Additional confirmatory evidence of its identity was obtained by reduction to the alcohol followed by oxidation to ketone **20**, which displayed the appropriate carbonyl frequency (1740 cm^{-1}) as well.[34]

Product studies carried out on unsaturated anti isomer **9b** showed it to be converted chiefly to the acetate of retained structure (**21**, 33%) and 7-acetoxy-1,3,5-cyclooctatriene (**22**,



9b 21 22 22'

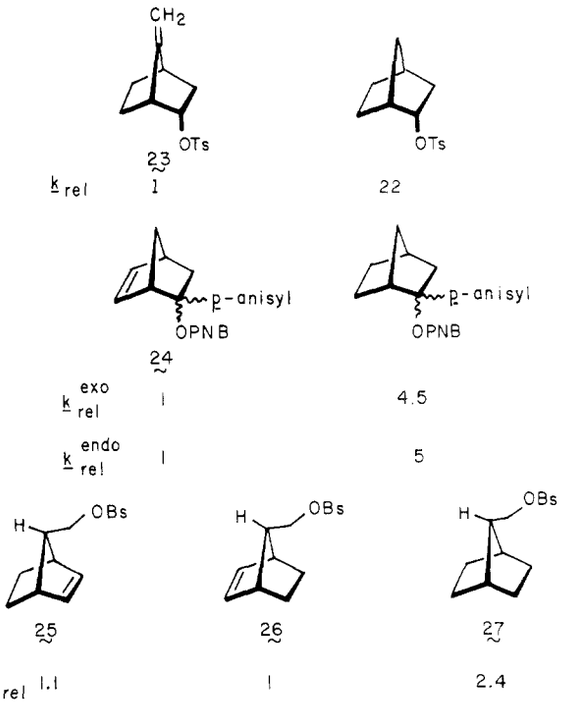
52%). Two more rapidly eluted components were also detected (3 and 12%) but were not characterized due to limited accessibility and serious peak overlap on attempted preparative VPC separation. Both Kröner[35] and Huisgen[36] have previously established that **22** is in equilibrium with bicyclic tautomer **22'** (53% at 60 °C). As with the authentic material, our sample of this acetate likewise exhibited two methyl singlets (~1:1) in the ^1H NMR spectrum. The reduction of cyclooctatrienone with 9-BBN and subsequent acetylation proved to be a serviceable route to **22**, although the yield was quite low (5%). Resubmission of **21** to the original reaction conditions also gave **22**. At the same temperature (90 °C), *syn*-acetate **5c** was converted somewhat more sluggishly to **22** as well. These ring openings may be simple thermal rearrangements, since the temperature involved is sufficiently elevated to promote such transformations. The saturated acetates **6c** and **10c** were inert to such treatment.

The product mixture formed upon acetolysis of **10b** consisted of **17** (66%) and **18** (34%), both of which had been previously identified.

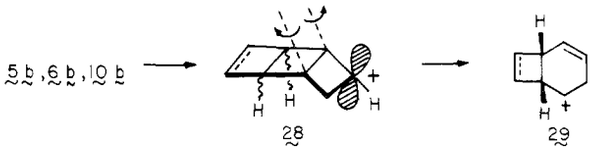
Discussion

It is seen (Table I) that all four tosylates undergo acetolysis at closely comparable rates, the difference between the fastest and slowest at 85 °C being merely a factor of 3.6. One might advance the argument that the similarities in the kinetic behavior of the saturated and unsaturated compounds within a given stereoisomeric subset may arise because of compensatory inductive factors operative principally in the latter. However, such rationalization appears unsatisfactory for several reasons. In unsaturated norbornyl systems such as **23**[37] and **24**,[38] where through-space interaction between the olefinic center and reaction site appears to be unimportant, the adverse inductive contribution of the π system leads to rate retardations on the order of 5–20. The introduction of another intervening carbon atom expectedly ameliorates this effect still more. Thus, Bly found that the acetolysis rates of brosylates **25–27** also fall within a very narrow range, the major product in each case being the acetate of retained structure.[39]

If a destabilizing mechanism of comparable magnitude were operative in the 7-tricyclo[4.2.0.$0^{2,5}$]octenyl ring systems, then the through-bond and/or through-space contributions to enhancement of the rate constants do not exceed a maximum of 2 to 3.5-fold. Clearly, such effects are too small to gain significance.



