Compound 15. A C_6D_6 solution of a 72:28 mixture of **15a–15b** was prepared, as described above, and was degassed and sealed in an nmr tube. The sample was placed in a high-temperature Colora Ultra Thermostat circulating oil bath preset and maintained at 130.0 ± 0.5° and it was removed periodically and rapidly cooled in an ice bath. The ratio of **15a–15b** was measured by pmr (at *ca.* 40°), using the relative absorption intensities of the ring methyl protons. Because of the small chemical-shift difference between these characteristic signals, direct electronic integration was not feasible, and therefore relative peak heights were used as a measure of **15a–15b**. Comparison of a few of these isomeric ratios with corresponding values obtained using a Du Pont Model 310 curve resolver verified the accuracy of the relative peak height method. After 26 days at 130.0°, the equilibrium mixture of **15a–15b** was 37.9:62.1. A least-squares treatment (correlation coefficient 0.999) of $\ln [(R - K)/(1 + R)]$ *vs.* t (eq 3) using ten data points, collected over a period of *ca.* 11 days, together with the value of K and the Eyring equation,[18] gave the values of $\Delta G^{\ddagger}$ for **15** reported in Table I.

Compound 16. A 90:10 mixture of **16a–16b** (160 mg) was prepared as described above and was dissolved in benzene (4 ml). Four 1-ml aliquots of this solution were placed in micro-Carius tubes and were degassed and sealed. The tubes were placed in a high-temperature Colora Ultra Thermostat circulating oil bath preset and maintained at 170.0 ± 0.5° and one tube was removed (quenched in ice-water bath) after 1, 8, 21, and 99 hr. Each tube was opened in a glove bag and methylene iodide (1 ml; *ca.* 50-fold molar excess) was then added. After 1–2 hr at *ca.* 50°, the four samples of **19** were isolated in essentially quantitative yield by precipitation with ether and were analyzed by pmr for purity and diastereomeric composition (with a Du Pont Model 310 curve resolver), using the characteristic signals of the iodomethyl protons for **19a** and **19b** (see above). The isomeric mixtures of **19**, which were derived from the aliquots removed after 21 and 99 hr, were the same (within experimental error) and gave an average value of 44:56 for **19a–19b**. Since the quaternization of **16** with methylene iodide to give **19** is stereospecific,[14] the equilibrium mixture of **16** was a 44:56 mixture of **16a–16b**. Setting the ratio of **16a–16b** at t_0 equal to 90:10 (see above), a least-squares treatment (correlation coefficient 0.996) of $\ln [(R - K)/(1 + R)]$ *vs.* t (eq 3) using three data points, together with the value of K and the Eyring equation,[1] gave the values for $\Delta G^{\ddagger}$ for **16** reported in Table I.

The Chlorinolysis of Medium-Ring Cycloalkyl 2,4-Dinitrobenzenesulfenates in Acetic Acid. Transannular Hydride Shifts[1]

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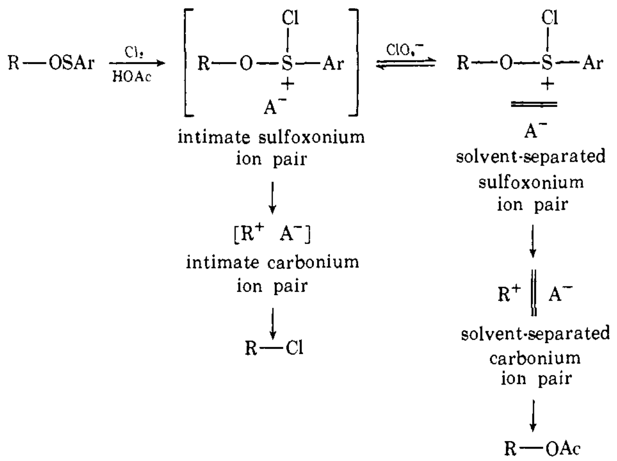
Abstract: A study of the chlorinolysis of deuterium-labeled cycloalkyl 2,4-dinitrobenzenesulfenates (ring sizes 8 and 10) in acetic acid has made possible the comparison of transannular hydride shifts occurring in different intermediate ion pairs. The dependence of product distributions on added lithium perchlorate has led to the conclusion that chloride product arises from intimate ion pairs and acetate from solvent-separated ones. The deuterium scrambling in the products implies that transannular hydride shifts occur to nearly the same extent in both ion pair species.

