Impact of High-Lying σ Orbitals and Extensive Through-Bond Interaction on Chemical Reactivity. 2. Solvolytic Studies of Hypostrophene Derivatives[1]

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Acetolysis of *exo*- and *endo*-tetracyclo[5.3.0.0^{2,6}.0^{3,10}]decan-4-yl tosylates (**6b** and **8b**) in buffered HOAc at 71 °C produced **16b** (together with 2% of **6c** in the endo case), but at rates estimated to differ by a factor of 170 (with **6b** faster). Comparable solvolysis of the unsaturated exo tosylate **3b** (at 25.9 °C) led rapidly to **18b** (50%), **19a** (5%), and **19b** (45%), a product distribution quite unlike that obtained from its endo epimer **5b** (**18b** accompanied by some polymer formation). These findings demonstrate that the frequently observed ability of a proximate double bond to engage in transannular participation has been overridden by lateral σ-bond participation. The kinetic and product data suggest that the first cation emanating from **5b** is classical, while that from **3b** is generated with anchimeric assistance and characterized by σ delocalization. Whereas acetolysis (71 °C) of *exo*-cyclopropyl derivative **10b** returned only **20a**, its endo counterpart **15b** gave a complex acetate product mixture at a rate approximately 440 times slower. The involvement of neighboring-group participation could again be implicated for **10b**, since interaction of the cationic center with the cyclopropane ring is effectively repressed. The rate constants and product distributions provide convincing demonstration of the effectiveness with which such anchimeric assistance can accelerate and control the ultimate outcome of cationic rearrangements.

Interest in hypostrophene (tetracyclo[5.3.0.0.^{2,6}.0^{3,10}]-deca-4,8-diene (**1**))[1-3] derives chiefly from its structural features, including its C_{2v} symmetry, the overriding by through-bond coupling of direct through-space π–π interaction,[4] and its obvious strain energy. The primary determinants of the observed level ordering in **1** are its exceptionally high-

1 **2**

lying lateral σ orbitals and their geometric relationship to the π bonds. Such symmetry-enforced indirect interaction between the double bonds should have significant consequences on chemical reactivity. This conclusion has received qualitative support from the response of **1** to attack by electrophilic reagents.[1,5]

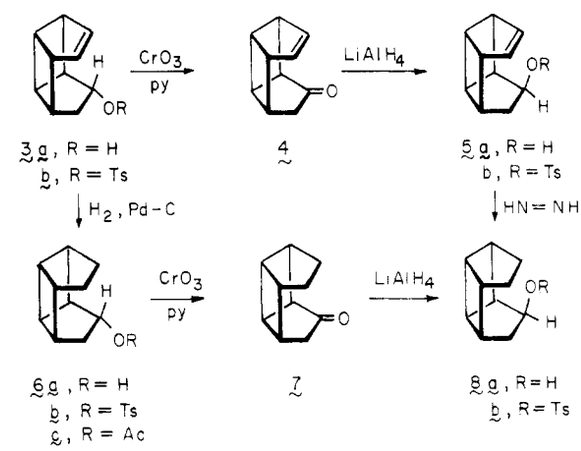
Hoffmann, Mollère, and Heilbronner have previously presented arguments supporting the notion that the exceptional unreactivity of 7-norbornyl cation precursors (**2**) is due not to the change in angle strain accompanying their ionization,[6] but to destabilization brought on by the inability of proper ribbon orbitals to interact suitably with the carbonium ion center.[7] This lack of interaction causes **2** to be less stable and more difficult to generate than it should otherwise be. At issue is whether similar phenomena would be observed in carbonium ions derived from **1** and allied structures.

The recent availability of efficient routes to **1** and the knowledge that carbocations are particularly sensitive to prevailing orbital interactions prompted a detailed kinetic study of the solvolytic behavior of a number of hypostrophene derivatives. In particular, a series of *exo*- and *endo*-*p*-toluenesulfonate esters have been prepared in which the transannular units positioned in close proximity to the leaving group vary from saturated ethano through etheno to edge cyclopropano. Their acetolysis forms the subject of this report.

Results

Synthesis. Oxidation of *exo*-alcohol **3a**, the monohydroboration product of hypostrophene,[1] gave ketone **4** which was reduced stereospecifically to **5a** with lithium aluminum hydride (Scheme I). Careful catalytic hydrogenation of **3a** led

Scheme I



to **6a** and subsequently to **8a** without complication. Diimide reduction of **5a** likewise provided **8a**.

Although the available **9**[1] could be cleanly converted to **10a** with 9-BBN, the somewhat limited accessibility of this hydrocarbon led us to develop a preferred route beginning with acetate **11**. Dichlorocarbene addition to **11** was conveniently achieved under phase-transfer conditions. The resulting adduct **12** was reduced sequentially with lithium aluminum hydride and sodium in liquid ammonia in good overall yield (Scheme II). Inversion of hydroxyl stereochemistry to provide **15a** was again achieved via an oxidation–reduction sequence.

Solvolysis Kinetics. Acetolyses of the *endo*-tosylates **5b**, **8b**, and **15b** were examined kinetically in buffered acetic acid (0.03 M in NaOAc) through use of the standard ampule technique and classical titrimetry. The method previously described by Wiberg and Hess[8] was utilized with *exo*-tosylates **6b** and **10b**. We highly recommend this technique in those situations where solvolysis is quite rapid or when the ionization process is complicated by substantial levels of early internal return. Its chief disadvantage, however, is the rather larger amounts of tosylate (~200 mg) required for a single run. As described in the Experimental Section, a procedural modification has been developed in the course of our study of **3b** which has proven reliable at the 20-mg level.