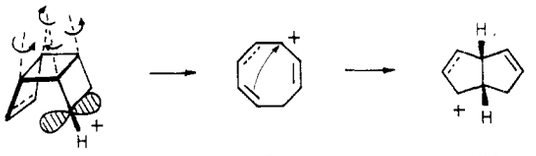
Furthermore, the product studies reveal that no obvious interaction occurs between the proximate π bond in **5b** or the peripheral cyclobutane bonds in **9b** and **10b** with the developing electron-deficient reaction center. Formation of the bicyclo[4.2.0]octyl acetates **12**, **17**, and **18** in three of the examples can be attributed to disrotatory opening of the adjoining internal bond[44] *after ionization* to attain maximum overlap with the vacant p orbital just produced. The resulting homoallylic cation (**29**) is trapped by acetate principally from



28 29

the exo direction as a consequence of prevailing steric conditions, solvent-separated ion pairing, and the like.

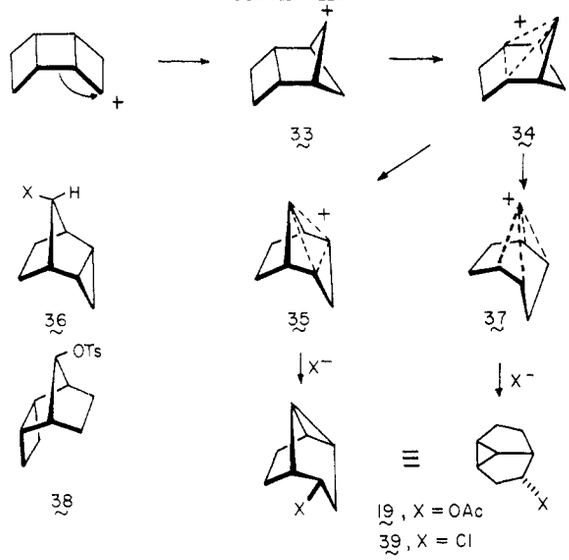
The origin of the bicyclo[3.3.0]octane ring system raises an interesting mechanistic question. Since this process occurs only when syn geometry is present, it is tempting to relate this product-forming step to the suitable orientation of the cyclobutane Walsh orbitals in the second distal internal bond such that its rupture occurs concomitantly with the first (cf. **30**). Subsequent transannular cyclization within **31** would give rise to **32**.



30 31 32

The acetolysis of **6b** leads principally to acetate **19**. As with *exo*-bicyclo[2.2.0]hex-2-yl tosylate,[41] ionization appears to be accompanied by lateral carbon–carbon bond migration to give initially **33** (Scheme III). In accord with the established solvolytic behavior of **38**,[45] delocalization of the proximal cyclobutane σ electrons can now be anticipated. Cation **34** is not a likely minimum on this potential surface and can be expected to experience "bridge flipping"[46] to arrive at trishomocyclopropenyl cation **35** or conversion to square-pyramidal ion **37**. The latter species has been generated by ionization of **36**-Cl and **39** and directly observed by NMR

Scheme III



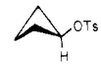
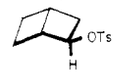
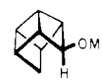
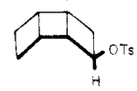
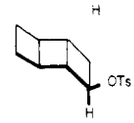
spectroscopy.[47] In any event, ions **35** and **37** are known to trap acetic acid to give **19** as the exclusive product.

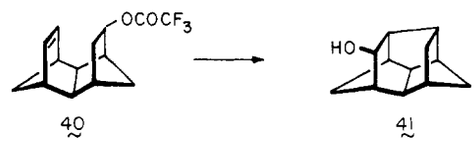
The ionization of **9b** leads to appreciable amounts of unrearranged acetate **21,** an observation which could be construed as a reflection of through-bond stabilization. If one were to consider the first-formed secondary carbocation as adequately stabilized by such an electronic mechanism, then capture of solvent with retention of configuration and without structural rearrangement might be expected. But this is not the only interpretation demanded by the experimental findings. Thermal ring opening of **21,** a process shown independently to occur under the reaction conditions, could account for the formation of **22.** While this is certainly a source of the triene, our observation that the ratio of **21** to **22** does not change significantly with time during the initial phases of the acetolysis of **9b** (VPC analysis) suggests that some **22** probably also comes directly from the tosylate.