The chlorinolysis of alkyl 2,4-dinitrobenzenesulfenates in acetic acid has provided useful information on the mechanistic studies of ionic reactions, as extensive characterization of ion pairing behavior has been made in a number of systems.[3] Generally, the arenesulfenate is chlorinated to form an intimate sulfoxonium ion pair which may lose a sulfinyl chloride fragment, before or after solvent reorganization, to form the corresponding carbonium ion pair. These carbonium ions (which form chloride, acetate, and olefin products) are "born in an inherited solvent environment"[3b] (see Scheme I). It has been shown that the chloride–acetate ratio decreases sharply in the presence of added lithium perchlorate,[3] a manifestation of a "special salt effect."[4] Since perchlorate anion has the

Scheme I[a]



[a] R = alkyl; Ar = 2,4-dinitrophenyl; A^- = anion (Cl^-, AcO^-, ClO_4^-), not necessarily identical at each appearance in the scheme.

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[1] (a) Based in part on the Ph.D. Dissertation of A. W. Foster, Louisiana State University, Baton Rouge, La., Jan 1971. (b) Supported in part by a grant (GP8228) from the National Science Foundation.

[2] (a) Recipient of Cities Service Graduate Fellowship, funded by the Cities Service Research and Development Company, 1968–1970. (b) Grateful acknowledgment is made to the Dr. Charles E. Coates Memorial Fund of the LSU Foundation donated by George H. Coates for financial aid toward the preparation of the Ph.D. Dissertation of Alan W. Foster.

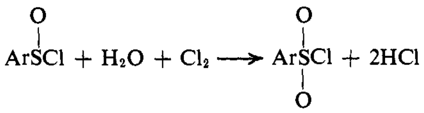
[3] (a) H. Kwart, E. N. Givens, and C. J. Collins, *J. Amer. Chem. Soc.*, **91**, 5532 (1969); (b) H. Kwart and J. L. Irvine, *ibid.*, **91**, 5541 (1969); (c) unpublished results arrived at independently by H. Kwart and J. G. Traynham and their coworkers.

[4] S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Amer. Chem. Soc.*, 76, 2597 (1954).

overall effect of enhancing the proportion of solvent-separated ions, the decrease in chloride–acetate ratio indicates that chloride is mainly a product of intimate ion pairing while acetate is formed from solvent-separated intermediates.

In the bicyclooctyl system, C–C bond shifts were shown to be rapid and equivalent in the processes leading to products derived from both intimate and solvent-separated ion pair intermediates.[3b] 7,2-Hydride shifts in this system[3b] and phenyl migrations in a substituted phenylethyl system,[3a] however, were shown to be slower and to be affected by added lithium perchlorate. We considered it of interest to ascertain the relative extents of transannular hydride shifts, which are common to medium rings,[5] in different medium-ring carbonium ion intermediates.

In this study transannular hydride shifts have been assessed by the nmr analysis of deuterium-scrambled products arising from the chlorinolysis of deuterium-labeled cycloalkyl (ring sizes 8 and 10) 2,4-dinitrobenzenesulfenates in acetic acid. All cycloalkyl 2,4-dinitrobenzenesulfenates were prepared from the corresponding cycloalkanols and 2,4-dinitrobenzenesulfenyl chloride.[6] Each ester was a neatly crystalline, bright yellow material, stable for extended periods of time at room temperature. The reaction of cycloalkyl arenesulfenates with a 2.5–3 molar excess of chlorine in acetic acid gives cycloalkyl chlorides, acetates, and elimination products (which add chlorine), and presumably 2,4-dinitrobenzenesulfinyl chloride as the aromatic fragment.[3a] Excess chlorine oxidizes the sulfinyl chloride to sulfonyl chloride, a reaction which occurs during the work-up procedure when water is added.[3a] Efforts



$$\mathrm{Ar}\overset{\mathrm{O}}{\overset{|}{\mathrm{S}}}\mathrm{Cl} + \mathrm{H_2O} + \mathrm{Cl_2} \longrightarrow \mathrm{Ar}\underset{\underset{\mathrm{O}}{|}}{\overset{\overset{\mathrm{O}}{|}}{\mathrm{S}}}\mathrm{Cl} + 2\mathrm{HCl}$$

to avoid addition of chlorine to cyclooctene (by varying the amount of available chlorine) were unsuccessful; the rate of addition was apparently very fast and preceded complete chlorinolysis of the arenesulfenate. The results for the chlorinolyses of cyclooctyl and cyclodecyl 2,4-dinitrobenzenesulfenates, both with and without added lithium perchlorate, are shown in Tables I and II, respectively.

