the same quantities of materials. The crude product was separated by column chromatography on alumina. The purified **9** (0.106 g, 55%) was distilled at 62–64° (6 mm); ir (neat) 5.79, 6.10, 8.08, and 8.20 μ; pmr (CCl_4) δ 0.01 (apparent t, 1), 0.73 (d, 3, J = 7.0 Hz), 1.02 (d, 3, J = 7.0 Hz), 0.82 (m, 1), 1.40 (m, 1), 1.81 (t, 3), 1.96 (s, 3), 2.27 (m, 1), 5.02 (broad abs, 1), and 5.40 (broad abs, 1).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.91; H, 9.44.

Preparation of 2-Methyl-5-isopropyl-5-acetoxymethyl-1,3-cyclopentadiene (11). Umbellulol (**5** or **6**) (0.775 g, 0.005 mol), 0.720 g (0.006 mol) of acetic anhydride, and 0.410 g (0.005 mol) of sodium acetate were heated at 125° for 2 days under nitrogen. After a similar work-up as in the preceding experiment, 0.737 g of residue was obtained. Analysis by gas chromatography (15% Carbowax 20 M column, 105°) showed two peaks with retention times of 5 and 18 min corresponding to **7** and **11**, respectively.

Chromatography of the mixture on neutral alumina gave two fractions. The fraction corresponding to peak two had bp 62–64° (6 mm); ir (neat) 5.76, 6.16, 8.08, and 12.48 μ; pmr (CCl_4) δ 0.8 (d, 3, J = 7.0 Hz), 0.9 (d, 3, J = 7.0 Hz), 1.92 (d, 3, J = 2.0 Hz), 1.96 (s, 3), 2.25 (m, 1), 3.92 (broad abs, 2), 5.8 (broad abs, 1), and 6.16 (d, 2, J = 2.0 Hz). On the basis of these spectral data, the structure assigned is 2-methyl-5-isopropyl-5-acetoxymethyl-1,3-cyclopentadiene (**11**).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.04; H, 9.43.

Treatment of 7 with Sodium Acetate in Acetic Acid at Room Temperature. 1-Isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**) (1.81 g, 0.012 mol) and 75 ml of 0.5 M sodium acetate in acetic acid were kept at room temperature for 3 days and extracted with a small amount of ether. The contents were filtered through a Büchner funnel to remove the excess sodium acetate, and the mixture was transferred to a separatory funnel containing a mixture of water and pentane. A work-up similar to that described above gave 1.58 g of residue. Gas chromatography showed one peak with a retention time of 5 min, and one broad peak with a retention time of 18 min.

Separation by chromatography on neutral alumina gave 1-isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**), corresponding to peak one. The fraction eluted with pentane–ether (9:1), corresponding to peak two, was a mixture of **9**, **10**, and **11** in the ratio of 2.2:3.4:1 (pmr).

Treatment of 7 with Sodium Acetate in Acetic Acid at 10°. Another reaction using the same amount of reagents as stated in the preceding experiment was carried out at a temperature of 10°. After a similar work-up, the crude material obtained showed two peaks on gas chromatography as well as absence of resonances at δ 3.92 and 6.16 in the pmr spectrum of the second fraction after chromatography. The second fraction contained **9** and **10** in the ratio of 1:1.75. None of the monocyclic acetate **11** was detected either by gas chromatography or pmr spectroscopy.

Tricyclic Alcohol (14 and 15). *cis*- (or *trans*-) Umbellulol (**6** or **5**) (3.5 g, 0.023 mol) and methylene iodide (7.7 g, 0.029 mol) were added dropwise to zinc–copper couple[18] (2.9 g) in ether containing methylene iodide (2.8 g) at 36°. The reaction mixture was stirred at reflux for 30 hr and cooled and saturated ammonium chloride was added. The ether was separated from the inorganic salts, and the salts were washed with ether. The combined ether extracts were washed with ammonium chloride, sodium bicarbonate, and sodium chloride solutions and dried and the ether was removed. Purification by column chromatography gave tricyclic alcohol: *cis*-**14** (1.34 g, 35%) bp 138–139° (7 mm); ir (neat) 2.98, 9.50, and 9.70 μ; pmr (CCl_4) δ 4.50 (d, 1, J = 7.0 Hz), 1.25 (s, 3), 0.28–1.5 (complex, 14); *trans*-**15** (1.27 g, 33%) bp 123–124° (10 mm); ir (neat) 2.94, 9.50, and 9.70 μ; pmr (CCl_4) δ 4.58 (d, 1, J = 7.0 Hz), 1.28 (s, 3), 0.20–1.30 (complex, 14).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: **14**, C, 79.30; H, 11.06. **15**, C, 79.72; H, 11.11.