Due to formation of extensive amounts of less reactive isomeric tosylates arising from internal recapture of *p*-toluenesulfonate anion, reliable instantaneous rate constants

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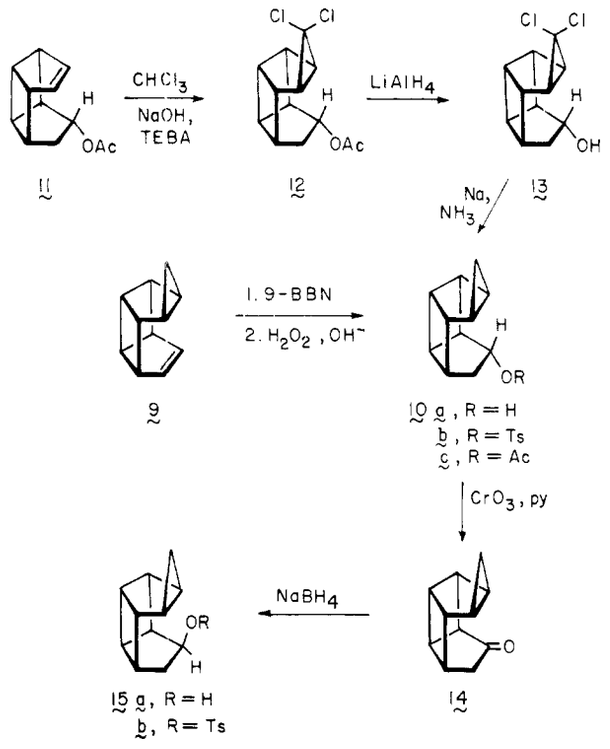
Table I. Rates of Tosylate Solvolysis in Buffered Acetic Acid

Compd	Registry no.	T, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel} (25.9 °C)
3b	65071-87-6	25.9	4.19×10^{-4}			1000
5b	65137-10-2	55.2	2.12×10^{-4}	21.2 ± 1.0	−11 ± 3	20
		51.1	1.46×10^{-4}			
		44.6	7.02×10^{-5}			
		25.9[a]	8.2×10^{-6}			
6b	65071-88-7	25.9	1.06×10^{-5}			25
8b	65137-11-3	83.6	1.42×10^{-4}	20.7 ± 0.9	−8.5 ± 2.5	1
		77.1	8.47×10^{-5}			
		71.0	4.62×10^{-5}			
		25.9[a]	4.3×10^{-7}			
10b	65071-89-8	25.9	1.71×10^{-5}			41
15b	65137-12-4	83.6	2.33×10^{-4}	23.8 ± 0.5	−8.7 ± 1.3	0.6
		77.1	1.19×10^{-4}			
		71.0	6.52×10^{-5}			
		25.9[a]	2.7×10^{-7}			

[a] Extrapolated values based on the activation parameters.

Scheme II



11 12 13 9 10 a, R = H; b, R = Ts; c, R = Ac 14 15 a, R = H; b, R = Ts

for **6b** and **10b** could be obtained only through the first 5− of reaction. For **3b**, the usable range was extendable to 20% conversion to products. Under the conditions employed, the internal return products were determined to be relatively inert. The rate constants given in Table I for these tosylates are therefore the k's for acetate formation only. In particular, they are believed to exclude any significant contributions from secondary acetolysis. The remaining three substrates underwent solvolysis according to simple first-order kinetics.

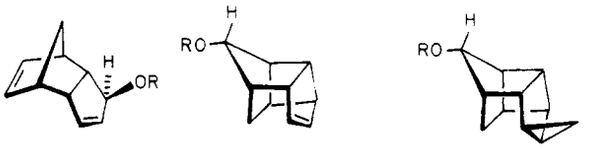
The kinetic data, together with relative rate factors and derived activation parameters (where assessable), are summarized in Table I.

Product Analysis. Upon preparative scale acetolysis at 71 °C, *endo*-tetracyclo[5.3.0.$0^{2,6}$.$0^{3,10}$]decan-4-yl tosylate (**8b**) was converted to a mixture of **16b** (98%) and **6c** (2%). Comparable treatment of the corresponding exo isomer (**6b**) led exclusively to **16b.** Upon lowering the reaction temperature for **6b** to 25.9 °C, the liberation of *p*-toluenesulfonate anion stopped after 15% acetolysis. The product mixture consisted of rearranged tosylate **16c** (85%) and the structurally related acetate **16b.** The structural assignment to **16b** and **16c** is based upon their rather characteristic ^{1}H NMR spectra (e.g., $J_{1,10} = J_{7,10} = 1.5$ Hz), lithium aluminum hydride reduction of **16b** to alcohol **16a,** and Eu(fod)$_3$ induced shifting of the latter. As expected of the *anti*-hydroxyl stereochemistry, the H_1, H_7, *exo*-H_8, H_9, and H_{10} protons in **16a** experienced the greatest

16 a, R = H; b, R = Ac; c, R = Ts 17

downfield shifting. Also clearly revealed was the geminal coupling of *exo*-H_8 with *endo*-H_8, as well as its vicinal coupling to H_7 and H_9 in accordance with dihedral angle estimates gained from molecular models. Additionally, Collins oxidation of **16a** gave ketone **17** whose intense paired carbonyl absorptions at 1780 and 1765 cm^{-1} compare closely to those of 7-norbornanone (1778 and 1740 cm^{-1}).[9]

The acetolysis of **5b** at 44.5 °C gave **18b** along with 30% polymer. The solvolytic reaction of unsaturated exo isomer **3b** (conducted at 25.9 °C) also led to **18b** (50%), but produced significant amounts of **19a** (5%) and **19b** (45%) as well. That



18 a, R = H; b, R = Ac 19 a, R = Ac; b, R = Ts 20 a, R = Ac; b, R = Ts

18b has the designated doubly unsaturated tricyclic structure is based upon its spectral parameters and independent synthesis by acetylation of the known alcohol **18a.**[10] One key feature of the ^{1}H NMR spectra of **19a** and **19b** is the clean narrow triplet (J = 1.5 Hz) which arises from the proton on carbon bonded to oxygen. That this multiplicity is again characteristic of a 7-norbornyl type proton was established by catalytic hydrogenation of **19b** to **16c.** Also, heating of **19b** in buffered acetic acid at 70 °C for 41 h returned exclusively **19a.**

Whereas the acetolysis (71 °C) of **10b** occurred with clean conversion to **20a,** its endo counterpart **15b** gave a more complex distribution of products under identical conditions. Thus, **10c** (8%) and three unsaturated acetates of still unes-

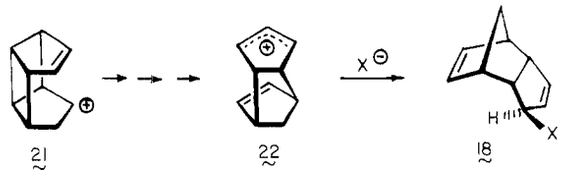
tablished structure (27, 20, and 5%) were isolated in addition to **20a** (40%). The great similarity of the downfield sector of the ^1H NMR spectrum of **20a** to those of **16b** and **19a** was taken as evidence that a comparable skeletal rearrangement had taken place.

