The Use of 5-Halocyclooctenes as a Radical Probe. Reactions with Lithium Aluminum Hydride

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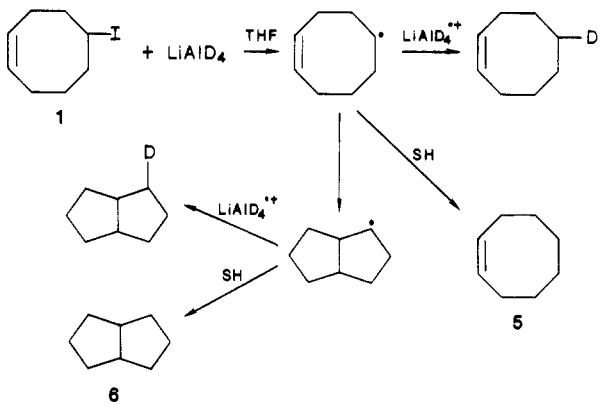
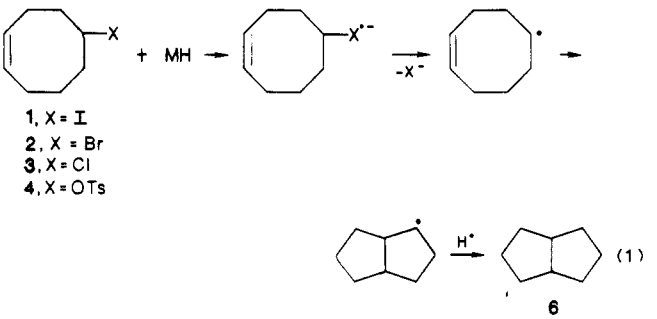
The 5-halocyclooctenes have been studied as a radical probe in their reactions with lithium aluminum hydride ($LiAlH_4$) in order to detect the occurrence of radical intermediates and also to evaluate the effectiveness of these compounds as radical probes. Also the 4-cyclooctenyl radical was trapped by dicyclohexylphosphine (DCPH), dicyclohexylphosphine deuteride (DCPD), and cyclohexadiene. For the iodide, and to a lesser extent the bromide, radical intermediates were found to be a major component in the reaction since the bicyclo hydrocarbon was the major product. No evidence for radical intermediates was found for reactions of the corresponding chloride or tosylate with $LiAlH_4$. It is concluded that 5-iodocyclooctene is an effective radical probe for those reactions where radical intermediates are involved.

In recent years, numerous studies concerning the reduction of organic halides by metal hydrides have appeared in the chemical literature.[1-3] A variety of mechanisms have been proposed to describe this reaction, e.g., a polar S_N2 pathway, a four-centered transition state, and a pathway involving a radical intermediate.[4-14] Recently, we were able to show by means of employing various cyclizable probes that radical intermediates are formed in the reduction of organic iodides by $LiAlH_4$ and AlH_3.[12] Since the cyclization of the 4-cyclooctenyl radical is a well-established radical rearrangement,[15-18] we decided to employ the 5-halocyclooctenes in the reaction with $LiAlH_4$ in order to provide a much more detailed evaluation of this system as a radical probe. Earlier, Posner[19] had observed that 5-bromocyclooctene cyclized when allowed to react with $LiCuMe_2$ and concluded that the formation of the bicyclic products in this reaction was due to the cyclization of the 4-cyclooctenyl radical. We also have recently used this system in the reaction of 5-iodocyclooctene with $LiEt_3BH$[20] and have found the expected bicyclo hydrocarbon product.

Scheme I



Herein, we would like to report detailed studies of the reduction of cyclizable alkyl halides with $LiAlH_4$, using the 4-cyclooctenyl group as a radical probe. Thus, if the cyclic product is produced in this reaction, the occurrence of a radical intermediate is suggested according to eq 1.



