was used. A 0.522-g sample of alumina (Woelm acid-washed grade 1 activated at 230° for 2 hr under vacuum) was stirred with 35 ml of petroleum ether (dried over a portion of above alumina) for 16 hr at room temperature. The alumina was then filtered and washed two times with ether (*ca.* 30 ml) and the clear ether solution set aside. The alumina was then washed two times with 20 ml of $CH_2Cl_2$ and this solution set aside. A third wash was done with two 15-ml portions of methanol and one 15-ml portion of ether to yield a yellow solution. Each solution was reduced on the steam bath and analyzed by glpc. The ether solution contained only ketone. The $CH_2Cl_2$ solution contained only ketone but in relatively small quantities, while the methanol solution contained only traces of ketone along with other unidentified compounds. The ketone was collected by glpc (column D, 135°) to yield 191 mg of clear oil (181 mg from ether solution, 10 mg from $CH_2Cl_2$ solution). The nmr ($CCl_4$) of the ketone agreed with the published one[17] showing one proton resonances at $\tau$ 2.48, 3.51, 3.70, 4.05, 6.12, and 6.66.

*endo-* **and** *exo-***Bicyclo[3.2.0]heptadienol (7a and 7b).** These alcohols were prepared according to Story and Fahrenholtz[17] by lithium aluminum hydride reduction of **6**. The reaction mixture was worked up by quenching with potassium sodium tartrate solution. The alcohols were collected by glpc (column E, 133°, 20 psi). **7a** had a retention time of 22.5 min and **7b**, 27 min. The ratio of **7a** to **7b** (peak areas) was 59 ± 2:41 ± 2, and by direct weighing of isolated alcohols the ratio was 58:42.

The nmr spectrum ($CD_2Cl_2$) of **7a** (endo) showed resonances at $\tau$ 3.37 (1 H, doublet, $J$ = 3 Hz), 3.90 (2 H, multiplet), 4.39 (1 H, doublet, $J$ = 6 Hz), 5.24 (1 H, doublet, $J$ = 10 Hz) (unresolved multiplets), 6.40 (2 H, multiplet), and 7.84 (1 H, singlet, OH). The exo epimer **7b** exhibited bands at $\tau$ 3.50 (1 H, doublet, $J$ = 2.5 Hz), 3.80 (2 H, multiplet), 4.20 (1 H, doublet, $J$ = 7 Hz), 5.50 (unresolved multiplet), 6.19 (1 H, multiplet), 6.87 (1 H, quartet, $J$ = 1.5, 3 Hz), and 8.00 (1 H, singlet, OH).

*endo-* **and** *exo-***Bicyclo[3.2.0]heptadienol-*2-d* (7c and 7d).** These alcohols were prepared exactly as **7a** and **7b** except lithium aluminum chloride was used as the reducing agent. High resolution mass spectra (calcd for $C_7H_8DO$, 108.05596) gave 108.05609 for **7c** and 108.0560 for **7d.**

**2-Methyl-*endo*-bicyclo[3.2.0]heptadienol (7e).** To a solution of 218 mg (2.06 mmol) of ketone **6** in 20 ml of dry ether was added dropwise 1.8 ml (2.9 mmol) of 1.6 *M* solution of methyllithium in ether (Foote Mineral Co.). During the addition, which lasted 5 min, the reaction mixture was cooled in an ice-water bath. After stirring the mixture for an additional 0.5 hr, it was quenched with a small quantity of water. Sodium sulfate was added, and the mixture was extracted with ether. The precipitated material was then dissolved in an excess of water and the aqueous phase was extracted well with more ether. The combined ether layers were dried over anhydrous potassium carbonate, filtered through anhydrous sodium sulfate, and concentrated. The product was purified by short-path distillation in a small sublimer. The nmr spectrum ($CD_2Cl_2$, internal $CH_2Cl_2$) showed bands at $\tau$ 3.40 (1 H, doublet, $J$ = 2.5 Hz), 3.85 (1 H, doublet, $J$ = 2.5 Hz), 4.08 (1 H, doublet of doublets, $J$ = 2.5, 5.5 Hz), 4.53 (1 H, doublet, $J$ = 5.5 Hz), 6.45 (1 H, multiplet), 6.75 (1 H, multiplet), 8.16 (1 H, singlet, OH), and 8.70 (3 H, singlet); high resolution mass spectrum 122.07283 (calcd for $C_8H_{10}O$, 122.07316).

**Acknowledgment.** The authors wish to express their great appreciation to Professor P. G. Gassman for samples of the 7-phenylnorbornenols, to Professors F. A. L. Anet, H. G. Richey, Jr., P. R. Story, and the late H. Dauben for helpful exchanges of information, to Dr. C. Watts for assistance with the deuterium exchange reaction, and to the National Science Foundation for partial support of this work.

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# Carbon-to-Metal Chlorine Exchange. IV. Mercuric Salt Promoted Acetolysis of *exo*-Norbornyl Chloride[1]

**James P. Hardy,*[2] A. F. Diaz, and S. Winstein[3]**

*Contribution from the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103.* *Received July 1, 1971*

**Abstract:** Mercuric salts enhance the rate of acetolysis of *exo*-norbornyl chloride, I-Cl. Rate constants have been measured for solvolysis, $k_t$, exchange of radiolabeled chlorine between mercuric chloride and I-Cl, $k_e$, and loss of optical activity, $k_\alpha$. Relative solvolytic rate constants for mercuric acetate, chloromercuric acetate, and mercuric chloride promoted reactions at 75° are 1820, 89, and 1, respectively. Since the rate enhancements are much greater than expected for normal salt effects, the mercuric salts must be intimately involved in the ionization process. For the mercuric chloride promoted reaction, $k_\alpha/k_t = 9.6$ indicating that some 90% of the ion pairs return to covalent I-Cl in the poorly dissociating acetic acid solvent. The ratio $k_{rac}/k_e = (k_\alpha - k_t)/k_e = 2.0$ for mercuric chloride can be interpreted in terms of one or more ion-pair intermediates $I^+HgCl_3^-$ of differing structure. In a manner similar to $HgCl_2$, $Hg(OAc)_2$ facilitates C–Cl bond heterolysis, and carries the solvent anion, $OAc^-$, into intimate contact with the incipient carbonium ion, which makes the chloromercuric diacetate anion a unique "leaving group."

Mercuric salt promoted reactions of alkyl halides have been known for some time. Mercuric halides have been studied most extensively, but some early work with mercuric nitrate and mercuric perchlorate has been reported.

Satchell[4–6] studied the racemization of optically active 1-phenylethyl chloride in the presence of high concentrations of mercuric halides in the aprotic solvents nitrobenzene and acetone. The rate of loss of optical activity could be fit by eq 1 up to 0.8 *M* mercuric salt.

$$\text{obsd } k_\alpha = k_i[HgHal_2] + k_{ii}[HgHal_2]^2 \qquad (1)$$

The first-order term is explained as simple electrophilic

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[3] Deceased Nov 23, 1969.

[4] R. S. Satchell, *J. Chem. Soc.*, 5963 (1963).

[5] R. S. Satchell, *ibid.*, 5464 (1964).

[6] R. S. Satchell, *ibid.*, 797 (1965).