Discussion

Evidence has been accumulated in the foregoing experiments that the various exo-substituted hypostrophene derivatives are characterized by enhanced solvolytic reactivity. Direct comparison of the apparent acetolysis rate constants given in Table I provides the following exo/endo rate ratios: unsaturated **3b/5b** = 51; saturated **6b/8b** = 25; and cyclopropanated **10b/15b** = 63 (all at 25.9 °C). Suitable control experiments conducted on **6b** and **10b** revealed internal return to be an important feature of their solvolytic chemistry. In contrast, their endo counterparts were not seen to rearrange to isomeric tosylates. In view of the typical product distributions which show **16c** and **20b** to be formed at least six times faster than the acetate products, the true rates of ionization for **6b** and **10b** ($k_{ion} = k_{solv} + k_{int\ ret}$) must in reality be some seven times larger than determined experimentally or 74×10^{-6} and 120×10^{-6}, respectively. If internal return to the starting tosylates is neglected, as it must be under the present circumstances, these *exo*-sulfonate esters are seen to exhibit substantial kinetic enhancement to ionization (170 and 440) relative to the endo-saturated and cyclopropanated derivatives.

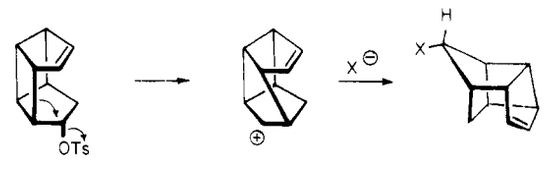
The behavior of **3b** in buffered acetic acid is such that internal return with skeletal rearrangement was again prominent, as reflected in the isolation of **19b** (45%) at 25.9 °C. But this tosylate is also the most reactive of the entire series and the true magnitude of k_{ion} was more difficult to establish conclusively in this instance. Notwithstanding, it is clear that acetolysis of the exo isomers is greatly accelerated by neighboring-group participation, or the endo isomers are unexpectedly slow. The former explanation seems the more reasonable to us, and the ensuing discussion makes clearer our reasons for this choice.

Observations made in earlier work[1] suggest that should **3b** or **5b** experience simple S_N1 ionization to cation **21,** there can

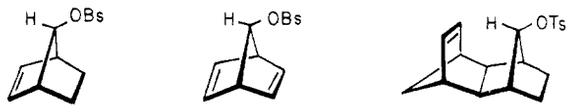


21 22 18

be expected to follow a rapid energy-releasing cascade to the substantially less strained *endo*-dicyclopentadienyl framework **22** and eventual nucleophilic capture of the latter to give **18.** Convincing evidence that the endo substitution plan in **5b** is conducive to transient generation of **21,** as expected, is found in its isomerization to **18b.** Although the very reactive **3b** experiences partial conversion to **18b** as well, there is also formed significant amounts of **19a** (5%) and **19b** (45%) at 25.9 °C. Consequently, the customarily overwhelming capability of the proximate double bond in **3b** to enter into transannular bonding[1] has been overridden by an alternative electronic realignment involving apparent 1,2-shift of a lateral edge bond. The competitive isomerization to **23** is considered to be



3b 23 19



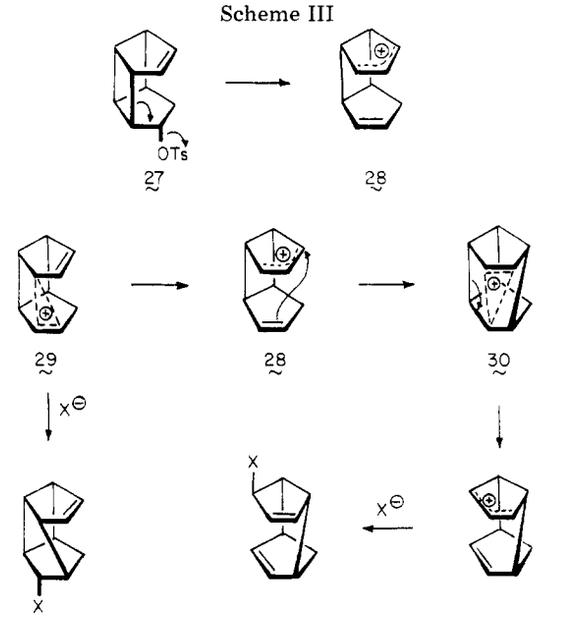
24 25 26

the combined result of an ideal antiplanar stereoelectronic arrangement and the effectiveness with which the electron-rich lateral cyclobutane bond can dissipate positive charge. It is particularly remarkable that the proximate double bond in **3b** does not find it possible to control the ionization in its entirety since one $p\pi$ orbital is tightly compressed to the anterior of the departing group. However, the isolation of **19a** and **19b** argues against such domination and provides indication that electronic factors within this hypostrophene derivative differ from that customarily found in such unsaturated molecules as the *anti*-7-norbornenyl (**24**),[11] 7-norbornadienyl (**25**),[12] and octahydrodimethanonaphthyl brosylates (**26**)[13] where through-space interaction is fully operative.

One may now question why the lateral σ bond in **3b** does not enter into electronic reorganization as illustrated in **27** to provide access to the assumedly more thermodynamically stable allylic cation **28** (Scheme III). The reader will undoubtedly be aware of the fact that demonstration of a rate enhancement in solvolysis is good evidence for participation in the transition state, but tells nothing about the structure of the intermediate cation formed. In the present instance, the available data does allow for the possibility that **3b** ionizes with *total* σ anchimeric assistance to produce the nonclassical or rapidly equilibrating ion **29** much in the manner characteristic of 2-norbornyl and related systems. Although bottom-side nucleophilic capture of **29** will lead to **19,** it is not inconceivable that allylic cation **28** can be formed from **29** after the rate determining step and experience subsequent electronic reorganization via **30** and **22** to give products of type **18** (Scheme III). Unfortunately, no labeling scheme will distinguish whether **18** arises from **21** or **29.** The results make it clear, however, that if **29** is the exclusive intermediate of kinetic control its partitioning between direct conversion to **19** and further rearrangement in the **28** → **30** → **22** → **18** manifold is approximately equal.