(1)

Results and Discussion

Reduction of the 5-halocyclooctenes, where (1) X = I, (2) X = Br, (3) X = Cl, or (4) X = OTs, by a variety of metal hydrides was carried out and the results are given in Table I (expts 1-7). Reaction of 1 with $LiAlH_4$ in THF (expt 1) gave a high yield (67%) of the cyclized product, bicyclo[3.3.0]heptane (6). Experiment 2 shows that the percentage of deuterium incorporation in the products of reaction of $LiAlD_4$ with 1 is 75% and 25% for 5 and 6, respectively. Clearly these data show that the hydrogen involved in the reductive of the halide comes from a source or sources in addition to the metal hydride. The deuterium incorporation study and the extent of cyclization reflected in the product suggest the occurrence of radical interme-

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Table I. Reduction of the 5-Halocyclooctenes 1–4 by Metal Hydrides at Room Temperature[a]

expt	time (h)	substrate	hydride	solvent	% yield of products 5	6	7
1	34	1 (X = I)	$LiAlH_4$	THF	30	67	0.0
2	48		$LiAlD_4$	THF	35 (75% d_1)[c]	65 (25% d_1)[c]	0.0
3	49		$LiAlH_4$	Et_2O	22	16	58.0
4	1.5		$LiAlH_4$	HMPA	93	1.5	0.0
5	192		AlH_3	THF	23	27	45.0
6	91	2 (X = Br)	$LiAlH_4$	THF	7.5	9.5[b]	0.0
7	124	3 (X = Cl)	$LiAlH_4$	THF	0	0[b]	0.0
8	124	4 (X = OTs)	$LiAlH_4$	THF	57	0[b]	0.0

[a] All reactions carried out were 0.1 M in both hydride and halide. [b] Recovered alkyl halide accounts for the material balance in expts 6, 7, and 8. [c] Numbers in parentheses indicate the % deuterium incorporation in the product.

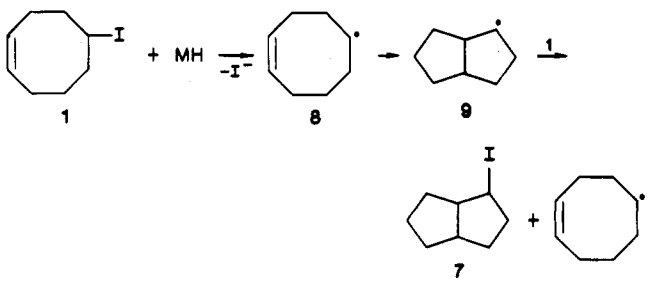
Table II. Rate Profile Studies of the Reaction of 5-Iodocyclooctene (1) with Various Reagents in THF at Room Temperature[a]

expt	reagent	time (min)	% recovered 1	% products 7	5	6
1	$LiAlH_4$	30	90	5	2	0
2		60	85	8	6	<1
3		90	22	57	20	4
4		120	trace	50	29	11
5		2040	0	0	30	67
6	AlH_3	1440	trace	68	23	13
7	$LiAlH_4 + AlH_3 + LiI$[b]	15	73	10	1	9
8		30	52	22	2	16
9		90	0	39	15	46
10	0.2 $LiAlH_4$	4320	20	75	5	<1

[a] All reactions carried out were 0.1 M in both hydride and halide. [b] 0.1 M of each reagent and halide was used.

diate precursors for both **5** and **6** which then abstract a hydrogen atom from either the solvent or the metal hydride (Scheme I). In Et_2O, the reaction of $LiAlH_4$ with **1** is considerably slower (expt 3) than that in THF. On the other hand, the reaction of $LiAlH_4$ with **1** in HMPA is considerably faster than that in THF and gives mostly the uncyclized product **5** (93%, expt 4). The fact that much less cyclization of the radical probe is observed in HMPA compared to Et_2O and THF does not necessarily imply that radical intermediates are not involved. Since cyclization of the probe takes place only outside of the solvent cage and since the viscosity of HMPA (η (20 °C) = 3.47) is considerably greater than that of Et_2O (η (20 °C) = 0.242) and THF (η (20 °C) = 0.55), more of the reaction in HMPA should take place in the solvent cage. We know from previous studies[12] that $LiAlH_4$ reduction of alkyl halides is much more rapid in HMPA than THF. Since electron transfer is the rate-determining step of the reaction and since cyclization of the 5-cyclooctenyl radical is significantly slower than the cyclization of the 2,2-dimethyl-5-hexenyl radical reported earlier (10^4 s^{-1} vs. 10^6 s^{-1}), it is not surprising that less cyclized product was observed in HMPA using the cyclooctenyl radical probe. Experiment 5 shows that the less reactive AlH_3 gives nearly an equal amount of **5** and **6** (23% and 27%), but this reaction is very slow. The formation of cyclized iodide **7** in the reaction of **1** with $LiAlH_4$ in Et_2O (expt 3) and with AlH_3 in THF (expt 5) is an important consideration in discussing the mechanism of this reaction and will be addressed later in this paper. The reduction of **2** (X = Br) by $LiAlH_4$ was examined in THF solvent (expt 6). The reaction proceeded very slowly, but produced nearly equal amounts of **5** (7.5%) and **6** (9.5%) over a period of 91 h. Clearly these data for the bromide indicate that a substantial portion of the reaction pathway involves the development of radical character sufficient for cyclization of the probe to occur. For **3** (X = Cl), no reduction product was obtained over a period of 124 h (expt 7), and for **4** (X = OTs), the only hydrocarbon product cyclooctene (**5**) was produced in 57% yield (expt 8) in 124 h. These data indicate that the reduction of **3** and **4** is probably a polar process and follows the rate order OTs ≫ Cl.