The relatively low solvolytic reactivity of **6b, 10b,** and *exo*-bicyclo[2.2.0]hex-2-yl tosylate compared to cyclobutyl tosylate (Table II) very likely has its origins in conformational factors. In the simple cyclobutyl example, ionization proceeds from the puckered conformation with anchimeric assistance provided by the β,γ σ bond, the orbital of which attains maximum overlap with the developing empty p orbital and gives rise to a stabilized bicyclobutonium intermediate.[48] In the bi- and tricyclic homologues, conformational flexibility is greatly reduced and disrotatory opening of the central bond concurrent with ionization is prohibited for steric and geometric reasons. However, when the leaving group is endo oriented, these restraints are not in force, bicyclobutonium ions can now intervene, and much of the added steric strain should be reflected in the rate constant. The large rate difference separating the *endo*- and *exo*-bicyclo[2.2.0]hex-2-yl derivatives (Table II) conforms nicely to this interpretation. The somewhat enhanced solvolytic behavior of the secocubyl mesylate has been attributed to steric strain release which develops upon ionization.[48]

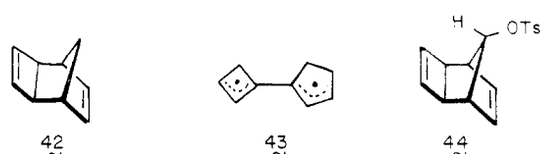
The rather unreactive nature of the tosylates examined in the present study would appear to exclude the likelihood that through-bond interactions can be kinetically demonstrated as in the case of hypostrophene derivatives.[1] Neither can the absence of through-space interaction in **5b** be attributed to dissymmetric orientation of the π bond with the developing cationic center. Winstein earlier found that trifluoroacetate **40** is ten times more reactive than the *anti*-7-norbornenyl derivative in spite of such dissymmetry.[49] In addition, the resulting product (**41**) arises from π participation. The mitigating factor in the cation derived from **5b** is more likely the distance between the π bond and the empty p orbital MINDO calculations for hydrocarbon **1** denote the transannular distance between the two closest nonbonded olefinic carbons to be 2.93 Å.[18] Bly has previously considered 2.8 Å to be beyond the range for possible π anchimeric assistance.[39]

Table II. Relative Solvolysis Rates

Compd	k_{rel}	Ref
	50	40
	5.5	41
	4.4×10^8	42
	13	43
	1	This work
	1.7	This work



The inefficiency of through-bond coupling in a structural framework within which photoelectron spectroscopy suggests facile σ-bond relay of electronic effects has been observed on one previous occasion. Thus, Haselbach[50] and Martin[51] have determined that *anti*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene (**42**) exhibits through-bond coupling in a manner somewhat comparable to **1.** A chemical consequence of this effect is the ready photolytic cleavage of the C_1–C_2 bond to give the bisallyl



radical **43.**[50] Notwithstanding, the 9-tosyloxy derivative **44** solvolyses eight times more slowly than *syn*-7-norbornenyl tosylate, indicating no accelerating effect due to coupling of the reaction center to the cyclobutenyl double bond via C_1–C_2 and C_5–C_6.[52]

The present results indicate that through-bond effects which are clearly evident upon photoelectron spectral analysis of a hydrocarbon system need not necessarily become apparent during solvolysis of a suitably functionalized derivative. Primary detractants from our more lucid understanding of bond assistance effects are steric factors and strain relief, which operate along a given reaction pathway. Understandably, these can sometimes mask those orbital interaction effects being sought and seriously cloud the mechanistic picture. However, a second, more serious complication is inherent to the present treatment. In all circumstances, neutral molecules have been employed as electronic models for the structurally related cations. But the former do not possess the added vacant p orbital which characterizes the latter. Since this p orbital is truly the focus of our interest, the parent systems do

not qualify as true models. This conclusion implies that each individual cation should be analyzed by computational methods in its own right, without necessary regard for the electronic properties of its hydrocarbon congener. Under these circumstances, a more direct correlation with solvolytic behavior might be seen.