Table I. Product Distribution from the Chlorinolysis of Cyclooctyl 2,4-Dinitrobenzenesulfenate[a]

$[\mathrm{LiClO_4}]$, *M*	Chloride	Acetate	RCl/ROAc	Olefin addition products: 1,2-*trans*-Dichloride	Olefin addition products: Others[b] (5)
None	59	18	3.3	12	12
0.08	14	39	0.36	25	23

[a] Each entry is the average (± 1 unit) of two separate experiments. [b] These components (5) were shown to arise from the addition of chlorine to cyclooctene in acetic acid (see Table IV, Experimental Section).

Table II. Product Distribution from the Chlorinolysis of Cyclodecyl 2,4-Dinitrobenzenesulfenate in Acetic Acid[a]

$[\mathrm{LiClO_4}]$, *M*	Chloride	Acetate	RCl/ROAc	Olefin[b] and addition products[c]
None	37	5	7.4	60
0.08	5.5	7.5	0.73	87

[a] Averages of two or three separate experiments. Gas-chromatographic (gc) area per cents are reported here; however, chloride and acetate have essentially the same molar response. [b] A mixture of *cis*- and *trans*-cyclodecene. [c] At least 13 addition products were found to be present; the only identified component was *trans*-1,2-dichlorocyclodecane, which constituted 25–35% of the olefin and addition products. These products were shown to arise from reaction of olefin and chlorine by comparing gc chromatograms with those obtained for the addition of chlorine to *cis*- and *trans*-cyclodecenes (see Experimental Section).

The effect of added lithium perchlorate on the ratio of chloride–acetate and chloride–olefin products is clear and persuasive. Without lithium perchlorate, the chloride product strongly predominates; however, in its presence the yield of chloride drops off sharply and the yields of acetate and olefin increase noticeably, the shift in chloride–acetate being about tenfold for both systems studied. In accord with data obtained earlier by others,[3a,b] these data suggest that acetate arises mainly from solvent-separated ion pairs, whereas chloride is apparently a product of intimate ion pairing.

For the cyclodecyl system, olefin is the major product, and the effect of $\mathrm{LiClO_4}$ is to increase the proportion of olefin still further at the expense of cyclodecyl chloride. The ratio of acetate–olefin (small) is about the same with and without added salt, implying that olefin and acetate are formed from a common precursor, which is (at least predominantly) a solvent-separated ion pair. The great preference of elimination over substitution is simply a reflection of the high strain associated with the ten-membered ring.[7] The products formed in the acetolysis of cyclodecyl tosylate have been shown to be almost exclusively olefins,[8] whereas the acetolysis of cyclooctyl tosylate has produced a 52:48 mixture of olefin and acetate.[9]

Completely separated ions have not been considered to be a contributing ionic species in the ionization scheme. Product distribution for the cyclooctyl arenesulfenate chlorinolysis has shown *no* dependence on the presence of lithium chloride, a salt which would cause increase in chloride product *via* a common ion effect, if completely separated ions were important in the process.[3a,b]

On the basis of the apparent ion pairing behavior of medium-ring carbonium ions generated during the chlorinolysis of cycloalkyl arenesulfenates, we undertook the assessment of the extents of transannular hydride shifts occurring in these intermediates. Nuclear magnetic resonance (nmr) analysis (integration ratio of methine–methylene protons) of the isotopically scrambled products arising from the chlorinolysis of α and β deuterium-labled arenesulfenates provides a measure of transannular hydride shift. Table III sum-

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(5) (a) V. Prelog and J. G. Traynham in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 9, and references therein; (b) A. C. Cope, M. Martin, and M. McKervey, *Quart. Rev., Chem. Soc.*, **20**, 119 (1966), and references therein.

(6) N. Kharasch, D. P. McQuarrie, and C. M. Buess, *J. Amer. Chem. Soc.*, **75**, 2658 (1953).

(7) E. Eliel, N. Allinger, S. Angyal, and G. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, p 193.

(8) (a) V. Prelog and S. Borcić, *Helv. Chim. Acta*, **41**, 199 (1958); (b) V. Prelog, W. Küng, and T. Tomlienovic, *ibid.*, **45**, 1352 (1962).

(9) N. Allinger and W. Szkrybalo, *Tetrahedron*, 4699 (1968).