Scheme II



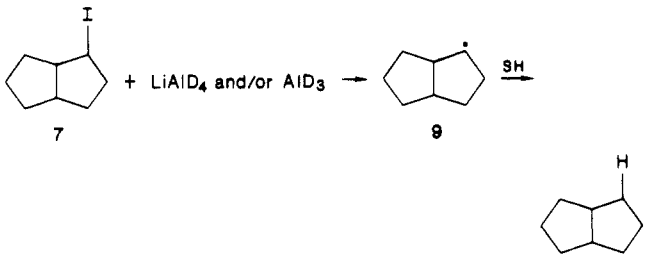
Next, we expanded the scope of these studies by carrying out a reaction profile study for the reduction of **1** by $LiAlH_4$ and AlH_3 (Table II). Note that in the reaction of **1** with $LiAlH_4$, the reduction product, bicyclo[3.3.0]-heptane (**6**), was formed only in the latter stages of the reaction. This result suggests that since LiI and AlH_3 are also formed in the latter stages of the reaction, they maybe participating in the cyclization of the starting material followed by reduction of the cyclized iodide **7** to the cyclized hydrocarbon product **6**. We examined the reaction of **1** with AlH_3 alone (expt 6) and with $LiAlH_4$ to which was added AlH_3 and LiI in THF (expt 7) before initiating the reaction. Clearly AlH_3 alone or the combination of AlH_3 and LiI with $LiAlH_4$ causes a rapid isomerization of

Table III. Action of Trapping Reagents on the Reduction of 5-Halocyclooctenes by $LiAlH_4$ and $LiAlD_4$ in THF[a]

expt	substrate	reagent	additive	time (h)	% products: 5	% products: 6
1	1 (X = I)	$LiAlH_4$	none	34	30	67
2		none	1 DCPH	72	0	0[a]
3		$LiAlH_4$	1 DCPH	2	93	6
4		$LiAlD_4$	none	48	35 (75% d_1)	65 (25% d_1)
5		$LiAlH_4$	1 DCPD	20	95 (47% d_1)	<1
6		$LiAlD_4$	5	69	66 (57% d_1)	4[b]
7		$LiAlD_4$	1 DCPH	30	88 (0.0% d_1)	9 (0.0% d_1)
8	4 (X = OTs)	$LiAlH_4$	none	124	57	0[b]
9		$LiAlD_4$	1 DCPH	124	59 (100% d_1)	0[b]

[a] All reactions carried out were 0.1 M in both hydride and halide. [b] Recovered alkyl halide accounts for the material balance in expts 2, 6, 8, and 9.

Scheme III



1 to iodobicyclo[3.3.0]heptane (7) (expt 6–9, Table II). The isomerization of 1 to its cyclic isomer 7 can be visualized as a radical chain process which is initiated by SET from $LiAlH_4$ and/or AlH_3 as in Scheme II.

In order to test for a radical chain process initiated by SET, we used a small amount of $LiAlH_4$ (20% relative to 1) in the reaction of 1 with $LiAlH_4$ in THF (expt 10, Table III). Cyclization of 1 to 7 took place in 75% yield, supporting the notion that the cyclization of the probe is a radical chain process.

It is important to realize that all of the cyclized product 6 is not formed as a result of a polar reduction of 7 by $LiAlH_4$ although 7 is formed rapidly in the reaction. This is clear from the data of expt 2, Table I, which shows that 75% of 6 and 25% of 5 were formed from a radical precursor in the reaction of $LiAlD_4$ with 1. The reaction with $LiAlD_4$ shows that part of the product must be formed by radical abstraction of hydrogen from the solvent. If the assumption is made that 7 is the major initial product, then one must explain the 35% yield of the uncyclized product 5 of which at least 25% is formed from a radical precursor. In addition, if the 65% yield of the cyclized hydrocarbon 6 is formation from 7, then the reaction of 7 with $LiAlH_4$ and/or AlH_3 must involve the formation of at least 75% of the product via a radical intermediate (9) (Scheme III).