Table I. Summary of $k$'s for Mercuric Chloride Promoted Reactions of *exo*-Norbornyl Chloride[a] in Acetic Acid at 75°

| | | $10^6k^{HgCl_2}$, $sec^{-1}$ | | |
|---|---|---|---|---|
| $HgCl_2$, $10^2$ $M$ | LiOAc, $10^2$ $M$ | $k_{1\alpha}$ | $k_{1t}$ | $k_{1e}$ |
| None | 1.00 | | 0.452 ± 0.013 | |
| None | 11.70 | | 0.604 ± 0.015 | |
| None | 11.70 | 5.15 ± 0.17[b] | | |
| 0.30 | 1.12 | | | 0.348 ± 0.019 |
| 1.10 | 11.70 | 9.58 ± 0.44[c] | | |
| 1.17 | 2.33 | | 1.02 ± 0.24 | 1.93 ± 0.12 |
| 2.20 | 2.15 | | 1.40 ± 0.04 | |
| 2.40 | 2.33 | | | 4.16 ± 0.27 |
| 4.02 | 7.90 | 20.3 ± 0.10[c] | | |
| 4.74 | 1.10 | | | 9.29 ± 0.96 |
| 4.82 | 1.94 | | 2.72 ± 0.05 | |
| 5.40 | 5.15 | 26.1 ± 0.18[d] | | |
| 5.75 | 2.08 | | 3.27 ± 0.09 | 11.9 ± 1.2 |
| 6.98[e] | 2.08 | | 5.40 ± 0.12 | 17.0 ± 1.5 |

[a] 0.0096–0.0117 $M$ I-Cl. [b] 0.31 $M$ I-Cl. [c] 0.20 $M$ RCl. [d] 0.54 $M$ RCl. [e] Contains 0.0184 $M$ $LiClO_4$.

assistance to ionization of the RCl and the second-order term as assistance to ionization by mercuric halide dimers present in solution at the higher salt concentrations.

Ledwith, Hojo, and Winstein[7] studied the mercuric chloride induced racemization and radiochloride exchange ($k_e$) of *p*-chlorobenzhydryl chloride in anhydrous acetone and reported that the rate of racemization proceeds three-halves times faster than the rate of radiochlorine exchange. This unique ratio of $^3/_2$ held for a range of mercuric chloride concentrations from 1 to $15 \times 10^{-3}$ $M$. The explanation offered was that RCl was regenerated from racemic $R^+HgCl_3^-$ ion pairs in which all three chlorine atoms are equivalent but so constituted that two of them are from the original labeled $HgCl_2$ and one is from the RCl. In contrast to Satchell's findings, the first-order constants increased linearly with mercuric chloride probably as a consequence of the lower salt concentrations.

In 80% aqueous acetone,[8] 55% of the *p*-chlorobenzhydryl cation ion pairs dissociate and collapse with water to produce carbinol product ($k_t$). However, the ion-pair intermediates involved maintain the same constitution as in anhydrous acetone since ion pair return to RCl occurs with racemization being three-halves faster than chlorine exchange. Racemization in the benzhydryl system is a difficult process since it requires that the $R^+HgCl_3^-$ ion pairs become sufficiently loose to permit the $HgCl_3^-$ anion to migrate from one face of the cation, $R^+$, to the other. This loss of rigidity in the ion pair is inevitably accompanied by randomization of the chlorine atoms on $HgCl_3^-$.

$$\left.\begin{array}{ll} d\text{-RCl} \xrightarrow{HgCl_2} dl\text{-RCl} & k_{rac} \\ d\text{-RCl} + \text{HOS} \xrightarrow{HgCl_2} dl\text{-ROS} & k_t \end{array}\right\} k_\alpha$$

$$\text{RCl} + HgCl_2{}^* \longrightarrow \text{RCl}^* + HgCl_2 \qquad k_e$$

Mercuric salts other than mercuric halides have received much less attention. Hammett and Roberts[9] studied reactions of benzyl chloride with mercuric nitrate in 60, 75, and 90% aqueous dioxane at 25°. The kinetics they observed were second order; first order in benzyl chloride and first order in mercuric nitrate. Hammett and Roberts postulated an unstable carbonium ion intermediate which reacted with water or nitrate to produce the observed benzyl alcohol and benzyl nitrate products.

Benfey[10] studied the solvolysis of several alkyl bromides in the presence of mercuric nitrate in 70% aqueous dioxane. The effects of structural changes on the salt promoted reaction were found to be similar to those in the unpromoted reaction.[11] Thus in the series ethyl, *n*-propyl, isobutyl, isopropyl, and cyclohexyl bromide the relative reactivities are 7.3, 3.6, 1.0, 106, and 282, respectively.

With these features of mercuric salt promoted reactions in mind, we felt it would be interesting to study the effect of mercuric chloride and mercuric acetate on the acetolysis of *exo*-norbornyl chloride. Recalling that racemization in the benzhydryl system is a difficult process, it became of interest to determine how well the randomization process of the chlorine atoms on $HgCl_3^-$ would compete with a racemization process which was considerably more facile. The system *exo*-norbornyl chloride seemed appropriate for this study since the ionization reaction proceeds with inevitable loss of optical activity due to the formation of the bridged cation with a plane of symmetry.[12] We now wish to present the results of such an investigation.

## Results

**Kinetics. Mercuric Chloride.** The racemization, exchange with radiolabeled mercuric chloride, and solvolysis of *exo*-norbornyl chloride (I-Cl) were studied in glacial acetic acid at 75.0°. In all cases, the acetic acid was buffered with sufficient lithium acetate to react with the HCl produced during solvolysis. The rate constants for solvolysis of I-Cl without mercuric chloride, $k_{1t}^0$, and in the presence of mercuric chloride, $k_{1t}^{HgCl_2}$, were followed by glc, by watching either the disappearance of starting material or the appearance of products. In one kinetic run, the two methods were compared and the two rate constants agreed within experimental error (±2.7%). Reasonable first-order kinetics were followed up to 65% reaction for $k_{1t}^0$ and

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(7) A. Ledwith, M. Hojo, and S. Winstein, *Proc. Chem. Soc., London*, 241 (1961).

(8) A. Diaz, I. L. Reich, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 7598 (1970).

(9) I. Roberts and L. P. Hammett, *ibid.*, **59**, 1063 (1937).

(10) O. T. Benfey, *ibid.*, 70, 2163 (1948).

(11) A. Diaz and S. Winstein, *ibid.*, **91**, 5635 (1969), and references therein.

(12) See the following and references therein: S. Winstein, *et al.*, *ibid.*, 87, 376 (1965); G. D. Sargent, *Quart. Rev., Chem. Soc.*, **22**, 301 (1966).