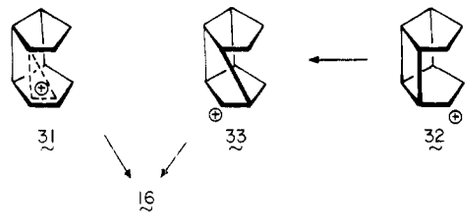
With the exception of 2% inversion of configuration in **8b,** the epimeric saturated tosylates **6b** and **8b** are converted to the same product (**16b**), although at widely differing rates. The formation of **16** further reveals the proclivity of hypo-

Scheme III



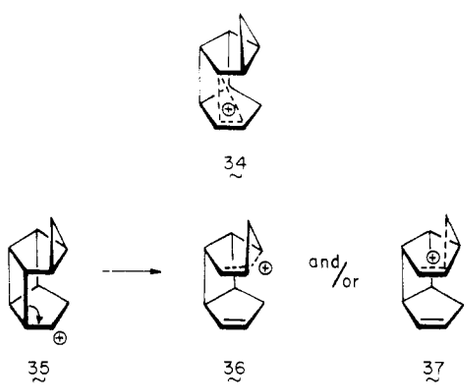
27 28 29 28 30 19 18 22

strophene derivatives for 1,2-migration of an edge cyclobutane bond. If, on the one hand, the position is taken that exo derivative **6b** undergoes acetolysis with anchimeric assistance and conversion to **31**, the rate difference can be attributed in large part to σ-electron delocalization. Alternatively, if it is accepted that the behavior of **6b** is normal and characterized by initial conversion to **33**, the slower rate of ionization ex-



hibited by **8b** must be attributed to steric inhibition of ionization. This analysis would require **6b** to differ phenomenologically from its unsaturated and cyclopropanated analogues (vide infra), a seemingly unwarranted distinction. More importantly, steric factors cannot be chiefly responsible for the slow rate of ionization of **8b**. Molecular models reveal that the pair of endo transannular hydrogens present in **8b** and **15b** and the attendant congestion in the inner sphere of the hypostrophene framework are not greatly different from that found in the endo unsaturated derivative **5b**, due principally to a reduction in conformational flexibility in the latter. Yet, the individual rates exhibited by this trio of *endo*-tosylates differ by only 33-fold, despite the presence of a π bond and cyclopropane ring in close proximity to the ionizing centers in **5b** and **15b** and the well-established capabilities of such groups to inhibit through induction the generation of nearby positive charge.[14] Consideration of the following ratios of acetolysis rate constants ($k_{3b}/k_{6b} = 40$; $k_{3b}/k_{10b} = 25$; $k_{5b}/k_{8b} = 20$; $k_{5b}/k_{15b} = 33$; $k_{8b}/k_{15b} = 1.7$; $k_{6b}/k_{10b} = 0.6$) reveals that *both* the exo-unsaturated and endo-unsaturated tosylates experience ionization some 20–40 times more rapidly than their saturated or cyclopropanated counterparts. In contrast, comparison of the saturated and cyclopropanated compounds lacking unsaturation generates ratios close to unity. Internal return aside, it therefore appears that the cations derived from **3b** and **5b** are stabilized. For the endo example, we attribute this to through-bond stabilization of classical cation **21**. The behavior of the exo system is adequately understood in terms of **29**.

With the *exo*-cyclopropyl derivative **10b**, efficient conversion to **20a** was noted. This behavior necessarily implicates **34** (or its rapidly equilibrating equivalent) since endo isomer **15b** gives a rather different product profile. The formation of several unsaturated acetates, for example, appears to be related to lateral bond cleavage within classical cation **35** to deliver **36** and/or **37** (this point remains to be unequivocally established). Evidently, the anchimeric assistance in **34** succeeds in repressing this rearrangement with its attendant greater release of strain energy.



The incursion of extensive σ-bond participation during ionization of the *exo*-hypostrophenyl derivatives affords the simplest explanation for both the high reactivities and stereospecific rearrangements described above. Rate-determining involvement of a lateral cyclobutane bond is appropriately in accord with highly effective through-bond coupling known to prevail in this ring system[4,16] and with partial strain relief. Before generalizations can be drawn concerning the extent to which through-bond interaction can be effective in the stabilization of cationic centers, there is a need to consider a variety of other structural types whose electronic structures are reasonably well characterized. The ensuing paper[17] constitutes a step in this direction.

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained on Varian T-60, A-60A, and HA-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were obtained with Perkin-Elmer Model 137 and 467 spectrometers, while mass spectra were measured with an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***exo*-Tetracyclo[5.3.0.0^{2,6}.0^{3,10}]dec-4-en-8-ol Tosylate (3b). General Procedure for Tosylate Formation.** A mixture of the alcohol (3.4 mmol) and *p*-toluenesulfonyl chloride (0.7 g, 3.6 mmol) in 7 mL of dry pyridine was stored in a refrigerator for 24 (exo derivatives) or 72 h (endo derivatives). Ice water (50 mL) was added and after 10 min (certain of the tosylates crystallized within this time) the product was extracted into ether (3 × 50 mL). The combined organic layers were washed with cold 10% hydrochloric acid (3 × 75 mL), saturated sodium bicarbonate solution, and brine prior to drying and solvent evaporation at 0 °C. The residue (oil or crystals) was dissolved in a minimum amount of hexane and stirred with charcoal for 30 min at 20 °C. After filtration and cooling to 0 °C, the tosylates were obtained crystalline and recrystallized to purity from hexane. In the case of **3b**, the white crystalline solid melted at 54–55 °C with decomposition. The individual ^{1}H NMR spectra showed all tosylates to be unrearranged relative to their alcohol precursors.