Table III. Extents of Hydride Shift Occurring in Medium-Ring Cycloalkyl Cations Generated from Different Substrates[a,b]

<table>
<tr><th rowspan="2">Substrate[b,c]</th><th rowspan="2">[LiClO₄], <i>M</i></th><th colspan="2">% olefin</th><th rowspan="2">% chloride</th><th rowspan="2">% acetate</th><th rowspan="2">Ref</th></tr>
<tr><th>Cis</th><th>Trans</th></tr>
<tr><td>$C_8SAr^{d,e}$</td><td></td><td colspan="2">10</td><td>44</td><td>50</td><td>This work</td></tr>
<tr><td>$C_8SAr^{e,f}$</td><td></td><td colspan="2">29</td><td>39</td><td>43</td><td>This work</td></tr>
<tr><td>C_8SAr^{d}</td><td>0.08</td><td colspan="2">34</td><td>42</td><td>50</td><td>This work</td></tr>
<tr><td>C_8SAr^{f}</td><td>0.08</td><td colspan="2">63</td><td>45</td><td>45</td><td>This work</td></tr>
<tr><td>$C_{10}SAr^{e,f}$</td><td></td><td colspan="2">27</td><td>30</td><td>29</td><td>This work</td></tr>
<tr><td>$C_{10}SAr^{f}$</td><td>0.08</td><td colspan="2">44</td><td></td><td></td><td>This work</td></tr>
<tr><td>C_8OBs^{f}</td><td></td><td>49</td><td></td><td></td><td>55</td><td><i>h</i></td></tr>
<tr><td>$C_{10}OTs^{g}$</td><td></td><td>29</td><td>12</td><td></td><td></td><td><i>i</i></td></tr>
<tr><td>$C_{10}OTs^{d}$</td><td></td><td></td><td>16</td><td></td><td></td><td><i>i</i></td></tr>
<tr><td>$C_{10}NH_2^{g}$</td><td></td><td>16.5</td><td></td><td></td><td>25</td><td><i>i</i></td></tr>
</table>

[a] Per cents of rearrangement estimated from product nmr data, which favor 1,5 shifts; see Experimental Section and Discussion for details. [b] Acetic acid solvent except for amine deamination (water solvent). [c] C_n represents an *n*-membered cycloalkyl ring; Ar = $2,4\text{-}(NO_2)_2C_6H_3-$; Bs = *p*-$BrC_6H_4SO_2-$; Ts = *p*-$CH_3C_6H_4SO_2-$. [d] 1-Deuteriocycloalkyl. [e] Average of two runs. [f] 1,2,2,*n*,*n*-Pentadeuteriocycloalkyl. [g] Cycloalkyl-*1*-^{14}C. [h] A. C. Cope and D. Gale, *J. Amer. Chem. Soc.*, **85**, 3747 (1963). [i] Reference 5a.

marizes the hydride-shift data obtained from the chlorinolysis of mono- and pentadeuterium-labeled substrates. These data reveal that the extents of rearrangement detected in the chloride and acetate products are nearly the same and are unaffected by added lithium perchlorate; *i.e.*, that hydride shifts occur to nearly the same extent in intimate and solvent-separated ion pair intermediates. These results strongly support the earlier assumption that the *carbonium* ion pairs generated in this system do not equilibrate with each other.[3a] Although it appears that less transannular rearrangement occurs in the cyclodecyl cation than in the cyclooctyl cation, additional data are necessary before extensive comparisons can be made.

On the basis of nmr data obtained with the pentadeuterium-labeled cyclooctyl system, we believe that essentially all of the transannular hydride shifts which occur during chlorinolysis are 1,5 shifts. Less apparent rearrangement in the pentadeuterium-labeled system than in the monodeuterium-labeled one (Table III) may indicate that a small amount of 1,2 hydride shift accompanies the transannular shifts.

Experimental Section

General. Gas-liquid chromatographic (glc) analyses were carried out on either a Beckman GC-5 or Hewlett-Packard 700 gas chromatograph, both instruments being equipped with hydrogen flame detectors and $^1/_8$-in. columns. Columns used included 10% Carbowax 20 M (10 ft) and 10% Ucon UC-W98 (6 ft). Nuclear magnetic resonance (nmr) spectra were obtained from a Varian A-60A nmr spectrometer with internal tetramethylsilane reference. Mass spectral data were recorded by Cheryl White of the Department of Chemistry, Louisiana State University, with a Varian M-66 spectrometer. Infrared (ir) spectra were recorded on a Perkin-Elmer 137 spectrophotometer. Melting points (open capillary) were obtained with a Thomas Hoover melting point apparatus and were corrected. Mr. Ralph Seab of the Department of Chemistry, Louisiana State University, performed all elemental microanalyses.