The possibility that a small amount of oxygen might produce a radical intermediate followed by cyclization was examined by the introduction of dry oxygen to the reaction vessel prior to mixing the reactants. However, no reaction was observed between 1 and $LiAlH_4$ in the presence of oxygen. In addition, the reaction of 1 with $LiAlH_4$, carried out in an oxygen-free drybox, gave a 66.8% yield of 6 and a 33.0% yield of 5 which is the same result obtained using Schlenk tube techniques (expt 1, Table I). Thus, in the case of addition of a small amount of oxygen, the result was not cyclization of the probe but rather inhibition of the reaction.

Having obtained evidence of a radical intermediate in the reduction of a cyclizable alkyl iodide by the use of a cyclizable radical probe, next we sought to obtain additional information by utilizing trapping agents in order to trap the intermediate radicals. Since Kuivila[15] has shown that dicyclohexylphosphine (DCPH) can be used as a trapping agent for alkyl radical intermediates (eq 2), the

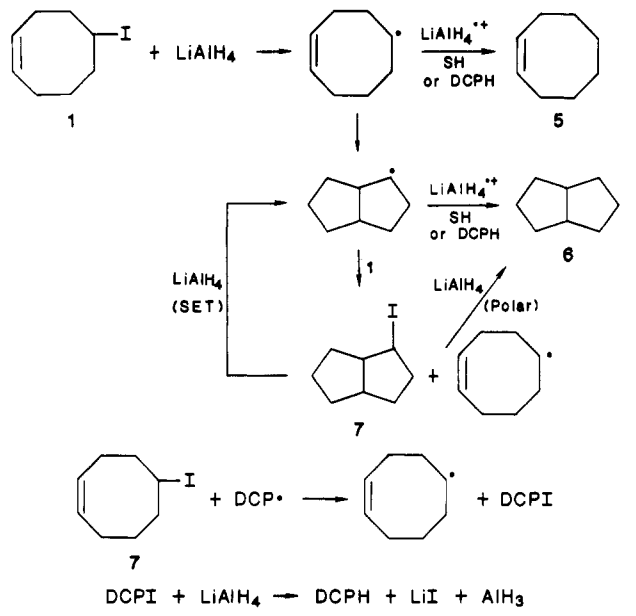
$$RX \xrightarrow{e^-} RX^{\cdot-} \rightarrow R^{\cdot} + X^- \xrightarrow{DCPH} RH \qquad (2)$$

ability of DCPH and other trapping agents such as DCPD and 1,4-cyclohexadiene were used in an attempt to trap intermediate radicals in the reduction of alkyl halides by metal hydrides. In order to observe the trapping of radical intermediates, one must employ $LiAlD_4$ as the reducing agent and then examine the products for the extent of deuterium incorporation. Or, one can use $LiAlH_4$ with a deuterated trapping agent such as DCPD and examine the products for deuterium incorporation. The reduction of 1 (X = I) and 4 (X = OTs) with $LiAlH_4$ and $LiAlD_4$ in the presence and absence of trapping agents were conducted and the results are given in Table III. Control experiments demonstrated that the alkyl halides employed were recovered quantitatively from THF solutions of trapping agents such as DCPH (expt 2, Table III) and that no reaction occured between $LiAlH_4$ and the trapping agents in the absence of the alkyl halides as determined by infrared spectroscopy (Al–H stretching band unperturbed on addition of DCPH). The reduction of the iodide 1 with $LiAlH_4$ in the presence of DCPH and DCPD is very interesting. The decrease in the formation of the cyclization product 6 from 67% to 6% and <1%, respectively, indicates that a significant amount of radical intermediate is produced which can abstract a H-atom from DCPH or a D-atom from DCPD (expts 3, 5). Abstraction of a D-atom from DCPD (expt 5) to give 47% d_1 in product 5 clearly shows that even noncyclized reduction product has, to a significant degree, a radical precursor.