***endo*-Tetracyclo[5.3.0.0^{2,6}.0^{3,10}]dec-4-en-8-ol (5a).** Dry chromium trioxide (600 mg, 6 mmol) was added to a magnetically stirred solution containing 949 mg (12 mmol) of anhydrous pyridine in 15 mL of freshly distilled methylene chloride. The flask was capped with a Drierite drying tube and the deep burgundy solution was stirred at room temperature for 15 min. A solution of 149 mg (1 mmol) of **3a** in a few milliliters of dry methylene chloride was added in one portion and a tarry black residue immediately formed. After 30 min, the solution was decanted into 10 mL of 5% sodium hydroxide solution and the residue was rinsed with ether. The combined organic layers were washed with two 10-mL portions of 5% sodium hydroxide solution, two 10-mL portions of 5% aqueous hydrochloric acid, 10 mL of saturated sodium bicarbonate, and 10 mL of brine. Drying of the solution, followed by filtration and evaporation of solvent, left 144 mg (97%) of ketone **4** as a pale yellow oil: IR ν_{max} (neat) 1730, 1392, 1343, 1259, 1075, 878, 803, and 739 cm^{-1}; *m/e* calcd 146.0732, found 146.0734.

The ketone was directly dissolved in 10 mL of anhydrous ether and treated with 38 mg (1 mmol) of lithium aluminum hydride followed by gentle refluxing under nitrogen for 1 h. The usual workup[1] provided 160 mg of white crystals which were purified by sublimation [45 °C (0.03 mm)] to give 77 mg (51%) of pure **5a**: IR ν_{max} (KBr) 3370, 1345, 1260, 1110, 1054, 1010, 815, 790, 755, and 733 cm^{-1}; NMR δ_{Me_4Si} ($CDCl_3$) 6.65 (dd, 1), 6.23 (dd, 1), 4.34 (m, 1), 3.60–2.80 (br m, 6), 2.52–2.00 (br m, 1), 2.02 (br s, 1), and 1.56 (dd, 1); *m/e* calcd 148.0888, found 148.0891.

The 3,5-dinitrobenzoate was prepared by the customary procedure and isolated as off-white crystals, mp 155–156 °C (from ether), in quantitative yield.

Anal. Calcd for $C_{17}H_{14}N_2O_6$: C, 59.65; H, 4.12; N, 8.18. Found: C, 59.68; H, 4.33; N, 8.12.

Tosylate **5b** was isolated as a colorless crystalline solid, mp 77–77.5 °C.

***exo*-Tetracyclo[5.3.0.0^{2,6}.0^{3,10}]decan-4-ol (6a).** A solution of **3a** (1.40 g) in 75 mL of purified hexane containing 100 mg of 5% palladium on charcoal was hydrogenated at atmospheric pressure (vigorous magnetic stirring) for 40 min. The catalyst was removed by filtration, the solvent was evaporated, and the residue was directly sublimed [55 °C (10 mm)] to give 1.25 g (89%) of **6a** as a waxy colorless solid; NMR

δ_{Me_4Si} ($CDCl_3$) 4.50 (dd, 1), 3.29–2.68 (br m, 6), 2.47 (dd, 1), and 2.00–1.20 (br m, 6); *m/e* calcd 150.1045, found 150.1047.

The 3,5-dinitrobenzoate was obtained in quantitative yield as off-white crystals, mp 135.5–136 °C (from ether).

Anal. Calcd for $C_{17}H_{16}N_2O_6$: C, 59.30; H, 4.68; N, 8.14. Found: C, 59.11; H, 4.80; N, 7.98.

Tosylate **6b** was isolated as a colorless crystalline solid, mp 72.5–73 °C.

***endo*-Tetracyclo[5.3.0.0^{2,6}.0^{3,10}]decan-4-ol (8a). A. Diimide Reduction of 5a.** A solution of **5a** (1.8 g, 12.2 mmol) in 150 mL of methanol containing 23.6 g (122 mmol) of potassium azodicarboxylate was cooled to 0 °C and treated dropwise with 20.6 ml of acetic acid during 1 h. Stirring was maintained at 0 °C until the yellow color faded. Then 100 mL of water was added, most of the methanol was evaporated, to give 1.7 g (94%) of **8a:** IR ν_{max} (KBr) 3320, 1110, 1062, 1020, 927, 908, and 890 cm^{-1}; NMR δ_{Me_4Si} ($CDCl_3$) 4.32 (m, 1), 3.20–2.48 (br m, 7), and 2.28–1.48 (br m, 6); *m/e* calcd 150.1045, found, 150.1047.

The 3,5-dinitrobenzoate was obtained as off-white plates, mp 148–149 °C (from ether).

Anal. Calcd for $C_{17}H_{16}N_2O_6$: C, 59.30; H, 4.68; N, 8.14. Found: C, 59.17; H, 4.79; N, 8.27.

The tosylate **8b** was obtained as a colorless crystalline solid, mp 44.5–45 °C.

B. Oxidation–Reduction of 6a. An 800-mg (5.3 mmol) sample of **6a** was oxidized with 3.2 g (32 mmol) of anhydrous chromium trioxide and 4.96 g of pyridine in 80 mL of methylene chloride as described above. The resulting ketone (0.71 g) was reduced with 0.18 g of lithium aluminum hydride in 15 mL of anhydrous ether and the semicrystalline product was sublimed to give 420 mg of a waxy colorless solid, the spectral features of which proved identical with those of **8a** as detailed above.

***exo*-Pentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{8,10}]undecan-4-ol (10a).** A solution of 100 mg of **9**[1] in 10 mL of anhydrous tetrahydrofuran was cooled to 0 °C under nitrogen and excess 9-borabicyclononane in tetrahydrofuran solution (10 mL of 0.5 M) was added dropwise during 30 min. Oxidative hydrolysis of this reaction mixture as before[1] gave **10a** in 60% yield. The alcohol was purified by preparative VPC on a 30% SE-30 column at 105 °C: IR ν_{max} (neat) 3380, 1055, 1009, and 900 cm^{-1}; NMR δ_{Me_4Si} ($CDCl_3$) 4.69 (dd, 1), 3.24–2.36 (br m, 7), 1.72–1.20 (br m, 4), 0.30 (dt, 1), and −0.25 (dt, 1).