Cycloalkyl 2,4-Dinitrobenzenesulfenates.[3a] To a solution of 15.5 g (0.066 mol) of 2,4-dinitrobenzenesulfenyl chloride (recrystallized from CCl_4; mp 95–98°) in 150 ml of 1,2-dichloroethane was added 0.073 mol of freshly distilled cycloalkanol followed by 15 ml of pyridine. The mixture was stoppered for 2 hr before the pyridinium salt was removed by suction filtration. The filtrate was concentrated to an oil by rotary evaporation, and finally a small amount of water was added to react with excess sulfenyl chloride. The oil was crystallized from ethanol.

Cyclooctyl 2,4-dinitrobenzenesulfenate was obtained in 60% yield: mp 100–102°; nmr ($CDCl_3$) δ 9.10 (d, 1, J = 2.5 Hz, arom), 8.50 (dd, 1, J = 9, J' = 2.5 Hz, arom), 7.97 (d, 1, J = 9 Hz, arom), 3.90 (m, 1, J = 6 Hz, C*H*OSAr), 2.05 (m, 4), and 1.58 (m, 10). *Anal.* Calcd for $C_{14}H_{18}N_2O_5S$: C, 51.5; H, 5.6; N, 8.6. Found: C, 51.2; H, 5.5; N, 8.5.

Cyclodecyl 2,4-dinitrobenzenesulfenate, prepared by the same procedure, was obtained in 62% yield: mp 80–82°; nmr ($CDCl_3$) δ 9.07 (d, 1, J = 2 Hz, arom), 8.51 (dd, 1, J = 9, J' = 2 Hz, arom), 8.00 (d, 1, J = 9 Hz, arom), 4.05 (m, 1, J = 6 Hz, C*H*OSAr), 1.97 (m, 4), and 1.55 (m, 14). *Anal.* Calcd for $C_{16}N_{22}N_2O_5S$: C, 54.2; H, 6.3; N, 7.9. Found: C, 54.4; H, 6.4; N, 8.1.

Pentadeuterium-Labeled Esters. Deuterium-labeled ketones were prepared by equilibration of the cycloalkanone (7–15 g) with deuterium oxide (25–75 g) containing potassium carbonate (3–6 g).[10] The mixtures were refluxed for 3 days, cooled, and extracted with ether. The ether extracts were dried ($MgSO_4$), concentrated, and either recycled or reduced to the cycloalkanol-d_5. Only two equilibrations were found to be necessary to replace essentially all of the active methylene hydrogens with deuterium. Two ketones were prepared by this procedure: **cyclooctanone-**$2,2,8,8$-d_4 [nmr ($CDCl_3$) δ 1.80 (m) and 1.45 (m), *no* absorption at 2.40 (α H); mass spectrum (70 eV) *m/e* (rel intensity) 130 (93) and 129 (7), which is equivalent to 93% d_4 and 7% d_3 species] and **cyclodecanone-**$2,2,10,10$-d_4 [nmr ($CDCl_3$) δ 1.80 (m) and 1.36 (m), *no* absorption at 2.55 (α H); mass spectrum (70 eV) *m/e* (rel intensity) 154 (0), 155 (0.5), 157 (3), and 158 (96), which is equivalent to 0.5% d_1 and d_2, 3% d_3, and 96% d_4].

Each labeled ketone was reduced with lithium aluminum deuteride in ether solution to the corresponding cycloalkanol, which was converted directly to the 2,4-dinitrobenzenesulfenate derivative. The two esters prepared were: **cyclooctyl-**$1,2,2,8,8$-d_5 **2,4-dinitrobenzenesulfenate** [mp 99–102°; nmr ($CDCl_3$) δ 9.08 (d, 1, J = 2.5 Hz, arom), 8.47 (dd, 1, J = 9, J' = 2.5 Hz, arom), 7.95 (d, 1, J = 9 Hz, arom), and 1.58 (m, 10)] and **cyclodecyl-**$1,2,2,10,10$-d_5 **2,4-dinitrobenzenesulfenate** [mp 79–81°; nmr ($CDCl_3$) δ 9.10 (d, 1, J = 2 Hz, arom), 8.48 (dd, 1, J = 9, J' = 2 Hz, arom), 7.97 (d, 1, J = 9 Hz, arom), and 1.53 (m, 14)].