Experimental Section

The ^1H NMR spectra were obtained with Varian T-60, Varian A-60A, and Bruker 90 (FT) spectrometers and apparent splittings are given in all cases. The Bruker 90 spectrometer was also employed for the recording of ^{13}C spectra. Mass spectral measurements were made on an AEI-MS9 spectrometer at an ionizing potential of 70 eV. Preparative VPC work was done on a Varian Aerograph A90-P3 instrument equippped with a thermal conductivity detector. A 6 ft × ¼ in. column packed with 10% OV-11 on 60/80 mesh Chromosorb G at 115 °C was used unless otherwise stated. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***syn*-Tricyclo[4.2.0.0^{2,5}]oct-7-en-*exo*-3-ol (5a).** To a magnetically stirred solution of **1** (2.08 g, 20 mmol) in 50 mL of tetrahydrofuran under nitrogen at 0 °C was added dropwise 45 mL of 0.5 *N* 9-borabicyclononane in tetrahydrofuran. Stirring was continued for 2 h, whereupon 15 mL of 15% aqueous sodium hydroxide solution followed by 15 mL of 30% aqueous hydrogen peroxide were added dropwise and the solution was allowed to warm to room temperature. The tetrahydrofuran was evaporated and the aqueous residue was extracted with ether (3 × 50 mL). The combined ether layers were washed with water (75 mL) and brine (75 mL), dried, and concentrated to leave a yellow oil. Chromatography on silica gel (elution with 15% ether–pentane) yielded a solid which was recrystallized from pentane to give 0.67 g (27%) of **5a** as white needles: mp 52–55 °C; NMR $\delta_{Me_4Si}(CDCl_3)$ 6.50 (m, 2), 4.18 (t, J = 6.0 Hz, 1), 3.40 (m, 2), 2.75 (m, 2), 2.39 (br s, 1), and 2.40–2.00 (m, 2); calcd for *m/e* 122.0732, found 122.0733.

Tosylate **5b** was prepared in the usual way, mp 61–62 °C, as was the 3,5-dinitrobenzoate derivative, mp 127.5–128.5 °C.

Anal. Calcd for $C_{15}H_{12}N_2O_6$: C, 56.96; H, 3.83; N, 8.86. Found: C, 57.10; H, 4.07; N, 8.64.

***anti*-Tricyclo[4.2.0.0^{2,5}]oct-7-en-*exo*-3-ol (9a).** To a magnetically stirred solution of **2** (2.08 g, 20 mmol) in 40 mL of dry tetrahydrofuran at 0 °C under nitrogen was added dropwise 40 mL (20 mmol) of 0.5 N 9-borabicyclononane in tetrahydrofuran over 1 h. Workup in the predescribed manner yielded 500 mg (25%) of **9a** as a clear oil: NMR $\delta_{Me_4Si}(CDCl_3)$ 6.32 (nm, 2), 4.21 (t, J = 6.2 Hz, 1), 3.13 (nm, 2), 2.40 (s, 1), and 2.36 (m, 4); calcd for *m/e* 122.0732, found 122.0733.

Tosylate **9b** was prepared in the usual way, mp 62–63 °C, as was the 3,5-dinitrobenzoate derivative, mp 151.5–153 °C.

Anal. Calcd for $C_{15}H_{12}N_2O_6$: C, 56.96; H, 3.2; N, 8.86. Found: C, 57.00; H, 3.90; N, 8.88.

***syn*-Tricyclo[4.2.0.0^{2,5}]octan-*exo*-3-ol (6a).** To a magnetically stirred solution of 1.8 g (14.8 mmol) of **5a** in 150 mL of methanol under nitrogen at 0 °C was added 19 g (100 mmol) of dipotassium azodicarboxylate in one portion. To the stirred slurry was added 15 mL of acetic acid via syringe and stirring was continued until the yellow color of the potassium salt was discharged. The methanol was evaporated, the product was taken up in ether (3 × 50 mL), and the combined organic layers were washed with saturated sodium bicarbonate solution (2 × 100 mL), water (100 mL), and brine (100 mL) before drying and evaporation. There was obtained 1.35 g (85%) of **6a** as a clear oil: NMR $\delta_{Me_4Si}(CDCl_3)$ 4.98 (t, J = 6.0 Hz, 1), 2.93 (m, 4), 2.66 (s, 1), and 2.36 (m, 6); calcd for $C_8H_{12}O$, *m/e* 124.0888, found 124.0890.