The 3,5-dinitrobenzoate was obtained as off-white clusters, mp 148–149 °C (from ether).

Anal. Calcd for $C_{18}H_{15}N_2O_6$: C, 60.67; H, 4.53; N, 7.86. Found: C, 60.43; H, 4.64; N, 7.79.

Tosylate **10b** was isolated as colorless crystals, mp 90–92 °C.

9,9-Dichloro-*exo*-pentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{8,10}]undecan-4-yl Acetate (12). A solution of **3a** (0.50 g) and acetic anhydride (0.65 mL) in 6 mL of pyridine was stirred at room temperature in a stoppered flask for 24 h, poured onto ice, and extracted with pentane (3 × 25 mL). The combined organic layers were washed with cold dilute hydrochloric acid, saturated sodium bicarbonate solution, and brine prior to drying. Removal of solvent left 0.6 g of **11** whose key ^1H NMR signals were seen [δ 6.25 (m, 2), 4.96 (dd, J = 7 and 2 Hz, 1), and 1.96 (s, 3)] in $CDCl_3$ solution.

To a solution of **11** (0.6 g) in chloroform was added 50 mg of benzyltriethylammonium bromide and 1.5 mL of 50% sodium hydroxide and the mixture was stirred at room temperature for 60 h. Dilution with water was followed by extraction with chloroform (3 × 15 mL). The combined organic layers were washed with brine, dried, and evaporated to give 750 mg (81.5% overall) of **12:** mp 98–99 °C (from cyclohexane); NMR δ_{Me_4Si} ($CDCl_3$) 5.50 (dd, 1), 3.45–2.5 (br m, 6), 2.4–2.02 (m, 2), 1.92 (s, 3), and 1.84–1.4 (m, 2).

This material was used directly without purification.

9,9-Dichloro-*exo*-pentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{8,10}] undecan-4-ol (13). To a stirred suspension of lithium aluminum hydride (120 mg) in 10 mL of anhydrous ether was added dropwise a solution of **12** (700 mg) in 10 mL of the same solvent. Stirring was maintained at room temperature for 1 h before sequential introduction of water (0.12 mL), 15% sodium hydroxide solution (0.12 mL), and water (0.36 mL). The precipitated solids were filtered and rinsed well with ether. The combined filtrates were washed twice with brine, dried, and evaporated. There was isolated 560 mg (94%) of **13;** NMR δ_{Me_4Si} ($CDCl_3$) 4.65 (dd, 1), 3.12–2.4 (br m, 6), 2.16–1.95 (m, 2), 1.85 (br s, 1), and 1.78–1.35 (m, 4).

This material was likewise utilized without further purification.

Reductive Dehalogenation of 13. To a solution of sodium metal (0.45 g) in 40 mL of liquid ammonia cooled to −75 °C under nitrogen was added 0.60 g of **13** dissolved in 5 mL of ether. Stirring was maintained for 30 min at this temperature before addition of solid ammonium chloride to discharge the blue color. The ammonia was allowed to evaporate, the residue was partitioned between water and ether, and the aqueous phase was twice reextracted with ether. The combined organic layers were dried and evaporated to afford 0.30 g (74%) of alcohol **10a,** which proved identical with the material prepared earlier.

***endo*-Pentacyclo [5.4.0.0^{2,6}.0^{3,11}.0^{8,10}] undecan-4-ol (15a).** Alcohol **10a** (322 mg) was oxidized with chromium trioxide–pyridine in the predescribed manner to give 78 mg of ketone **14;** IR ν_{max} (neat) 1730 cm^{-1}. Its direct reduction with sodium borohydride (100 mg) was carried out in 3 mL of absolute methanol at 0 °C for 10 min. After stirring at room temperature for 1 h, the mixture was processed in the customary fashion to give 57 mg of oil which crystallized on standing. Preparative gas chromatography on a 6 ft 5% SE-30 column at 110 °C gave 31 mg (39%) of **15a** as colorless crystals; IR ν_{max} (neat) 3340, 1447, 1347, 1330, 1312, 1298, 1110, 1062, 1035, 1010, 910, 827, and 804 cm^{-1}; NMR δ_{Me_4Si} ($CDCl_3$) 4.40 (m, 1), 2.90 (m, 6), 2.52 (m, 2), 2.20 (m, 1), 1.81 (m, 1), 1.29 (m, 1), 0.42 (dt, 1), and −0.18 (dt, 1).

The dinitrobenzoate was prepared in the usual manner and obtained in 93% yield as off-white blades, mp 184.5–185.5 °C (from ether).

Anal. Calcd for $C_{18}H_{16}N_2O_6$: C, 60.67; H, 4.53; N, 7.86. Found: C, 60.46; H, 4.50; N, 7.85.

Tosylate **15b** did not crystallize and was utilized in the form of a colorless viscous oil.

Kinetic Measurements for *endo*-Tosylates. In the case of **5b, 8b,** and **15b,** the usual ampule technique was used. Approximately 40 mg of tosylate was dissolved in 10 mL of buffered acetic acid (0.03 M in NaOAc) and transferred in 1.25-mL portions into eight ampules. These were sealed and placed simultaneously into a constant temperature bath. After 15 min, the first ampule was removed and inserted immediately into an ice bath. After 2 min, the ampule was transferred to a room temperature water bath where it was maintained for 3 min. Exactly 1.0 mL of this solution was titrated with 0.0075 M perchloric acid in acetic acid to give V_0; V_∞ was taken after 10 half-lives. Additional ampules were removed at appropriate time intervals and handled comparably. The rate constants were obtained by least-squares analysis of $\ln (V_\infty - V_0/V_\infty - V)$ vs. time with the aid of a Wang computer program.