Cyclooctyl-*1-d* 2,4-Dinitrobenzenesulfenate. Cyclooctanol-*1-d*, prepared by lithium aluminum deuteride reduction of cyclooctanone, was converted to the 2,4-dinitrobenzenesulfenate in 67% yield. The ester melted at 100–102°: nmr ($CDCl_3$) δ 9.08 (d, 1, J = 2.5 Hz, arom), 8.48 (dd, 1, J = 9, J' = 2.5 Hz, arom), 7.95 (d, 1, J = 9 Hz, arom), 2.00 (m, 4), and 1.57 (m, 10). *Anal.* Calcd for $C_{14}H_{17}DN_2O_5S$: C, 51.4; H (D), 5.8; N, 8.6. Found: C, 51.2; H (D), 5.5; N, 8.6.

Chlorinolyses of Cycloalkyl 2,4-Dinitrobenzenesulfenate in Acetic Acid.[3a] **A. Without Added Salts.** Chlorinolyses of cycloalkyl arenesulfenates followed the general procedure described below for the cyclooctanol derivative. Into a solution of 1.0 g (3.06 mmol) of cyclooctyl arenesulfenate in 30.6 ml of acetic acid (0.1 *M* solution) was bubbled 0.34 ml (7.5 mmol) of dry chlorine through a capillary tube extending beneath the surface of the acetic acid solution. (The chlorine was dried by being passed through concentrated surfuric acid and was collected in a tube chilled in a Dry Ice–acetone bath.) During the addition of chlorine, which required approximately 6 min, the reaction vessel was maintained at a temperature of 20 ± 1°, and the flask was covered to exclude light. After all of the chlorine had been added, the inlet tube was replaced with a stopper, and the reaction mixture was allowed to stir for an additional 0.5 hr. When the cover was removed from the flask, it was noted that the intense yellow-orange color

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(10) See Table III, footnote *h*.

of the sulfenate had been replaced by the yellow-green color of chlorine. The reaction mixture was then poured into 200 ml of water and extracted with 50 ml of pentane. After the phases had separated, the slightly colored solid which had formed at the interface was removed by filtration, and the aqueous layer was extracted twice more with 50-ml portions of pentane. The pentane extracts were combined, washed twice with sodium bicarbonate, and dried ($MgSO_4$). The products were concentrated by rotary evaporation to yield 0.38 g of products. The solid which had separated during the work-up is believed to be 2,4-dinitrobenzenesulfonyl chloride[3a] (mp 101–103°) (lit.[3a] mp 102°); however, only 0.061 g could be collected as much of it adhered to the glassware.

The products were subjected to glc analysis, and components were identified, qualitatively and quantitatively, by the comparison of retention times and relative response factors with those of authentic samples. The product distributions obtained are summarized in Tables I and II. The yields were 70–78%.

It was necessary to separate the products in pure form for nmr analysis when deuterated arenesulfenates were chlorinated. This separation was accomplished by chromatographing the distilled product mixture on a 2.5 ft × $^5/_8$ in. alumina column (4% water deactivated) with pentane–ethyl ether mixtures as developing solvents. The proportion of ether was slowly increased so as to increase the solvent polarity. It was usually possible to obtain chlorides, acetates, and dichlorides in ≥99% purity in this manner. Occasionally, microdistillation had to be employed to further purify the samples. The isolated products were analyzed by nmr spectroscopy to determine the extents of intramolecular hydride shifts which had occurred. The method consisted essentially of comparisons of the intensities of the signals for HCX and CH_2.[11] The data are summarized in Table III.

B. With Added Lithium Perchlorate. To a solution (0.08 *M*) of lithium perchlorate (0.52 g, 4.9 mmol) in acetic acid (61.2 ml) was added 6.12 mmol of cycloalkyl 2,4-dinitrobenzenesulfenate. Chlorinolysis was effected as described above. The product distributions are summarized in Tables I and II.

C. With Added Lithium Chloride. To a solution (0.1 *M*) of lithium chloride (0.13 g, 3.06 mmol) in acetic acid (30.6 ml) was added 1.0 g (3.06 mmol) of cyclooctyl 2,4-dinitrobenzenesulfenate. The chlorinolysis was carried out as before. Gc analysis of the resulting product mixture indicated that *no* appreciable shift in product distribution had occurred.