Table II. Summary of Mercuric Salt Promoted Reactions of *exo*-Norbornyl Chloride in Acetic Acid

| Salt | Temp, °C | $10^4k_t$, $M^{-1}$ sec$^{-1}$ [a] | $k_t$ (rel) | $10^4k_\alpha$, $M^{-1}$ sec$^{-1}$ | $10^4k_e$, $M^{-1}$ sec$^{-1}$ | $k_\alpha/k_t$ [e] | $k_{rac}/k_e$ [e] |
|---|---|---|---|---|---|---|---|
| $Hg(OAc)_2$ | 25.0 | 10.4 | | 12.6 | | 1.2 | |
| $Hg(OAc)_2$ | 50.0 | 124 | | | | | |
| $Hg(OAc)_2$ | 75.0 | 737 | 1820 | 884 [d] | | | |
| $Hg(OAc)Cl$ [b] | 75.0 | 36 [c] | 89 | | | | |
| $HgCl_2$ | 75.0 | 0.405 | 1 | 3.9 | 1.8 | 9.6 | 2.0 |
| None | 75.0 | (0.452 × $10^{-6}$ sec$^{-1}$) [d] | | (5.15 × $10^{-6}$ sec$^{-1}$) [d] | | 11.4 | |

[a] I-Cl *ca.* 0.01 *M;* LiOAc 0.01–0.02 *M.* [b] Ratio of $HgCl_2/Hg(OAc)Cl$ varied from *ca.* 0 to 10. [c] Rate constant estimated from initial rates. Mean error of average rate constants is ±45%. [d] Estimated using $k_\alpha/k_t$ ratio of 1.2 measured at 25.0°. [e] First-order rate constants.

up to 56% reaction for $k_{1t}^{HgCl_2}$. The *k* values are listed in Table I.

When $k_{1t}^{HgCl_2}$ is plotted against mercuric chloride concentration (Figure 1), it shows a linear dependence on mercuric salt up to at least 0.057 *M*, where the slope of the line through the fixed intercept, 0.452 × $10^{-6}$ sec$^{-1}$, provides the second-order rate constant, $k_{2t}^{HgCl_2}$, equal to 0.405 × $10^{-4}$ $M^{-1}$ sec$^{-1}$ (see Table II).

A word at this point will clarify the symbols used for rate constants. The superscript will designate the electrophilic species while the letter subscript indicates the reaction being followed: solvolysis is designated by "t," the subscript "e" will denote exchange rate constants, and "α" indicates polarimetric rate constants. The number subscript designates the kinetic order of the rate constant as calculated.

Chlorine-36 labeled mercuric chloride exchanges labeled chloride with I-Cl, concurrent with solvolysis. The first-order exchange rate constants, $k_{1e}^{HgCl_2}$, were calculated using a modified form of the equation of Swart and le Roux[13] (eq 2). The quantity "*a*" is the initial molarity of I-Cl, "*b*" is the initial *normality* of radiolabeled chloride (there are 2 equiv of chloride per mole of mercuric chloride), and γ is the ratio of radiolabeled I-Cl, at any time, to the total amount of radiolabeled chloride. Reasonable kinetics were observed up to 50% exchange and the $k_{1e}^{HgCl_2}$ values are collected in Table I.

$$k_{1e}^{HgCl_2} = \frac{-2.303b}{t(a+b)}\log\left[1 - \gamma e^{k_{1t}^{HgCl_2}t}\left(1 + \frac{b}{a}\right)\right] \quad (2)$$

These first-order rate constants plot linearly against mercuric chloride concentrations up to at least 0.02 *M* (Figure 1). At 0.0575 *M* salt, the linear dependence no longer holds, and the rate constant is some 22% high. The slope of the linear portion of the curve through the origin provides the second-order rate constant, $k_{2e}^{HgCl_2}$, equal to 1.8 × $10^{-4}$ $M^{-1}$ sec$^{-1}$.

The loss of optical activity of levorotatory I-Cl ($k_{1\alpha}^{HgCl_2}$), followed on a Bendix automatic polarimeter, showed good first-order kinetics up to 70% loss of optical activity. The rate constants are collected in Table I and show a linear dependence on [$HgCl_2$] up to 0.054 *M* salt. The slope of the line through the fixed intercept, 5.15 × $10^{-6}$ sec$^{-1}$, provides the second-order rate constant equal to 3.9 × $10^{-4}$ $M^{-1}$ sec$^{-1}$ (Figure 1).

The initial slopes for the exchange and solvolysis reactions are rather shallow. Thus, at 0.01 *M* mercuric chloride, only 39% of the solvolysis is proceeding by the promoted reaction. It is of interest to note that the $k_{2\alpha}^{HgCl_2}/k_{2t}^{HgCl_2}$ ratio is 9.6, indicating that ion-pair return is just as important as in the unpromoted reaction where the $k_{1\alpha}^0/k_{1t}^0$ ratio is 11.4.

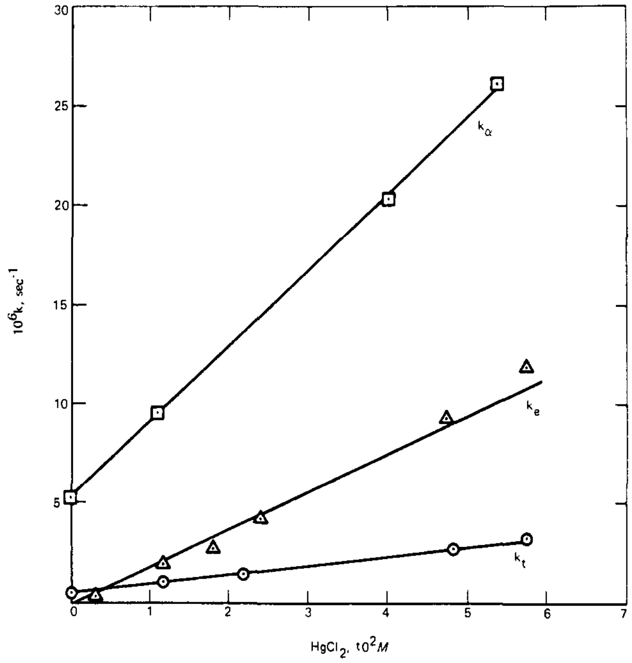
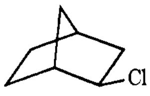
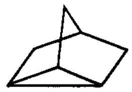


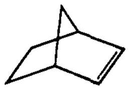
Figure 1. Dependence of $k_\alpha$, $k_e$, and $k_t$ on mercuric chloride for *exo*-norbornyl chloride in acetic acid at 75°.

The effect of $LiClO_4$ on the solvolysis and exchange reactions was studied briefly. Added $LiClO_4$ produced a rate increase where the *b* value calculated as shown in eq 3 is 19 and 9 for the solvolysis and exchange reactions, respectively. The value used for $k_{\text{no salt}}$ is the rate constant in the presence of $HgCl_2$ and LiOAc only. The effect of $LiClO_4$ on the polarimetric rate was not investigated.

$$k_{\text{salt}} = k_{\text{no salt}}(1 + b[LiClO_4]) \quad (3)$$


I-Cl


II


III

**Products. Mercuric Chloride.** The major product from the mercuric chloride assisted solvolysis of I-Cl is norbornyl acetate, which, although not shown, is most likely exclusively exo in configuration. In addition to the I-OAc, some elimination is observed where the elimination product was mainly nortricyclene (II)

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[13] E. R. Swart and L. J. le Roux, *J. Chem. Soc.*, 2110 (1956).