Kinetic Measurements for *exo*-Tosylates. The method described by Wiberg[8] was utilized to obtain the solvolysis rates of **6b** and **10b.** The tosylate (~200 mg) was dissolved in 1 mL of dry carbon tetrachloride. Independently, increasing amounts of accurately weighed anhydrous sodium acetate were placed into ten test tubes. The final volume in each was adjusted to 8 mL through addition of anhydrous acetic acid. After 2 drops of a 1% bromophenol blue solution in acetic acid was introduced to each tube, they were stoppered and placed in a constant temperature bath for 15 min. Then a 0.095-mL portion of the tosylate solution was added to the first test tube via syringe and the time for complete indicator change was noted (zero time was taken subsequent to addition). The process was repeated for each test tube, covering a range of 5% reaction. The rate constants were then obtained from a least-squares analysis of $\ln [ROTs]_0/[ROTs]_t$ vs. t.

The following modification was employed for **3b.** Approximately 20 mg of the tosylate was weighed into a vial and 0.1 mL of carbon tetrachloride was added. The vial was placed in a constant temperature together with a second vial containing 8 mL of acetic acid and 2 drops of 1% bromophenol blue in acetic acid. After 15 min, the acetic acid was rapidly transferred to the tosylate solution. A timer was started, 0.100 mL of a standard NaOAc/HOAc solution (viz., 0.9812 × 10^{-3} mmol of NaOAc) was added and the time necessary for complete decolorization was noted. A second 0.100 mL of the NaOAc solution was added and the procedure was repeated. This cycle was extended to cover 20% of reaction and data analysis was achieved as above.

Acetolysis of 8b. A solution containing 0.40 g of **8b** and 0.10 g of sodium carbonate in 10 mL of glacial acetic acid was heated at 71 °C for 40 h. After cooling, neutralization was effected with saturated sodium bicarbonate solution. The products were extracted into ether (3 × 50 mL) and the combined organic extracts were washed with saturated $NaHCO_3$ solution and brine before drying and evaporation. Analysis of the residue (0.20 g) on a 6 ft × 0.25 in. 10% SE-30 column (150 °C) showed the oil to consist of **16b** (98%) and **6c** (2%). Preparative scale isolation gave the pure components.

For **16b:** NMR δ_{Me_4Si} ($CDCl_3$) 4.82 (br s, 1), 2.8–2.05 (br m, 5), 2.00 (s, 3), and 1.9–1.2 (m, 7); *m/e* calcd 192.1154, found 192.1150.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.95; H, 8.48.

For **6c:** NMR δ_{Me_4Si} ($CDCl_3$) 4.83 (m, 1), 3.0–2.05 (br m, 8), 2.00 (s,

3), and 1.95–1.4 (m, 4). This oil proved identical with that obtained from direct acetylation of **6a.**

Acetolysis of 6b. A solution of **6b** (0.10 g) in 6 mL of glacial acetic acid was kept at 71 °C for 25 min. The solvent was removed at 25 °C and 0.1 mm to leave a dark residue (0.085 g) which was dissolved in warm hexane, filtered to remove *p*-toluenesulfonic acid, and cooled to −20 °C. The precipitated solid was recrystallized twice more from hexane to give 0.04 g of pure **16c:** mp 80–80.5 °C; NMR δ_{Me_4Si} ($CDCl_3$) 7.78 (d, J = 5 Hz, 2), 7.31 (d, J = 5 Hz, 2), 4.59 (t, J = 1.5 Hz, 1), 2.75–2.5 (m, 2), 2.45 (s, 3), 2.38 (br m, 3), and 1.8–1.4 (m, 7); *m/e* calcd 304.1133, found 304.1139.

Anal. Calcd for $C_{17}H_{20}O_3S$: C, 67.07; H, 6.62. Found: C, 67.16; H, 6.68.

In a second experiment, a mixture of **6b** (0.10 g), anhydrous sodium carbonate (0.05 g), and glacial acetic acid was maintained at 71 °C for 96 h. After the usual workup, there was isolated 0.06 g of **16b** as the only product.

Sequential Reduction–Oxidation of 16b. A solution of **16b** (0.14 g) in 5 mL of anhydrous ether was added dropwise to a stirred slurry of lithium aluminum hydride (0.055 g) in the same solvent (10 mL). After 2 h at room temperature, there followed the usual workup and isolation of 0.08 g of **16a.** The ^1H NMR spectrum of this alcohol was extensively decoupled prior and subsequent to incremental amounts of $Eu(fod)_3$.

Alcohol **16a** (0.03 g) was added to a solution of chromium trioxide (0.12 g) and pyridine (0.19 mL) in 4 mL of methylene chloride and stirred at room temperature for 30 min. The solution was decanted, the residue was rinsed twice with ether, and the combined organic phases were washed with 5% sodium hydroxide solution (3 × 20 mL), 5% hydrochloric acid (3 × 20 mL), and brine. Drying and evaporation afforded 0.025 g of **17:** IR ν_{max} (Nujol) 1780 and 1765 cm^{-1}.

Acetolysis of 5b. A mixture comprised of **5b** (0.40 g), anhydrous sodium carbonate (0.20 g), and glacial acetic acid (10 mL) was kept at 36 °C for 96 h. After the usual workup, 0.23 g of an oil was obtained, VPC analysis of which indicated it to consist of **18b** (70%) and polymeric material (30%). For **18b:** NMR δ_{Me_4Si} ($CDCl_3$) 6.1–5.8 (m, 2), 5.6–5.45 (m, 2), 4.96 (m, 1), 3.4–2.5 (m, 5), 2.17 (s, 3), and 1.7–1.2 (m, 1).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.70; H, 7.36.

Acetolysis of 3b. A solution comprised of **3b** (0.20 g), anhydrous sodium carbonate (0.06 g), and glacial acetic acid (10 mL) was kept at 25.9 °C for 1.5 h. After neutralization with sodium bicarbonate solution, the products were extracted into ether (3 × 40 mL). The combined organic layers were processed in the usual manner to leave a mixture of **18b** (50%), **19a** (5%), and **19b** (45%) (combined ^1H NMR and VPC analysis). The volatile acetates were removed under vacuum [25 °C (0.1 mm)] overnight.