Addition of Chlorine to Cyclooctene in Acetic Acid. To a solution (0.05 *M* in olefin) of 0.4 g (0.004 mol) of cyclooctene in 8 ml of dry acetic acid was added 0.5 ml (0.011 mol) of dry chlorine in the manner described for sulfenate ester chlorinolyses. Table IV compares the product distribution obtained here with those from sulfenate ester chlorinolyses.

Table IV. Reaction of Chlorine with Cyclooctane Derivatives in Acetic Acid Solution[a]

Substrate	[$LiClO_4$], *M*	*trans*-1,2-Dichloride	Unknowns[b] A	B	C	D + E[c]
Cyclooctene		55	13	6	18	8
Sulfenate ester[d]		52	13	5	21	9
Sulfenate ester[d]	0.08	50	12	5	24	9

[a] Relative gc area percentages are reported here. [b] Believed to be dichlorides and chloro acetates, lettered in order of increasing retention time on a 6 ft × $^1/_8$ in. 10% Ucon UC-W98 column at 160°. [c] These components were not resolved. [d] Monochloride and -acetate products are not included here.

Addition of Chlorine to *cis*- and *trans*-Cyclodecene in Acetic Acid. The addition of chlorine to *cis*- and *trans*-cyclodecenes in acetic acid (0.05 *M* in olefin) produced at least 13 products which were shown to correspond to the unidentified products in the cyclodecyl 2,4-dinitrobenzenesulfenate chlorinolyses. These are believed to be various dichlorides and chloro acetates which are position isomers and stereoisomers.

Discussion

In solvolytic processes, intimate and solvent-separated **carbonium** ion pairs are formed sequentially,[4] but in the chlorinolysis reactions studied here, they are formed from the corresponding **sulfoxonium** ion pairs.[3a] The extents of hydride shifts accompanying product formation from intimate and solvent-separated ion pairs (chloride and acetate products, respectively) in these cycloalkyl systems are the same and are unaffected by added lithium perchlorate (Table III). This lack of dependence of hydride shift on the presence of lithium perchlorate supports the hypothesis that, in this reaction, no interconversion between carbonium ion pairs occurs.[3a] To assume that solvent-separated carbonium ion pairs formed from intimate carbonium ion pairs would be more extensively scrambled than those generated from a sulfoxonium ion precursor appears reasonable, because of the different life expectancies of the carbonium ions possible by the two routes. Sequential formation of the solvent-separated carbonium ion pair from the intimate one would almost surely lead to more extensive rearrangement in the acetate product than in the chloride product, especially so in the presence of lithium perchlorate since return to intimate carbonium ion pairs would be suppressed or eliminated.[4]

The carbonium ion pair born as a solvent-separated pair will be longer lived (more stable) than the one born as an intimate ion pair.[3a,b] With the more stable ion pair, both hydride shift and product formation will proceed more slowly. (Charge is more dispersed in the transition states for both processes than in the "ground-state" carbonium ion.) These processes are but little different in energy requirements, however, and the difference in difference of activation energy requirements is likely to be, as required by the deuterium-scrambling data, inconsequential.

The fact that olefin rearrangement *is* dependent on lithium perchlorate is interesting, and suggests that olefin is a product of two different intermediates. The increase in the amount of olefin (dichloride) with added salt indicates that at least part of the olefin is formed by elimination from solvent-separated ion pairs. The relatively small extent of rearrangement in the olefin when no salt is present[12] is possible evidence for some olefin formation *via* a mechanism other than E1. A mechanism which is consistent with the data involves, in addition to an E1 process with rearrangement in a solvent-separated carbonium ion pair, an elimination (without rearrangement) from an intimate sulfoxonium ion pair in which the chloride ion can abstract a proton[14] (see Scheme II). This scheme accounts for limited rearrangement in the absence of lithium perchlorate and more extensive rearrangement when the salt is added.