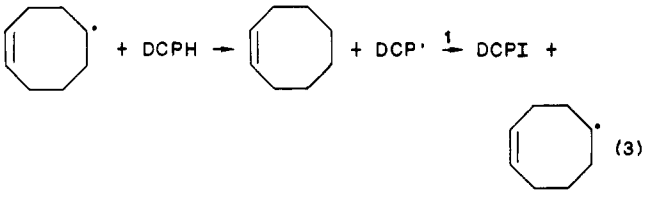
The reduction of 1 by $LiAlD_4$ also gives some very interesting results. First of all, deuterium incorporation in the reduction products is greatly reduced by the presence of DCPH (0% d_1 in each product, expt 7) and 1,4-cyclohexadiene (from 75% d_1 to 57% d_1, expt 6). Secondly, the decrease of cyclized product 7 in the presence of DCPH and cyclohexadiene (expt 5 and 6) further indicates the ability of the trapping agent to trap the radical intermediate before it can cyclize to produce 6. Note that the rate of reduction of 1 is much greater in the presence of DCPH as shown by comparison of expt 4 with expt 5.

The rate increase produced in the reaction of 1 with $LiAlH_4$ in the presence of DCPH is further evidence of a radical chain process (Scheme II) in which the radical product from 1 produced by electron transfer from $LiAlH_4$

Scheme IV



or AlH_3 can also be formed by reaction of **1** with DCP· formed in the reaction (eq 3, 4). For further evidence of



$$DCPI + LiAlH_4 \rightarrow DCPH + LiI + AlH_3 \quad (4)$$

the existence of a radical intermediate, we utilized compound **4** (X = OTs) in the reduction by $LiAlD_4$ in the presence of DCPH (expt 9) and found that no radical intermediate could be trapped in this case (100% d_1 in **5**). This result is consistent with an S_N2 pathway for the tosylate. Thus, although it is clear that reduction of alkyl iodides proceed by SET when allowed to react with $LiAlH_4$, it appears that chlorides and tosylates react by an S_N2 pathway with the bromide possibly reacting by both pathways. An overall mechanistic scheme to account for all the data is presented in Scheme IV.

Conclusion

A variety of methods have been utilized in order to evaluate the occurrence of an electron-transfer pathway for the reduction of organic halides by $LiAlH_4$. The reduction of a unique cyclizable system, the 5-substituted cyclooctenes, as a radical probe was examined. It appears that the tosylate and the chloride are reduced by an S_N2 pathway. However, for the iodide, overwhelming evidence exists to substantiate the occurrence of radical intermediates. In the case of the bromide, it appears that both S_N2 and SET are competing processes.

Experimental Section

Materials. Solvent grade pentane and hexane were stirred over concentrated H_2SO_4, washed with water, dried over $MgSO_4$, and distilled from $NaAlH_4$ under nitrogen before use. Reagent grade diethyl ether (Fisher) and reagent grade tetrahydrofuran (THF) were distilled under nitrogen from deep purple solutions of sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from sodium at reduced pressure. Cyclooctene was obtained in 99% purity from Aldrich and used as received. An authentic sample of *cis*-bicyclo[3.3.0]octane (**6**) [^{1}H NMR 1.12–1.7 ppm (12 H, m), 2.3–2.4 (2 H, m); mass spectrum, *m/e* (relative intensity) 110 (3.90). Anal. Calcd: C, 87.17; H, 12.83. Found: C, 86.95; H, 12.87.] was obtained by preparative GLC of a hydrolyzed sample of the reaction mixture of **1** with $LiAlH_4$. A sample of 2-iodo-*cis*-bicyclo[3.3.0]octane (**7**) [^{1}H NMR 1.1–2.45 ppm (10 H, m), 2.5–2.6 (2 H, m), 3.76–4.9 (1 H, m); mass spectrum, *m/e* (relative intensity) 236 (30.78). Anal. Calcd: C, 40.69; H, 5.56. Found: C, 40.70; H, 5.57.] was obtained by preparative HPLC (benzene as an eluent) of a hydrolyzed sample of the corresponding reaction mixture of **1** with $LiAlH_4$. Aldrich's 1,5-cyclooctadiene (bp 149–150 °C) and cyclohexadiene were obtained and distilled from CaH_2 under nitrogen before used.

Solutions of $LiAlH_4$, $LiAlD_4$, and AlH_3 were prepared according to known procedures. Solutions of hydride reagents were analyzed for active hydride by hydrolysis of samples on a standard vacuum line equipped with a Teopler pump. Aluminum analysis was performed by EDTA titration.