Table III. Elimination Products from Mercuric Salt Promoted Acetolysis of *exo*-Norbornyl Chloride[a]

| Temp, °C | Mercuric salt | Mercuric salt, $10^2$ *M* | % reaction salt promoted | Total %[b] nortricyclene | % nortricyclene,[c] promoted reaction | Norbornene |
|---|---|---|---|---|---|---|
| 25.0 | $Hg(OAc)_2$ | 1.98 | 100 | 6.26 ± 0.34 | | ~0 |
| 25.0 | $Hg(OAc)_2$ | 2.04 | 100 | 6.30 ± 0.24 | | ~0 |
| 50.0 | $Hg(OAc)_2$ | 2.03 | 100 | 7.23 ± 0.45 | | ~0 |
| 75.0 | $Hg(OAc)_2$ | 1.05 | 100 | 6.65 ± 1.11 | | 0 |
| 75.0 | Hg(OAc)Cl[d] | 1.03[d] | 100 | 10.0 ± 1.2 | | ~0 |
| 75.0 | $HgCl_2$ | 5.75 | 86.3 | 10.1 ± 0.6 | 9.1 | <1.5% |
| 75.0 | $HgCl_2$ | 2.20 | 67.8 | 13.7 ± 2.7 | 12.5 | <1.5% |

[a] 0.01 *M* RCl and 0.021 *M* LiOAc. [b] Total per cent calculated assuming only I-OAc and II are produced by acetolysis of I-Cl. [c] Per cent II from promoted reaction based on calculation that unpromoted reaction produced 16.1% II. [d] $HgCl_2$, 0.105 *M*, and $Hg(OAc)_2$, 0.00513 *M*, are assumed to give 0.01020 *M* Hg(OAc)Cl and 0.100 *M* $HgCl_2$.

Table IV. Summary of *k*'s for Mercuric Acetate Promoted Reactions of *exo*-Norbornyl Chloride[a] in Acetic Acid

| $Hg(OAc)_2$, $10^2$ *M* | Average[b] salt, $10^2$ *M* | LiOAc, $10^2$ *M* | Temp, °C | $10^2 k_{2t}^{Hg(OAc)_2}$,[c] $M^{-1}$ sec$^{-1}$ | $10^4 k_{1t}^{Hg(OAc)_2}$,[d] sec$^{-1}$ |
|---|---|---|---|---|---|
| 1.08 | 0.49 | None | 75.0 | 7.68 ± 0.21 | 3.76 ± 0.10 |
| 1.03 | 0.57 | 1.08 | 75.0 | 6.36 ± 0.50 | 3.71 ± 0.29 |
| 1.05 | 0.58 | 2.15 | 75.0 | 8.45 ± 0.84 | 4.84 ± 0.48 |
| 1.45 | 1.11 | 2.15 | 75.0 | 6.29 ± 0.04 | 6.95 ± 0.04 |
| 2.06 | 1.48 | 1.08 | 75.0 | 8.09 ± 0.22 | 11.98 ± 0.30 |
| 1.98 | 1.70 | 2.08 | 25.0 | 0.0944 ± 0.0052 | 0.106 ± 0.009 |
| 2.04 | 1.63 | 2.15 | 25.0 | 0.113 ± 0.0037 | 0.184 ± 0.006 |
| | | | | $10^2 k_{2\alpha}^{Hg(OAc)_2}$, $M^{-1}$ sec$^{-1}$ | |
| 6.90 | | 9.86 | 25.0 | 0.154 ± 0.009[e] | |
| 11.8 | | 25.8 | 25.0 | 0.0974 ± 0.007[f] | |

[a] 0.010–0.012 *M* I-Cl. [b] Average mercuric acetate concentration within a run. [c] Using the average of all rate constants at each temperature, the activation parameters for $k_{2t}^{Hg(OAc)_2}$ are: $\Delta H^{\ddagger} = 16.9$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -15.1$ eu. [d] $k_{1t}^{Hg(OAc)_2}$ calculated by mutiplying $k_{2t}^{Hg(OAc)_2}$ by the average mercuric acetate concentration. [e] 0.00646 *M* I-Cl. [f] 0.187 *M* I-Cl.

with trace amounts of norbornene (III). If norbornene were produced in an amount as high as 10% of the nortricyclene, the norbornene would still account for less than 1.5% of the total products. This amount is detectable by our methods of analysis. The per cent of II is dependent upon the mercuric chloride concentration. This is expected since the reaction is a mixture of salt assisted and unassisted paths, each contributing a different fraction of II. These results are listed in Table III.

Vogelfanger[14] investigated elimination products in the norbornyl system with different leaving groups at 75.0 and 100.0° and found that less elimination occurred at lower temperatures. However, the elimination products from I-Cl were measured only at 100.0°. Assuming the elimination reactions with I-Cl and *exo*-norbornyl *p*-bromobenzenesulfonate, I-OBs, have the same temperature dependence, we can estimate the amount of II produced from the salt assisted reaction of I-Cl as follows: I-OBs yields 11.2 and 7.2% II at 100.0 and 75.0°, respectively; I-Cl yields 24.9% II at 100.0° and we can estimate 16.1% II is produced by the unassisted acetolysis of I-Cl at 75.0°. Using this value, we estimate that the $HgCl_2$ assisted acetolysis produces approximately 10.8 ± 1.6% nortricyclene where the extra *ca.* 1.1% arises from the unpromoted reaction.

**Kinetics. Mercuric Acetate.** The rate of solvolysis of *exo*-norbornyl chloride in the presence of mercuric acetate was measured in acetic acid at 25.0, 50.0, and 75.0°. The progress of the reaction was followed by glc analysis by watching the disappearance of starting material, or the appearance of products. Acceptable second-order kinetics were observed up to 80% reaction. The calculations were made according to eq 4 assuming that 1 mol of mercuric acetate reacts with 1 mol of I-Cl. *a* and *b* are the concentrations of I-Cl and mercuric acetate initially, and *x* is the amount of either which has reacted in a given time. In most cases, the rate was followed by watching the formation of I-OAc only. The various rate constants are summarized in Table IV.

$$(k_{2t}^{Hg(OAc)_2})t = \frac{2.303}{(b-a)} \log \frac{a(b-x)}{b(a-x)} \tag{4}$$

The pseudo-first-order rate constants, $k_{1t}^{Hg(OAc)_2}$, were calculated using the average $[Hg(OAc)_2]$ present in the run and the calculated second-order constant, $k_{2t}^{Hg(OAc)_2}$. These values are plotted against the average mercuric acetate concentration in Figure 2. The slope of the best straight line through the origin provides the value for $k_{2t}^{Hg(OAc)_2}$ equal to $7.37 \pm 0.84 \times 10^{-2}$ $M^{-1}$ sec$^{-1}$ with an average error of ±11%.

It should be noted that $k_{2t}^{Hg(OAc)_2}/k_{2t}^{HgCl_2} = 1820$ at 50.0°. Mercuric acetate is obviously a much more reactive species than mercuric chloride. The question then arises as to the reactivity of chloromercuric acetate relative to mercuric acetate.

To probe the effect of chloromercuric acetate on the rate of acetolysis of I-Cl, three kinetic measurements were made in which mixtures of mercuric chloride and mercuric acetate were present. It is assumed that 2 mol of HgClOAc is produced from 1 mol of $HgCl_2$ plus 1 mol of $Hg(OAc)_2$. In all three cases, the initial

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[14] E. Vogelfanger, Doctoral Dissertation, University of California at Los Angeles, 1963.