Tosylate **6b** was prepared in the usual way, mp 44–45 °C, as was the 3,5-dinitrobenzoate derivative, mp 144.0–144.5 °C.

Anal. Calcd for $C_{15}H_{14}N_2O_6$: C, 56.60; H, 4.43; N, 8.86. Found: C, 56.57; H, 4.50; N, 8.71.

***anti*-Tricyclo[4.2.0.0^{2,5}]octan-*exo*-3-ol (10a).** To a magnetically stirred solution of 1.1 g (9.0 mmol) of **9a** in 100 mL of methanol at 0 °C under nitrogen was added 13.9 g (72 mmol) of dipotassium azidocarboxylate in one portion. Subsequently, 9.7 mL of acetic acid was added slowly over 1 h and stirring was continued until the yellow color was discharged. Through workup as described above, there was isolated 590 mg (53%) of **10a** as a clear oil: NMR $\delta_{Me_4Si}(CDCl_3)$ 4.26 (t, J = 6.0 Hz, 1), 2.88–1.83 (m, 4), 2.65 (m, 6), and 2.01 (s, 1); calcd for *m/e* 124.0888, found 124.0890.

The tosylate (**10b**) was prepared in the usual way and used directly as a clear oil.

***syn*-Tricyclo[4.2.0.0^{2,5}]oct-7-en-*endo*-3-ol (8).** To a magnetically stirred solution containing 218 mg (1.64 mmol) of *N*-chlorosuccinimide in 10 mL of methylene chloride cooled to 0 °C under nitrogen was added 102 mg (1.68 mmol) of dimethyl sulfide via syringe. A white precipitate formed and the mixture was cooled to −23 °C. Alcohol **5a** (100 mg, 0.82 mmol) in 3 mL of methylene chloride was added in one portion and stirring was continued for 2 h, whereupon 84 mg (0.84 mmol) of triethylamine was introduced. The mixture was allowed to warm to room temperature and poured into ether (15 mL) and water (50 mL). The aqueous phase was separated and the organic layer was washed with water (2 × 25 mL), dried, concentrated, and transferred to a 25-mL round-bottom flask. Lithium aluminum hydride (50 mg, 1.3 mmol) was added and the mixture was stirred at room temperature for 1 h. Saturated sodium sulfate solution was added dropwise until the supernatant liquid became clear and the precipitated aluminum salts were filtered and washed amply with ether. The filtrate was dried and concentrated to leave 30 mg (30%) of **8** as a clear oil: NMR $\delta_{Me_4Si}(CDCl_3)$ 6.62 (nm, 1), 6.40 (nm, 1), 4.16 (m, 1), 3.52 (br d, 2), 2.56 (m, 2), and 2.17 (m, 2).

Kinetics Procedure. A ~0.02 M solution of tosylate (accurately weighed) in 0.0510 N sodium acetate in acetic acid was prepared in a 20-mL volumetric flask. Aliquots of this solution were removed and sealed in glass ampules which had been washed sequentially with 10% hydrochloric acid, 10% ammonium hydroxide, and water, and dried at 70 °C overnight. The ampules were simultaneously placed in a constant temperature bath and after 10 min the first ampule was removed and quenched in ice water. At this point an accurate timer was started. The ampule then was allowed to warm to room temperature for ~5 min and exactly 1.985 mL of solution was removed via an automatic pipet and titrated with standard perchloric acid in acetic acid. Three drops of bromphenol blue was used as indicator and the end point was considered to be reached when the yellow solution turned clear. The remaining ampules were removed at appropriately timed intervals and treated as above. Points were taken through 1–2 half-lives and an infinity titer was taken after 10 half-lives.

Preparative Scale Solvolysis of 5b. A magnetically stirred solution of 1.0 g (3.63 mmol) of **5b** and 530 mg (5.0 mmol) of sodium carbonate in 25 mL of acetic acid was heated at 90 °C for 18 h (10 half-lives). The solution was cooled, poured into 100 mL of water, and extracted with ether (3 × 30 mL). The combined ether layers were washed with 50-mL portions of 10% aqueous sodium hydroxide solution (2×), water, and saturated aqueous sodium chloride solution before decolorization with charcoal, filtration through Celite, drying, and evaporation. There remained 560 mg (95%) of a clear oil, analysis of which by VPC showed four components to be present, two of which could be preparatively separated.