General Procedures. Reactions were performed under nitrogen at the bench with the use of Schenk-tube techniques or in a glovebox equipped with a recirculating system using manganese oxide columns to remove oxygen and dry ice–acetone traps to remove solvent vapors. Calibrated syringes equipped with stainless steel needles were used for transfer of reagents. Glassware and syringes were flamed and cooled under a flow of nitrogen. All melting points and boiling points are uncorrected.

Reactions were carried out in round-bottomed flasks equipped with T-bore stopcocks attached to male 20/40 standard taper joints and a Teflon-coated magnetic stirring bar. The appropriate amounts of solvents and reagents were syringed into the flask under a nitrogen flush. After complete reaction, the mixture was hydrolyzed with a saturated aqueous solution of NH_4Cl under nitrogen atmosphere. In some cases the ether layer was separated, dried over anhydrous $MgSO_4$, and filtered, and the solvent was removed under vacuum. In other cases the organic layer was analyzed directly by an appropriate method.

Gas chromatographic analyses were conducted on a Varian instrument equipped with an FID detector using a 30-m capillary column and preparative separations were performed on an F&M Model 720. Quantitative GLC analyses were obtained with the use of response-factor corrected peak areas using internal standards. Proton NMR were recorded on a Varian T-60 instrument with chemical shifts reported relative to tetramethylsilane (Me_4Si). Quantitative NMR studies were carried out by using nitromethane as the internal standard. For gas chromatographic analyses, the following column and conditions were used: 30-m capillary column of DB.1, 130 °C, 25 mL/min, *cis*-bicyclo[3.3.0]octane, cyclooctene, *n*-decane, 5-chlorocyclooctene, 5-bromocyclooctene, 2-iodo-*cis*-bicyclo[3.3.0]octane, 5-iodocyclooctene. Mass spectra were obtained on a Varian MAT 1125 and carbon–hydrogen microanalyses were conducted by Altantic Microlabs, Inc., Atlanta, GA.

Preparations. Deuterated dicyclohexylphosphine (PCPD) was prepared analogous to Issleib's method for DCPH.[22]

Tosylate of 5-Hydroxycyclooctene (4). The title compound was prepared from 5-hydroxyl-1-cyclooctene according to a known procedure.[23] The product exhibited the following: mp 46.5–47 °C (lit.[24] mp 47–48 °C); ^{1}H NMR 1.08–2.30 ppm (10 H, m), 2.40 (3 H, s), 4.40–4.80 (1 H, m), 5.48–5.72 (2 H, m), 7.20–7.78 (4 H, m); mass spectrum, *m/e* M^+ = 280.

5-Chloro-1-cyclooctene (3). In a 150-mL, three-neck flask, containing 1.0 mL of $SnCl_4$, was added 50 mL (0.4 mol) of 1,5-cyclooctadiene. This mixture was cooled to 0 °C and then dry HCl gas was passed through the mixture for a period of 60 min. The mixture was washed with water (150 mL), extracted with pentane (250 mL), washed with a solution of $NaHCO_3$ (3 × 250 mL), dried over magnesium sulfate, and then concentrated under vacuum. Fractional distillation yielded 20.5 g (34% yield) of analytically pure **3**, which exhibited the following: bp 71–72 °C at 10 mmHg; ^{1}H NMR 1.38–2.95 (10 H, m), 3.98–4.48 (1 H, m), 5.58–6.0 (2 H, m); GLC purity 99% on a 30-m capillary DB.1

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column at 130 °C; mass spectrum $M^+ = 144$.

5-Bromo-1-cyclooctene (2). In a 150-mL, three-neck flask, containing 1.0 mL of $SnCl_4$, was added 50 mL (0.4 mol) of 1,5-cyclooctadiene. This mixture was cooled to 0 °C, and then dry HBr (gas) was passed through the mixture for a period of 60 min. The mixture was washed with water (150 mL), extracted with pentane (250 mL), washed with a solution of $NaHCO_3$ (3 × 250 mL), dried over $MgSO_4$, and then concentrated under vacuum. Fractional distillation yielded 18.8 g (24.2% yield) of analytical pure **2**, which exhibited the following: bp 65–66 °C at 0.1 mmHg; ^1H NMR 1.38–2.96 (10 H, m), 4.18–4.62 (1 H, m), 5.58–6.0 (2 H, m); GLC purity 99% on a 30-m capillary DB.1 column at 130 °C; mass spectrum, m/e (relative intensity) $M^+ + 2 = 190$ (1.40), $M^+ = 188$ (1.28). Anal. Calcd: C, 50.81; H, 6.94. Found C, 51.00; H, 7.01.