Table V. Initial Rate Constants for Acetolysis of *exo*-Norbornyl Chloride and Mercuric Acetate

| $Hg(OAc)_2$, $10^2$ $M^a$ | $HgCl_2$, $10^2$ $M^a$ | I-Cl,[a] $10^2$ $M$ | LiOAc,[a] $10^2$ $M$ | Hg(OAc)Cl,[b] $10^2$ $M$ | $HgCl_2$/ Hg(OAc)Cl | Initial, $10^3k$,[c] $M^{-1}$ $sec^{-1}$ |
|---|---|---|---|---|---|---|
| 0.500 | 10.5 | 1.01 | 2.14 | 1.00 | 10 | 6.1 |
| 0.502 | 4.5 | 1.02 | 2.02 | 1.04 | 4 | 2.3 |
| 0.514 | ~0[d] | 1.05 | 1.09 | 0.514 | 0 | 2.3 |

[a] Initial amount of weighed material. [b] Calculated concentration based on the assumption that 1 mol of $HgCl_2$ reacts quantitatively with 1 mol of $Hg(OAc)_2$ to produce 2 mol of Hg(OAc)Cl. [c] Best straight line through initial points of plot of $(x/a)(a - x)$ against time. [d] Rate constant calculations were made after 0.00514 $M$ I-Cl had reacted assuming 1 mol of chloride reacts quantitatively with 1 mol of $Hg(OAc)_2$ to produce 1 mol of Hg(OAc)Cl.

concentrations of I-Cl and chloromercuric acetate were equal. The rates were treated for second-order kinetics assuming 1 mol of I-Cl reacts with 1 mol of HgClOAc. The rate constants drift down within a run, but the reaction does go to completion so the drift is not a manifestation of a reversible reaction. Since the rate constants decrease within a run, only the initial slopes of the plots of $(x/a)/(a - x)$ against time are recorded in Table V. These calculated initial second-order rate constants are, within a rather large experimental error (±45%), at least an order of magnitude smaller than those for mercuric acetate. This justifies the assumption made for the calculation of $k_{2t}^{Hg(OAc)_2}$ that chloromercuric acetate promoted acetolysis does not compete with acetolysis promoted by $Hg(OAc)_2$. Also, the assumption that the equilibrium is largely on the side of chloromercuric acetate is justified, since the initial rate constant is reasonably constant, within the large experimental error, even though the mercuric chloride concentration is varied drastically.

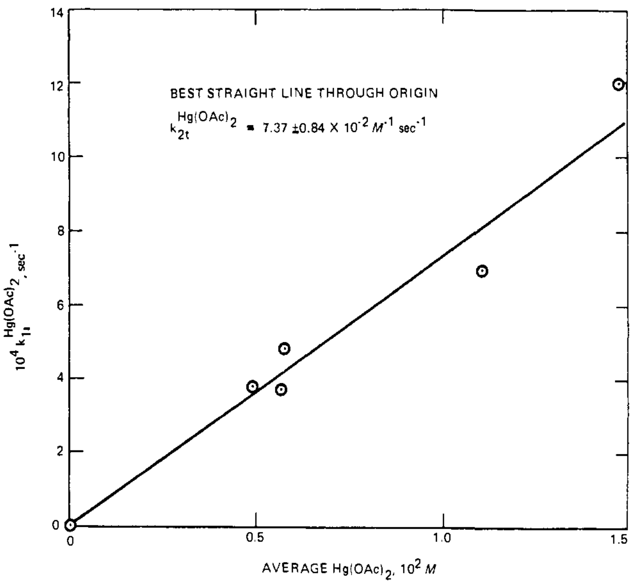

Figure 2. Dependence of $k_{1t}^{Hg(OAc)_2}$ on mercuric acetate for *exo*-norbornyl chloride in acetic acid at 75°.

The rate of loss of optical activity at any time is proportional to the concentration of (−)-I-Cl and $Hg(OAc)_2$ (eq 7).

Since the concentration of (−)-I-Cl is proportional to α, the measured optical rotation of the solution, eq 8 is easily written from eq 7. From a plot of α against time the slope, dα/d*t*, is measured at various times. Then the values of $(d\alpha/dt)/\alpha$ are plotted against the corresponding mercuric acetate concentrations calculated from $k_{2t}^{Hg(OAc)_2}$. A least-squares line for this plot provides the value for $k_{2\alpha}^{Hg(OAc)_2}$ (Figure 3). The average of this constant for two runs is 12.6 ± 2.8 × $10^{-4}$ $M^{-1}$ $sec^{-1}$.

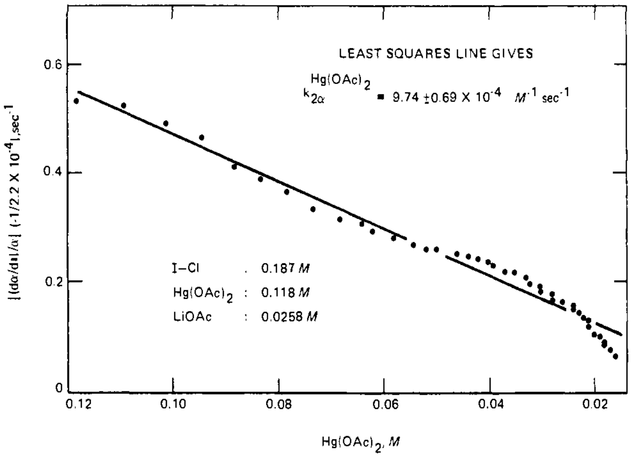

Figure 3. Plot of $(d\alpha/dt)/(\alpha)$ *vs.* $[Hg(OAc)_2]$ for the loss of optical activity of (−)-*exo*-norbornyl chloride in the presence of mercuric acetate in acetic acid at 25.0°.

The polarimetric infinity was measured carefully in order to determine residual optical activity. Within experimental error, essentially no activity was measured. The (−)-I-Cl was prepared from *endo*-norbornyl acid phthalate which was 48.7% resolved; therefore the maximum possible optical purity of the I-OAc product is 48.7%. This would correspond to a final polarimetric reading of 0.0138° in our experiments.[15] We estimate our error in polarimetric readings is less than 0.0008°; therefore if the final products had 0.0008° residual rotation, this would amount to a 94% loss of optical activity.

$$(-)\text{-I-Cl} + Hg(OAc)_2 \xrightarrow{k_{rac}} \text{racemic I-Cl} + Hg(OAc)_2 \quad (5)$$

$$(-)\text{-I-Cl} + Hg(OAc)_2 \xrightarrow{k_{2t}^{Hg(OAc)_2}} \text{racemic I-OAc} + Hg(OAc)Cl \quad (6)$$

$$-d[(-)\text{-I-Cl}]/dt = (k_{rac} + k_{2t}^{Hg(OAc)_2})[(-)\text{-I-Cl}][Hg(OAc)_2] \quad (7)$$

$$(-d(\alpha)/dt)/\alpha = k_{2\alpha}^{Hg(OAc)_2}[Hg(OAc)_2] \quad (8)$$

**Products. Mercuric Acetate.** The major products from the reaction of I-Cl with mercuric acetate in acetic acid are I-OAc and nortricyclene (II). No norbornene was detected, whereas 1.5% norbornene is detectable. In the presence of $Hg(OAc)_2$, nortricyclene

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(15) S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, 74, 1147 (1952).

is unstable and produces I-OAc. This reaction is faster by two powers of ten than addition of neutral acetic acid to II[14] and does not fit either first- or second-order kinetics. Nevertheless, the rate of disappearance of II is roughly ten times slower than the rate of solvolysis of I-Cl in the presence of mercuric acetate, and the products can be assumed stable under the conditions of the reaction except for the extended times required for the determination of experimental infinities where appropriate corrections can be made based on product distribution. The distribution of products between I-OAc and II showed little variation with temperature (Table III).