The first compound to be eluted was identified as **12** (6.5%): NMR $\delta_{Me_4Si}(CDCl_3)$ 6.34 (nm, 1), 6.14 (nm, 1), 6.03 (d, J = 4.5 Hz, 2), 5.55 (nm, 1), 3.00 (AA'BB', 2), 2.38 (t with fine splitting, J = 8.0 Hz, 1), and 2.06 (s, 3).

The third component was **11** (85%) as shown by comparison of its ^1H NMR features to those published:[31] NMR $\delta_{Me_4Si}(CDCl_3)$ 6.05 (dd, J = 2.0 and 5.5 Hz, 1), 5.80–5.50 (m, 3), 5.40 (m, 1), 3.65 (m, 1), 3.30 (m, 1), and 2.00 (s, 3); calcd for $C_{10}H_{12}O_2$, *m/e* 164.0837, found 164.0839.

Two other components (3 and 6%) could not be separated in a pure state due to coincidental elution with **11**.

Preparative Scale Acetolysis of 6b. A solution of 1.25 g (4.5 mmol) of **6b** and 500 mg (4.7 mmol) of sodium carbonate in 25 mL of acetic acid under argon was heated at 90 °C for 63 h (10 half-lives). The usual workup yielded 500 mg (68%) of a clear oil which exhibited five peaks upon VPC analysis. These were preparatively separated. The first two compounds to elute were collected together and shown to be **15** (21%) and **16** (11%). The third and fourth components were likewise collected together and identified as **17** (11%) and **18** (5%).

The final acetate proved to be **19** (52%): NMR $\delta_{Me_4Si}(CDCl_3)$ 4.97 (d of t, J = 6.46 and 9.00 Hz, 1), 2.67–1.12 (series of m, 10), and 2.00 (s, 3); ^{13}C NMR ($CDCl_3$) 170.36, 79.82, 44.23, 31.29, 27.07, 26.69, 26.17, 23.71, 21.06, and 19.31 ppm.

Preparative-Scale Acetolysis of 9b. A magnetically stirred solution of 600 mg (2.18 mmol) of **9b** and 500 mg (4.73 mmol) of sodium carbonate in 25 mL of acetic acid was stirred at 90 °C under argon for 26 h (10 half-lives). The usual workup yielded 250 mg (69%) of a clear oil containing four components (VPC analysis). The two major compounds could be separated. The first was identified as **21** (23%) by comparison of ^1H NMR and VPC retention times with those of an authentic sample. The second component was shown to be **22** (65%) by comparison of its ^1H NMR data with those of an authentic sample:[36] NMR $\delta_{Me_4Si}(CDCl_3)$ 5.95 (m, 2), 5.80 (m, 3), 5.15 (m, 1), 3.15–3.00 (m, 1), and 2.50 (m, 2); calcd for $C_{10}H_{12}O_2$, *m/e* 164.0837, found 164.0839.

The two remaining components (5 and 7%) eluted almost simul-

taneously and could not be obtained in a state pure enough for identification.

Preparative-Scale Acetolysis of 10b. To a solution of 1.1 g (4.0 mmol) of **10b** in 10 mL of acetic acid under argon was added 424 mg (4.0 mmol) of sodium carbonate and the solution was stirred at 90 °C for 30 h (10 half-lives). The reaction mixture was processed as before to leave 500 mg (58%) of a clear oil which was purified by preparative VPC. There was isolated a mixture of **17** (66%) and **18** (34%).