Tricyclic Ketone (16 and 17). To chromium trioxide–pyridine complex prepared from chromium trioxide (2.01 g, 0.02 mol) and pyridine (18 ml) was added tricyclic alcohol (**14** or **15**) (1.34 g, 0.008 mol) in pyridine (12 ml) and the reaction mixture was stirred at room temperature overnight. Addition of water was followed by extraction with ether. The ether extract was washed with water, 3% hydrochloric acid, and sodium bicarbonate solution and dried and the ether was removed. The crude product was purified by column chromatography: **17**, 1.20 g, 91%; ir (neat) 5.85, 9.68, and 9.84 μ; pmr (CCl_4) δ 0.87 (d, 3, J = 7.0 Hz), 0.90 (d, 3, J = 7.0 Hz), 1.43 (s, 3); mass *m/e* 164; **16**, 1.08 g, 82%; ir (neat) 5.85, 9.68, and 9.84 μ; pmr (CCl_4) δ 0.81 (d, 3, J = 7.0 Hz), 0.93 (d, 3, J = 7.0 Hz), 1.27 (s, 3).

The pmr spectrum, gas chromatographic retention time, and tlc R_f value of **17** were identical with those of a ketone prepared from umbellulone by Eastman's procedure.[9]

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: **17**, C, 80.53; H, 9.91. **16**, C, 80.30; H, 9.79.

Acknowledgment. We thank Mr. L. Strausser of Beckman Instruments for the preliminary analysis of the cymene mixture (24 ft 5% Bentone-34 plus 5% OS-124 column at 110°).

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Bridged Polycyclic Compounds. LXXII. Salt Effects in Acetolysis of *syn*-7-Chlorobenzonorbornadiene[1]

Stanley J. Cristol, Allen L. Noreen, and Guenter W. Nachtigall

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received February 23, 1971*

Abstract: *syn*-7-Chlorobenzonorbornadiene (**1**-Cl) solvolyzes in acetic acid to **1**-OAc about 10^3 times as fast as its anti epimer **2**-Cl gives **2**-OAc. Acetolysis of **1**-Cl, but not of **2**-Cl, is accelerated dramatically by potassium acetate. Possible bimolecular mechanisms and salt effects are considered, but in view of results with lithium perchlorate, which is more effective at rate acceleration than is potassium acetate, bimolecular mechanisms are excluded. The results are interpreted as "special salt" effects.

It was recently reported[2] that acetolyses of *syn*- (**1**-Cl) and *anti*-7-chlorobenzonorbornadiene (**2**-Cl) proceed with retention of configuration. Acetolysis of **1**-Cl is faster than that of **2**-Cl by a factor of 10^3, not including accelerative effects of potassium acetate, and the rate of acetolysis of **1**-Cl, but not that of **2**-Cl,

(1) Paper LXXI: S. J. Cristol, J. K. Harrington, T. C. Morrill, and B. E. Greenwald, *J. Org. Chem.*, **36**, 2773 (1971).

(2) S. J. Cristol and G. W. Nachtigall, *J. Amer. Chem. Soc.*, 90, 7132 (1968).

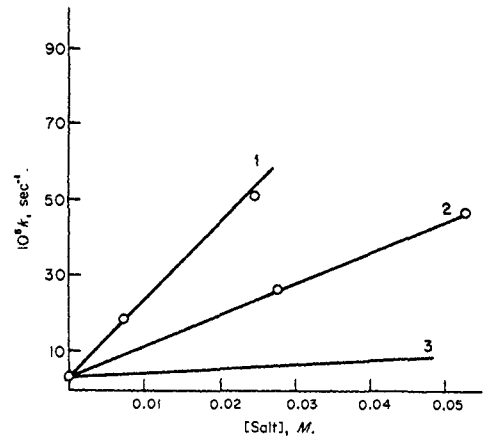
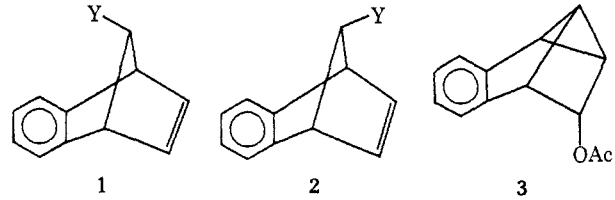


Figure 1. Salt effect curves: (1) curve observed for the acetolysis of **1**-Cl at 81.9° with $LiClO_4$ as the added salt; (2) curve observed for the acetolysis of **1**-Cl at 81.9° with KOAc as the added salt; (3) calculated normal salt effect curve with $b = 40$.

was accelerated substantially by potassium acetate. The rate enhancement could have several interpretations, and the herein described study was conducted to scrutinize this.