## Discussion

The enhanced rates of reaction of I-Cl in the presence of mercuric chloride or mercuric acetate in acetic acid are more than general salt effects. Using eq 3, one calculates *b* values to be 95–100 for mercuric chloride and 1.7–1.8 $\times$ $10^5$ for mercuric acetate! Such enormous *b* values are not consistent with normal values observed in the acetolysis of *exo*-norbornyl derivatives (Table VI). Even lithium perchlorate, which has been shown to be a very efficient salt for enhancing solvolysis,[16] is less effective than mercuric chloride in enhancing solvolytic rates. Clearly the mercuric salts are not demonstrating normal salt effects but are intimately involved in the ionization process. The mercuric salt promoted reactions are, however, susceptible to normal salt effects with lithium perchlorate or lithium acetate. The effect of $LiClO_4$ on the $HgCl_2$ promoted solvolysis and exchange of I-Cl is in line with normal salt effects as seen in Table VI.

**Table VI.** Calculated *b* Values for Acetolysis of *exo*-Norbornyl Derivatives

| Substrate | Salt | *b* | Ref |
|---|---|---|---|
| I-OBs | LiOBs | 4.5 | 22 |
| I-OBs | $LiClO_4$ | 38 | 22 |
| I-Br | LiBr | 3–7 | 30 |
| I-Br | $LiClO_4$ ($k_t$) | 14.5 | 30 |
| I-Br | $LiClO_4$ ($k_\alpha$) | 5.4 | 30 |
| I-Cl | LiOAc | 3 | This work |
| I-Cl ($HgCl_2$)[a] | $LiClO_4$ ($k_{1t}{}^{HgCl_2}$) | 19 | This work |
| I-Cl ($HgCl_2$)[a] | $LiClO_4$ ($k_{1e}{}^{HgCl_2}$) | 9 | This work |
| I-Cl | $HgCl_2$ | 95–100 | This work |
| I-Cl | $Hg(OAc)_2$ | 1.7–1.8 $\times$ $10^5$ | This work |

[a] Mercuric chloride and lithium perchlorate were present in the reaction. The *b* value calculation was based on lithium perchlorate enhancement of the mercuric chloride promoted reaction.

**Kinetics.** Acetolysis of I-Cl in the presence of mercuric chloride follows pseudo-first-order kinetics. The $HgCl_2$ promoted acetolysis of *p*-chlorobenzhydryl chloride also shows first-order kinetics.[17] On the other hand, the solvolysis of *p*-chlorobenzhydryl chloride in 80% acetone containing $HgCl_2$ is fit by second-order kinetics.[8] The formal stoichiometry of the second-order reaction in 80% acetone is expressed by eq 9 and 10.

$$RCl + HgCl_2 + H_2O \longrightarrow ROH + H^+ + HgCl_3^- \quad (9)$$

$$HgCl_3^- \rightleftarrows HgCl_2 + Cl^- \quad (10)$$

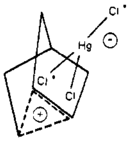
Anantaraman and coworkers[18,19] studied the mercuric chloride assisted hydrolysis of benzyl chloride in 80% aqueous acetone and treated the reaction as a first-order process. Table VII displays their data and our recalculation of their data on a second-order basis. It can be seen that the second-order treatment yields a somewhat better fit, eliminating the downward drift observed in the calculated first-order constants.

Since the observed kinetics for benzyl chloride solvolysis are fit by a second-order treatment with an average error of 1.2%, $HgCl_3^-$ must be highly associated and effectively inactive as a catalyst. Thus, eq 10 must lie far to the left.

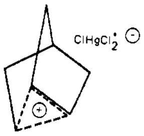
In acetolysis, lithium acetate is present in the medium to consume the hydrogen chloride produced. The formal stoichiometry of the reaction can be expressed by eq 11.

$$RCl + LiOAc + HgCl_2 \longrightarrow ROAc + LiCl + HgCl_2 \quad (11)$$

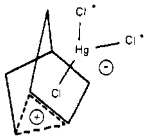
In acetic acid the lithium cation, present as lithium acetate, strongly affects the observed kinetics by competing successfully with mercuric chloride for the chloride ion produced during solvolysis.[20] Hence the mercuric chloride is not consumed by conversion to the inactive $HgCl_3^-$. Because the norbornyl system is internally compensated,[12] the polarimetric rate constant, $k_\alpha$, is a good measure of ionization. The $k_\alpha/k_t$ ratio of 9.6 for the promoted reaction indicates that some 90% of the ion pairs return to covalent I-Cl and only 10% yield solvolysis products. If we consider the character of only those ion pairs which return to covalent I-Cl, we find racemization exceeds exchange by a factor of 2, as indicated by the ratio $k_{rac}/k_e = (k_\alpha - k_t)/k_e = 2.0$. This simple ratio of 2.0 is most easily explained by regenerating I-Cl from the racemic ion pair **1** where only two chlorine atoms of the $HgCl_3^-$ anion are associated equivalently with the bridged norbornyl cation. One of the two equivalent chlorines is labeled and is from the originally labeled $HgCl_2$. The other is unlabeled and from I-Cl. Regeneration of racemic I-Cl from this ion pair where the two chlorine atoms do not further randomize with other chlorine atoms will incorporate radiochlorine only once out of two chances. The $k_{rac}/k_e$ ratio of 2.0 may also be the result of a blend of intermediates such as **2** or **3** in addition to **1**. Intermediate **2** would have a $k_{rac}/k_e = 1.5$ and is similar to the intermediate postulated for mercuric chloride promoted reactions of *p*-chlorobenzhydryl chloride[7,8] where all three chlorine atoms are equivalent with respect to return to the bridged cation. Two of the chlorines from the $HgCl_2$ are labeled and the third from I-Cl is unlabeled. Intermediate **3** would show no exchange upon ionization ($k_{rac}/k_c = \infty$). The



**1**



**2**



**3**

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[16] S. Winstein, P. Klinedinst, and G. C. Robinson, *J. Amer. Chem. Soc.*, **83**, 885 (1961).

[17] A. Diaz, unpublished results.

[18] S. Koshy and R. Anantaraman, *J. Amer. Chem. Soc.*, **82**, 1574 (1960).

[19] R. Anantaraman and K. Saramma, *J. Sci. Ind. Res., Sect. B*, **21**, 598 (1962).

[20] S. Bruckenstein and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **78**, 2974 (1956).