Bridged carbonium ions, in which participation by transannular hydrogen is involved, are not believed to

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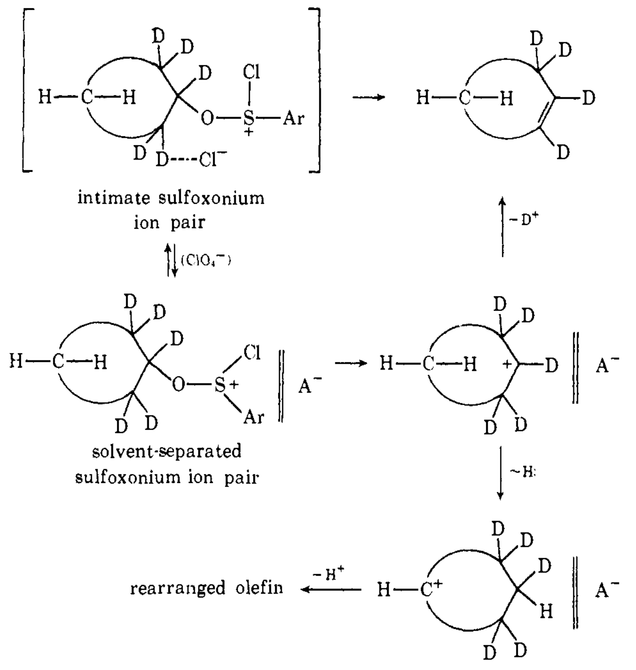
(11) For details and examples of calculations, see ref 1a.

(12) Rearrangement in the dichlorocyclooctane derived from monodeuterated arenesulfenate amounted to only 9–11%, although the extents of rearrangements in the chloride and acetate products were comparable to those obtained with d_5-labeled substrate. This difference in olefin rearrangement is a reflection of primary isotope effects which are involved in the elimination of deuterium to form olefin. Deuterium is lost at a slower rate than is hydrogen, thus allowing the transannular hydride shift to be a more highly competitive process. Since the initially generated cation reluctantly undergoes elimination of deuterium, there should be a decrease in the amount of olefin produced when deuterium is in the β positions.[13] This decrease is in fact observed; it amounts to 30–40% with the eight-membered ring, and 20–30% with the ten-membered ring.

(13) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(14) The latter process is reminiscent of elimination from an ion pair in which a gegenion abstracts hydrogen from a diazonium cation; T. Cohen and A. R. Daniewski, *J. Amer. Chem. Soc.*, **91**, 533 (1969).

Scheme II[a]



[a] $A^- =$ anion (Cl^-, ClO_4^-, AcO^-).

constitute a significant portion of the intermediates formed in the chlorinolysis of arenesulfenates. Such bridged cations are apparently of minor importance in the acetolysis of unsubstituted cyclooctyl tosylate (*p*-toluenesulfonate),[9] and bridged cyclodecyl cations have been excluded as contributing species in tosylate acetolysis also.[5] Although the mechanism of arenesulfenate chlorinolysis does not necessarily parallel that of tosylate solvolysis, the evidence indicates that unsubstituted medium-ring carbonium ions undergo hydride shifts from transannular positions to fully developed carbonium ion centers, regenerating a classical ion.

1,5-Hydride shifts have been shown to be the major mode of rearrangement in cyclooctyl-*1,2,2,8,8*-d_5 brosylate acetolysis, with 1,2-, 1,3-, and 1,4-hydride shifts being inappreciable.[10] Nmr data indicate that at least the bulk of hydride shift occurring prior to substitution of cyclooctyl cations generated from chlorinolysis is also 1,5 in nature. The pentadeuterium-substituted scrambled chloride and acetate products show the same shaped nmr methine absorption pattern as the *un*labeled derivatives. Since 1,4-hydride shifts have been shown to be uncommon,[5b] the only transannular hydride shift remaining, which accounts for products whose methine protons are in an environment similar to that of unlabeled products, is 1,5-hydride shift. 1,3-Hydride shift would place the methine proton adjacent to deuterium, decreasing the vicinal hydrogen–hydrogen couplings. This diminished coupling would narrow the methine absorption, an effect which would alter the shape of the nmr methine absorption pattern.

The methine multiplet appears to be better resolved for the pentadeuterium-labeled cyclooctyl products than for the monolabeled or unlabeled cyclooctyl products. The van der Waals radius of deuterium is smaller than that of hydrogen,[15] a factor which appreciably decreases the transannular interactions in the medium ring when five deuteriums are present. This decreased strain lowers the energy barrier for conformational changes, thus increasing the rate of flipping. The *β* hydrogens can therefore average more easily on the nmr time scale so that the lines in the methine multiplet sharpen noticeably when the ring has deuterium labels present. When a sample of scrambled monodeuterium-labeled cyclooctyl chloride (which displays the same resolution as unlabeled chloride) is warmed, the methine multiplet in the nmr spectrum sharpens to resemble that in the spectrum of the scrambled pentadeuterium-labeled chloride.

(15) A. R. Ubbelohde, *Trans. Faraday Soc.*, **32**, 525 (1936).