***endo*-2-Acetoxybicyclo[4.2.0]octa-4,7-diene (14).** To a solution of 200 mg (1.64 mmol) of bicyclo[4.2.0]octa-4,7-dien-2-one (**13**) in 25 mL of methanol at −20 °C under argon was added 248 mg (6.5 mmol) of sodium borohydride in two 124-mg portions at a 10-min interval. The solution was allowed to warm to room temperature, stirred for 5 h, and poured into 150 mL of water. The aqueous solution was extracted with ether (3 × 50 mL) and the combined ether layers were washed with water (2 × 75 mL) and saturated sodium chloride solution (75 mL) before drying and evaporation. The resulting yellow oil was dissolved in 5 mL of pyridine, 1.4 g (13.8 mmol) of acetic anhydride was introduced, and stirring at room temperature was maintained for 24 h. The solution was poured into 50 mL of water and the water layer was extracted with ether (3 × 30 mL). The combined organic layers were washed with 50-mL portions of water, 10% aqueous hydrochloric acid (2×), saturated aqueous sodium bicarbonate solution, and saturated aqueous sodium chloride solution prior to decolorization with charcoal, filtration through Celite, drying, and concentration. There remained 238 mg (85%) of the acetate as a clear oil: NMR δ_{Me_4Si} ($CDCl_3$) 6.23 (d, J = 3.0 Hz, 1) 5.70 (m, 2), 4.86 (d of t, J = 7.0 and 10.0 Hz, 1), 3.58 (m, 2), 2.82 (m, 2), and 2.07 (s, 3); calcd for $C_{10}H_{12}O_2$, m/e 164.0837, found 164.0839.

Control Experiments Concerned with the Stability of Acetates 15–18. A 50-mg (0 09 mmol) sample containing 66% of **15** and 34% of **16** was dissolved in 2 mL of acetic acid and heated at 90 °C under nitrogen for 48 h. The solution was poured into 25 mL of water and extracted with ether (3 × 10 mL). The combined ether layers were washed with 15-mL portions of 15% aqueous sodium hydroxide solution (2×), water, and brine. Drying and evaporation left 30 mg (66%) of a mixture of **5** and **16**, the ^{1}H NMR spectrum of which was identical with that of the starting sample.

The identical treatment of 30 mg (0.18 mmol) of a mixture of **17** and **18** (66:34) yielded after workup 25 mg (83%) of the unchanged starting mixture.

Control Experiments Concerned with the Stability of Acetates 5c and 21. To a solution of 82 mg (0.2 mmol) of **5c** in 2 mL of acetic acid under argon was added 2.2 mg (0.2 mmol) of sodium carbonate. This solution was stirred at 90 °C for 18 h (10 half-lives). The usual workup afforded 80 mg (98%) of a mixture of starting acetate (55%) and **22** (45%) by integration of the olefinic signals in the ^{1}H NMR.

Identical treatment of **21** (100 mg, 0.55 mmol) yielded 70 mg (70%) of **22**.

Control Experiments Concerned with the Stability of Acetates 6c and 10c. To 100 mg (0.6 mmol) of **6c** in 5 mL of acetic acid was added 63.6 mg (0.6 mmol) of sodium carbonate and this solution was heated for 48 h at 90 °C under argon. Upon workup, 85 mg (85%) of starting acetate was obtained. Identical treatment of **10c** (200 mg, 1.2 mmol) yielded 160 mg (80%) of unchanged acetate.

Reductive Cleavage and Oxidation of 19. A solution of **19** (30 mg) in anhydrous ether (2 mL) cooled to 0 °C was treated with 19 mg of lithium aluminum hydride and stirred at room temperature for 20 h. Saturated sodium sulfate solution was added dropwise, the precipitate was separated by filtration, and washed thoroughly with ether. The combined filtrates were evaporated to leave the alcohol, which was taken up in dichloromethane (2 mL) and added to a mixture of chromium trioxide (100 mg) and pyridine (158 mg) at 0 °C. After 45 min, the reaction mixture was poured into 10% sodium hydroxide solution and the salts were washed with ether. After further ether extraction, the combined organic phases were washed with 10% hydrochloric acid, water, and sodium bicarbonate solution before drying and evaporation. The resulting pale yellow ketone **20** exhibited a carbonyl stretching frequency at 1740 cm^{-1}.[34]

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Registry No.—**1**, 20380-30-7; **2**, 20380-31-8; **5a**, 65085-74-7; **5b** 3,5-DNP derivative, 65085-75-8; **6a**, 65085-76-9; **6b** 3,5-DNP derivative, 65085-77-0; **8**, 65137-68-0; **9a**, 65137-69-1; **9b** 3,5-DNP derivative, 65137-70-4; **10a**, 65137-71-5; **11**, 36257-89-3; **12**, 65085-78-1; **13**, 65085-79-2; **14**, 65165-51-7; **19**, 24221-98-5; **22**, 16326-82-2.

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