**Table VII.** Recalculation of Data for the Hydrolysis of Benzyl Chloride in the Presence of Mercuric Chloride in 80% Aqueous Acetone at 82.85° [a,b]

| $10^{-4}$ sec | Titer[c] | $x$ | $(a - x)$ | $(b - x)$ | $10^4k_2$, $M^{-1}$ sec$^{-1}$ | $10^5k_1$,[b] sec$^{-1}$ |
|---|---|---|---|---|---|---|
| 0 | 0.23 | 0.0000 | 0.0485 | 0.149 | | |
| 0.72 | 1.60 | 0.0064 | 0.0421 | 0.143 | 1.40 | 1.95 |
| 1.02 | 2.14 | 0.0089 | 0.0396 | 0.140 | 1.37 | 1.98 |
| 1.14 | 2.31 | 0.0096 | 0.0389 | 0.139 | 1.33 | 1.95 |
| 1.38 | 2.71 | 0.0115 | 0.0370 | 0.137 | 1.36 | 1.97 |
| 1.56 | 3.00 | 0.0128 | 0.0357 | 0.136 | 1.38 | 1.98 |
| 1.68 | 3.16 | 0.0136 | 0.0349 | 0.135 | 1.38 | 1.96 |
| 1.80 | 3.38 | 0.0146 | 0.0339 | 0.134 | 1.42 | 2.00 |
| 2.04 | 3.68 | 0.0160 | 0.0325 | 0.133 | 1.42 | 1.97 |
| 2.16 | 3.87 | 0.0169 | 0.0316 | 0.132 | 1.44 | 1.99 |
| 3.30 | 5.07 | 0.0224 | 0.0261 | 0.127 | 1.40 | 1.89 |
| 4.74 | 6.24 | 0.0279 | 0.0206 | 0.121 | 1.37 | 1.80 |
| 7.68 | 7.97 | 0.0359 | 0.0126 | 0.113 | 1.40 | 1.76 |
| | 10.67 | 0.0485 | | | Mean 1.39 ± 0.02 | 1.93 ± 0.05 |

[a] Calculated from the equation: $k_2 = [2.303/t(b - a)] \log (a/b)[(b - x)/(a - x)]$, where $x$ is the amount of benzyl chloride reacted. [b] Data taken from ref 18. [c] Titers are expressed in ml of 0.0232 $M$ NaOH per 5 ml aliquot of reaction mixture.

chlorine removed from I-Cl would retain its identity and remain pointing toward the bridged ion.

It may be in instructive to discuss at this point the results in formic acid[21] at 25.0° where the various reactions display the same kinetic behavior as in acetic acid. The increase in $k_t$ due to added $HgCl_2$ (up to 0.0450 $M$) is fit by a least-squares line with slope $13.9 \pm 0.2 \times 10^{-4}$ $M^{-1}$ sec$^{-1}$ and intercept $15.0 \pm 0.2 \times 10^{-6}$ sec$^{-1}$. Similarly, the $k_e$ values are linearly dependent on $[HgCl_2]$ where the slope of the line through the origin is $2.66 \pm 0.05 \times 10^{-4}$ $M^{-1}$ sec$^{-1}$. Finally the dependence of $k_\alpha$ on $[HgCl_2]$ provides the second-order constant equal to $27.1 \times 10^{-4}$ $M^{-1}$ sec$^{-1}$, where $k_\alpha$ in the absence of $HgCl_2$ is $60.7 \pm 1.5 \times 10^{-6}$ sec$^{-1}$.

On going from acetic to formic acid, the importance of ion-pair return in the promoted reaction is reduced; $k_\alpha/k_t$ diminishes from 9.6 to 1.95—indicating that only half of the *exo*-$R^+HgCl_3^-$ ion pairs return to covalent RCl. The amount of chlorine exchange that accompanies the racemization of RCl is also less in formic acid (*ca.* 20%). These results are in line with racemization in acetic acid proceeding *via* two intermediates, a "solvent-separated" ion pair like **2** which dissociates and gives product in the more dissociating solvent formic acid, and an "intimate" ion pair like **3** which is less susceptible to dissociation.[22–24]

In contrast to the racemization process of the benzhydryl derivatives,[8] the front side rearrangement in the $HgCl_2$ promoted reactions of the *exo*-norbornyl chloride does not proceed *via* ion-pair intermediates where all the chlorine atoms in $HgCl_3^-$ become equivalent. Instead the bridged cations in the ion-pair intermediates scrutinize the chlorine atoms and the one originally from *exo*-RCl remains pointed toward the cation some of the time.

**Mercuric Acetate Promoted Reactions.** Mercuric acetate is an unusual species, for it not only facilitates carbon–chlorine bond heterolysis, but it also carries the solvent anion, acetate, into intimate contact with the incipient carbonium ion. This indeed makes the chloromercuric diacetate anion a unique "leaving group." As we noted earlier, solvolysis promoted by mercuric acetate proceeds some 1820 times faster than that promoted by mercuric chloride.

A better estimate of the relative abilities of $Hg(OAc)_2$ and $HgCl_2$ to promote the ionization of *exo*-norbornyl chloride by electrophilic assistance is provided by the polarimetric rates which correct for ion-pair return. This estimate can be approximated from the values listed in Table II. Thus $k_\alpha$ with $Hg(OAc)_2$ at 75.0°, estimated from $k_t^{Hg(OAc)_2}$ and the $k_\alpha/k_t$ ratio with $Hg(OAc)_2$ at 25.0° (1.2), is $884 \times 10^{-4}$ $M^{-1}$ sec$^{-1}$ (Table II). This value makes $Hg(OAc)_2$ 228 times more effective than $HgCl_2$ in promoting the ionization of *exo*-norbornyl chloride.

The $k_\alpha/k_t$ ratio of 1.2 with $Hg(OAc)_2$ indicates that *ca.* 17% of the collapse of the cation ion pair is with the original chlorine. This behavior gives a measure of the degree of affiliation between the cation and the chlorine on mercury in ion pair intermediates such as **3**.

While we have no way of measuring the origin of I-OAc products, it is possible that some if not most of it is derived by internal return from the *exo*-norbornyl chloromercuric diacetate ion pair. This view is further suggested by the apparent low amount of ion-pair return accompanying the reaction with $Hg(OAc)_2$ ($k_\alpha/k_t = 1.2$), whereas ion-pair return is very important in the reaction of *exo*-norbornyl chlorine with $HgCl_2$ ($k_\alpha/k_t = 9.6$) and in the acetolysis of *exo*-norbornyl *p*-bromobenzenesulfonate ($k_\alpha/k_t = 4.6$).[25]

## Experimental Section

**Acetic Acid.** Reagent grade acetic acid was purified using acetic anhydride as previously described.[26] Stock acetic acid solvent and solutions were checked periodically by the Karl Fischer test.[27]

**Lithium Acetate.** An acetic acid solution of this salt was prepared using dried lithium carbonate. An amount of redistilled acetic anhydride, sufficient to react with the water produced in the neutralization, was added.

**Pentane.** Reagent grade petroleum ether was purified as previously described.[28]

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(21) J. P. Hardy, A. Ceccon, A. F. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 1356 (1972).

(22) S. Winstein, E. Clippinger, A. Fainberg, and G. C. Robinson, *ibid.*, **76**, 2597 (1954); *Chem. Ind. (London)*, 664 (1954).

(23) S. Winstein, E. Clippinger, A. Fainberg, R. Heck, and G. C. Robinson, *J. Amer. Chem. Soc.*, **78**, 328 (1956).

(24) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(25) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965).

(26) A. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(27) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).

(28) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1955.

**Norbornene.** Commercial grade norbornene was refluxed over sodium chips for 1 hr and then distilled, bp 95–98° (740 mm) (lit.[29] 96.0° (760 mm)).

**Bicyclohexyl.** Practical grade bicyclohexyl was washed with concentrated sulfuric acid, water, 1 *N* potassium hydroxide, and water again, and dried over anhydrous calcium sulfate. The bicyclohexyl was distilled under reduced pressure, bp 128.5° (33.2 mm). Glc analysis, using conditions employed in the kinetic analysis, showed no impurities.