One half of the residue (0.06 g) consisting of **19b** was hydrogenated over 10% palladium on charcoal in hexane during 3 h. Filtration and evaporation of solvent left 0.025 g of crystalline **16c.**

The other half of the residue was dissolved in 5 mL of acetic acid containing 0.03 g of sodium carbonate and heated at 70 °C for 41 h. After the usual workup, 0.035 g of an oil was obtained whose only volatile component was **19a;** NMR δ_{Me_4Si} ($CDCl_3$) 6.11 (dd, 1), 5.76 (dd, 1), 4.83 (br s, 1), 2.95–2.80 (m, 4), 2.7–2.0 (br m, 1), 2.02 (s, 3), and 1.95–1.3 (m, 2).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.68; H, 7.69.

Acetolysis of 10b. Subsequent to heating 0.2 g of **10b,** 0.1 g of sodium carbonate, and 7 mL of acetic acid at 71 °C for 72 h and processing the reaction mixture in the usual manner, there was isolated 0.1 g of **20a:** NMR δ_{Me_4Si} ($CDCl_3$) 4.73 (br s, 1), 2.7–1.95 (m, 8), 2.00 (s, 3), 1.90–0.85 (m, 4), and 0.35 to −0.14 (m, 2); *m/e* calcd 134.1095, found 134.1097.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 74.19; H, 9.34. Found: C, 73.94; H, 9.18.

In a second experiment, a 0.05-g sample of **10b** was dissolved in 5 mL of acetic acid and kept at 71 °C for 30 min. After cooling and evaporation of solvent at 20 °C (0.1 mm), there was obtained 0.035 g of a dark oil which was dissolved in warm hexane and filtered to remove *p*-toluenesulfonic acid. On cooling at −20 °C, there was precipitated 0.03 g of **20b:** mp 76.5–77 °C (from hexane); NMR δ_{Me_4Si} ($CDCl_3$) 8.1 (d, 2), 7.5 (d, 2), 4.50 (s, 1), 2.65–1.5 (m, 6), 2.46 (s, 3), 1.3–0.90 (m, 4), and 0.3 to −0.15 (m, 2); *m/e* calcd 316.1133, found 316.1137.

Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.32; H, 6.37. Found C, 68.04; H, 6.45.

Acetolysis of 15b. A solution of **15b** (0.25 g) and anhydrous sodium carbonate (0.1 g) in acetic acid (8 mL) was heated at 71 °C for 30 h. After the usual workup, 0.15 g of an oil was isolated which contained five components in the ratio of 8:40:27:20:5 (6 ft × 0.25 in. 10% SE-30, 160 °C). The individual components were isolated and the most rapidly eluted acetate was shown to be **10c** by spectral comparison. The major constituent was **20a.** The more slowly eluted trio of acetates were unsaturated compounds, the structures of which remain to be ascertained.

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Registry No.—3a, 65071-67-2; **4,** 65071-90-1; **5a,** 65137-13-5; **5b** 3,5-DNP derivative, 65137-14-6; **6a,** 65071-91-2; **6b** 3,5-DNP derivative, 65071-92-3; **6c,** 65071-86-5; **8a,** 65137-15-7; **8b** 3,5-DNP derivative, 65137-16-8; **9,** 65071-71-8; **10a,** 65071-74-1; **10b** 3,5-DNP derivative, 65071-75-2; **11,** 65085-84-9; **12,** 65071-76-3; **13,** 65071-77-4; **14,** 65071-78-5; **15a,** 65137-08-8; **15b** 3,5-DNP derivative, 65137-09-9; **16a,** 65071-79-6; **16b,** 65071-80-9; **16c,** 65071-81-0; **17,** 65071-82-1; **18b,** 65071-83-2; **19a,** 65071-84-3; **19b,** 65071-85-4; **20a,** 65102-59-2; **20b,** 65102-60-5; *p*-toluenesulfonyl chloride, 98-59-9.

References and Notes

(1) Part 1: L. A. Paquette, D. R. James, and G. Klein, *J. Org. Chem.*, preceding paper in this issue.
(2) J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *J. Am. Chem. Soc.*, **93,** 4957 (1971).
(3) L. A. Paquette, R. F. Davis, and D. R. James, *Tetrahedron Lett.*, 1615 (1974).
(4) W. Schmidt and B. T. Wilkins, *Tetrahedron*, **28,** 5469 (1972).
(5) G. Klein and L. A. Paquette, *Tetrahedron Lett.*, 2419 (1976).
(6) P. v. R. Schleyer and R. C. Nicholas, *J. Am. Chem. Soc.*, **83,** 182 (1961); P. v. R. Schleyer, *ibid.*, **86,** 1854 (1964); C. S. Foote, *ibid.*, **86,** 1853 (1964).
(7) R. Hoffmann, P. D. Mollère, and E. Heilbronner, *J. Am. Chem. Soc.*, **95,** 4860 (1973).
(8) K. B. Wibert and B. A. Hess, Jr., *J. Am. Chem. Soc.*, **89,** 3015 (1967).
(9) P. G. Pape, M. S. Thesis, The Ohio State University, 1962, p 36.
(10) (a) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5,** 70 (1959); (b) L. A. Paquette and J. S. Ward, *J. Org. Chem.*, **37,** 3569 (1972).
(11) S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78,** 592 (1956); S. Winstein, A. K. Lewin, and K. C. Pande, *ibid.*, **85,** 2324 (1963); H. Tanida and T. Tsushima, *ibid.*, **92,** 3397 (1970).
(12) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82,** 2084 (1960); P. R. Story and M. Saunders, *ibid.*, **84,** 4876 (1962).
(13) S. Winstein and R. L. Hansen, *Tetrahedron Lett.*, **No. 25,** 4 (1960).
(14) J. C. Martin and B. R. Ree, *J. Am. Chem. Soc.*, **92,** 1660 (1970); V. Buss, R. Gleiter and P. v. R. Schleyer, *ibid.*, **93,** 3927 (1971).
(15) See, for example: A. Streitwieser, "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962, p 92; P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77,** 2806 (1955); P. D. Bartlett and T. T. Tidwell, *ibid.*, **90,** 4421 (1968); J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickson, and H. C. Brown, *ibid.*, **96,** 1969 (1974); W. G. Dauben and L. N. Reitman, *J. Org. Chem.*, **40,** 835 (1975).
(16) Collaborative research with Professor R. Gleiter.
(17) L. A. Paquette and M. J. Carmody, *J. Org. Chem.*, following paper in this issue.