5-Iodocyclooctene (1). To 150 mL of acetone were added 20 g of NaI and 8.0 g of the crude 1-cyclooctenetosylate. After refluxing for 48 h, the mixture was cooled, diluted with pentane, and subjected to standard workup. Distillation yielded 4.0 g (45% yield) of analytically pure **1**, which exhibited the following: bp 73–74 °C at 0.1 mmHg; 1H NMR 1.38–2.95 (10 H, m), 4.28–4.78 (m, 1 H), 5.58–5.90 (2 H, m); GLC purity 99% on a 30-m capillary DB.1 column at 130 °C; mass spectrum, m/e (relative intensity) $M^+ = 236$ (100) (CI). Anal. Calcd: C, 40.69; H, 5.56. Found: C, 40.89; H, 5.57.

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Registry No. **1** (X = I), 103620-47-9; **2** (X = Br), 17223-82-4; **3** (X = Cl), 1855-55-6; **4** (X = OTs), 7212-64-8; **4** (X = OH), 31598-74-0; **5**, 931-88-4; **5** (free radical), 103620-46-8; **5** (75% deuterated), 97797-83-6; **6**, 1755-05-1; **6** (free radical), 103620-49-1; **6** (25% deuterated), 103620-48-0; **7** (X = I), 92285-04-6; DCPH, 829-84-5; DCPD, 91523-73-8; $LiAlD_4$, 14128-54-2; $LiAlH_4$, 16853-85-3; AlH_3, 7784-21-6; cyclohexadiene, 29797-09-9; 1,5-cyclooctadiene, 111-78-4.

The Predominance and Quantification of Steric Effects in the Solvolysis of Secondary Aliphatic Esters[1]

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The solvolysis rates of 35 tosylates in hexafluoroisopropyl alcohol are measured and compared to MM2 calculated strain energies, ΔSI, between weighted sp^3 states and the lowest sp^2 state. For unhindered (pseudo)equatorially substituted cycloalkyl tosylates a linear correlation, free from ambiguities involved, e.g., with the leaving group simulation, is obtained which shows a sensitivity of $m = 1.04 \pm 0.05$, indicating an extremely late transition state or limiting behavior. Based on the corresponding equation, it is shown that alkyl substituents in the γ- and in the β-position do not promote significant rate increases, even when there is an antiperiplanar disposition between the leaving group and a migrating β-methyl substituent. Instead, these substituents can lead to substantial ΔG^* increase (by up to 5 kcal/mol in comparison to the ΔSI prediction), which is related to steric hindrance of solvation and/or hindrance for elimination. 17-(Tosyloxy)androstanes show extremely large epimeric rate ratios of >30 000; these are not due to anchimeric assistance but only to the exceedingly slow reaction of the hindered 17β isomer, whereas the fast reaction of the 17α tosylate (e.g., 200 times higher than cyclopentyl tosylate) is in line with the ΔSI calculation. *endo*-Bicyclo[2.2.1]heptane esters show evidence for steric hindrance; *exo*-norbornyl tosylate has, however, a ΔG^* value lower by 4 kcal/mol than predicted. k_s/k_c values, obtained by rate comparison in 80% ethanol and 97% HFIP, vary between 0.5 and 300, mainly as a result of different steric hindrance to rearside nucleophilic substitution.

In recent years there has been a strong tendency to associate large reactivity differences in solvolytic reactions with a different degree of charge delocalization in the corresponding transition states.[2] Such claims are usually made on the grounds of what is considered to be an abnormally fast reaction, requiring a nonclassical charge dispersion in a bridged transition state. The prevailing arbitrariness, however, in the decision of what is regarded to be a "normal", that is sterically controlled reaction is most vividly illustrated by many reports on the norbornyl cation problem.[3] Other major efforts in recent years have been directed toward the study of carbocations under free ion conditions, which are also amenable to molecular orbital calculation.[3,4] Several studies demonstrated the formation of substantially delocalized bridged structures, even with the aid of "hard" C–H bonds, e.g., in the transannular position of medium rings.[5] It should, however, be borne in mind that the presence of solvolytic media is expected to change the nature of the intermediates by providing effective charge delocalization not only for the leaving group anion but also for the cationic in-

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