**Cyclohexane.** Cyclohexane (Matheson Coleman and Bell) was used directly from the bottle after glc analysis showed no impurities to be present.

**Nortricyclene.** The catalytic conversion of norbornene to nortricyclene is patterned after the work of Schleyer.[29] Freshly purified norbornene, 30 g, was placed in a 50-ml, one-necked flask fitted with an air-cooled condenser. Approximately 30 pellets of Houdry silica–alumina catalyst (Grade A Kaolin pellets, regular size) were added and the mixture was refluxed for 12 hr. The resulting yellow oil was roughly 70% nortricyclene and 30% norbornene mixed with some polymeric materials. The most volatile portion was transferred, bulb-to-bulb at 0.1 mm pressure, into a flask cooled in liquid nitrogen. This white solid was taken up in pentane and washed eight times with 10-ml portions of aqueous silver nitrate (1 g/ml) to extract the norbornene. The progress of the extraction was monitored by glc using conditions described in the Experimental Section under Product Analysis. The pentane layer was washed twice with water; the second wash gave no precipitate with aqueous sodium chloride. The pentane layer was dried over anhydrous potassium carbonate and filtered and the pentane carefully distilled away. The material was then fractionated through a 12-in. center tube column and the fraction boiling at 101° (740 mm) was kept. Vpc analysis showed it to be 97.8% nortricyclene and 2.2% norbornene.

***exo*-Norbornyl Chloride.** Approximately 150 ml of purified pentane and 24.6 g of freshly distilled norbornene were mixed and the solution was cooled by a Dry Ice–acetone bath to −70°. Anhydrous hydrochloric acid was bubbled through a gas dispersion tube into the solution for approximately 50 min. The flask was removed from the bath and 100 ml of water was slowly added with stirring.

The pentane layer was washed and dried over anhydrous sodium carbonate and magnesium sulfate. The solution was filtered, and the solvent was rapidly distilled away. The *exo*-norbornyl chloride was distilled through a 21-in. spinning band column (reflux ratio 12:1) under reduced pressure, and the center fraction, bp 62.9–60.0° (30.2 mm), yielded 13.3 g (41%) of the chloride. Glc analysis showed the material to be greater than 99% pure. Under these glc conditions, those employed for kinetic measurements, the exo and endo epimers are not separated.

**(−)-*exo*-Norbornyl Chloride.** Preparation was according to the methods of Winstein and Trifan[15] for the *endo*-norbornyl acid phthalate, and according to Clippinger[30] for the conversion of the *endo*-norbornyl acid phthalate to the *exo*-norbornyl chloride.

Approximately 10 g of 48.7% resolved *endo*-norbornyl acid phthalate, $[\alpha]^{25}\text{D}$ +2.44° (*c* 4.72, chloroform), was used to prepare optically active *exo*-norbornyl chloride. The material was approximately 99% pure by glc. The major impurity is probably nortricyclene, present to the extent of less than 1%.

**Preparation of Radiolabeled Mercuric Chloride ($^{36}$Cl).** To a solution of 394 mg of resublimed mercuric chloride (B & A Lot No. 24369) in 15 ml of acetone in a 50-ml round-bottom flask, was added 0.15 ml of radiolabeled ($^{36}$Cl) hydrochloric acid (2.64 *N* in water supplied by Oak Ridge National Laboratory). The solution was allowed to stand for 5 hr, after which time it was transferred to a vacuum sublimator. The solvent was carefully pumped away and the solid sublimed to yield 314 mg of recovered solid. This was mixed with 661 mg of unlabeled mercuric chloride and again sublimed to yield 984 mg of radiolabeled mercuric chloride with an activity of 99.8 cpm/mg.

**Kinetic Procedure.** A typical kinetic run is described. *exo*-Norbornyl chloride, 64.6 mg, and 48.0 mg of a 91:09 mixture of bicyclohexyl–cyclohexane as internal glc standards, are weighed into a 10-ml volumetric flask. An acetic acid solution of 0.107 *M* lithium acetate is added to the mark. An aliquot, 4.980 ml, of this solution is delivered into a 25-ml volumetric which contains 149.2 mg of mercuric chloride dissolved in approximately 15 ml of glacial acetic acid. The volumetric is filled to the mark with acetic acid and mixed. Aliquots, greater than 2 ml, are sealed in rate tubes. These are placed in a thermostated bath, agitated for 45 sec, and at the kinetic zero point removed and immediately plunged into an ice–water slush. The remaining tubes are similarly withdrawn at appropriate time intervals.

The rate tubes are broken open; a 2-ml aliquot is removed and added to a 25-ml separatory funnel containing 5 ml of cold water and 8 ml of cold pentane. The pentane layer is washed with an additional 2.5 ml of cold water and stored over anhydrous potassium carbonate awaiting glc analysis on a Wilkens Hy-Fi (flame ionization detector) under the following conditions: 1 m × $^1/_8$ in., 5% XF-1150 on 80–100 mesh Chromosorb W (nonacid washed), nitrogen carrier gas (No. 15), 40° oven and 90° injector.

The amounts of *exo*-norbornyl chloride and *exo*-norbornyl acetate are determined relative to the internal standard, bicyclohexyl.

**Kinetic Procedures for Radiolabeled Mercuric Chloride Exchanges.** The exchange reaction mixtures are made up exactly as described for a normal kinetic run with the exception that the mercuric chloride used is radiolabeled. An aliquot of 2 ml of acetic acid solution was removed from the rate tube and added to a separatory funnel containing 5 ml of cold water and 8 ml of cold pentane. The funnel was shaken vigorously 40 times and the aqueous layer drained quantitatively into a 10-ml volumetric flask. The aqueous portions were combined in a 10-ml volumetric flask; the organic layer was collected in another 10-ml volumetric flask. The funnel was rinsed with 1 ml of cold pentane which was added to the volumetric flask.

The contents of the volumetric flasks were brought to volume with the appropriate solvents, and aliquots of approximately 8 ml were withdrawn and delivered into the counting well of a Geiger–Muller counter.

Duplicate counts of at least 1600 counts each were made of each solution; the precision of the calculated counts per minute was within ±5%. The average of the separate determinations was taken, and each of the averaged counts per minute was corrected for background radiation; the ratio of the organic counts per minute to the total counts per minute, $\gamma$, was calculated for each kinetic point.

The pentane solution remaining in the 10-ml volumetric flask, after the aliquot had been removed for counting, was dried with anhydrous potassium carbonate and subjected to glc analysis. In this way, the exchange and solvolysis reactions were followed concurrently.

Control experiments showed that I-Cl was partitioned completely into the organic phase and $HgCl_2$ into the aqueous phase within experimental error.

**Polarimetric Procedure.** An appropriate amount of levorotatory *exo*-norbornyl chloride was weighed into a 5-ml volumetric flask, and a solution of mercuric chloride and lithium acetate in acetic acid was added to the mark. This solution was transferred to a 0.2-dm polarimeter tube, and the tube was sealed. The polarimeter tube was placed in a thermostated holder (±0.5°) in the Bendix automatic recording polarimeter, and the change in optical rotation of the solution was recorded on a strip-chart recorder; readings were later taken from the chart.

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[29] P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 80, 1700 (1958).

[30] E. Clippinger, Doctoral Dissertation, University of California at Los Angeles, 1955.