1 2 3

When **2**-Cl was acetolyzed, good first-order kinetics were observed, but first-order rate constants for acetolysis of 0.03 *M* **1**-Cl in glacial acetic acid containing 0.03 *M* potassium acetate fell off rapidly during the course of the reaction (see Table I). It seemed possible that this was the result of a common-ion rate depression,[3] and, indeed, when one-half of the initial acetate was replaced by the same concentration of chloride (Table I, run 3), the intitial instantaneous rate constant was approximately that of the standard reaction (run 2) after 50% reaction, and was depressed further as the reaction progressed. However, the observed decrease in rate could also be attributed to the decrease in acetate concentration, and this latter hypothesis was verified. Thus addition of 0.014 *M* tetramethylammonium chloride (TMAC) to a standard run (run 4 *vs.* run 2) had little effect on the rate constant, while doubling the concentration of potassium acetate (run 5) almost doubled the initial rate constant.

Table I. Instantaneous Rate Constants for the Acetolysis of 7-Chlorobenzonorbornadienes in Acetic Acid at 81.9°

Run No.	Compd	M^a	Salt	M^a	k_{inst}, sec^{-1}	% reaction
1	**2**-Cl	0.0277	KOAc	0.0277	3.1×10^{-6}	11[b]
2	**1**-Cl	0.0277	KOAc	0.0277	2.5×10^{-4}	0
					1.1×10^{-4}	50
					0.72×10^{-4}	75
3	**1**-Cl	0.0277	KOAc	0.0139	1.3×10^{-4}	0[c]
			TMAC[d]	0.0139	0.93×10^{-4}	20
					0.58×10^{-4}	40
4	**1**-Cl	0.0275	KOAc	0.0275	2.7×10^{-4}	0[c]
			TMAC	0.0139	1.9×10^{-4}	20
					1.1×10^{-4}	50
5	**1**-Cl	0.0280	KOAc	0.0560	4.8×10^{-4}	0[c]
					2.7×10^{-4}	50
					2.1×10^{-4}	75
6	**1**-Cl	0.0277	None[e]		0.3×10^{-4}	0[c]

[a] Initial molarity at room temperature. [b] Determined by vpc. [c] Extrapolated to 0% reaction. [d] TMAC = tetramethylammonium chloride. [e] Standard potassium acetate added to aliquots prior to titration.

In the absence of added base, **1**-Cl and **1**-OAc reach equilibrium ($K = 0.025$ mol/l.). The rate constant for acetolysis in the absence of potassium acetate was determined from an appropriate rate plot (run 6).

The data in Table I for runs 6, 2, and 5 are plotted in curve 2 of Figure 1 and fit a kinetic expression with a component first order in [**1**-Cl] and zero order in [KOAc], and one first order in [**1**-Cl] and first order in [KOAc]. Normal salt effects[4] follow the relationship

$$k_t = k_t^0[1 + b(\text{salt})] \quad (1)$$

where k_t is the observed "first-order" constant, k_t^0 is the constant at zero salt concentration, and b a constant for a given substrate, salt, and solvent medium. These are not readily distinguishable from superimposed bimolecular plus unimolecular reactions following eq 2,

$$k' = k_1 + k_2(\text{salt}) \quad (2)$$

if one assumes that the bimolecular reaction involves potassium acetate ion pairs rather than free ions. While the overall retention of configuration noted in the conversion of **1**-Cl to **1**-OAc (and *vice versa*) seemed incompatible with a bimolecular displacement reaction, the value of b of 250 calculated from curve 2 of Figure 1 was well outside the range of typical b values (0–40) reported by Winstein and his coworkers for salts in acetic acid.[5]

An alternate possibility for a bimolecular process involved participation of KOAc in a homo-SN2′ reaction with **1**-Cl to give **3** directly, which under the conditions of the solvolysis might be anticipated[6,7] to rearrange rapidly to **1**-OAc. If a bimolecular process indeed obtained, substitution of acetate by the weakly nucleophilic ion perchlorate would be predicted to decrease the homo-SN2′ process, and the rate might be anticipated to be about the same as in the absence of added salt. In fact, however, at comparable concentrations, lithium perchlorate was about twice as effective at rate acceleration as potassium acetate (see Figure 1).

The results then would seem to be best considered in terms of salt effects rather than in terms of a bimolecular displacement process.

There are two types of salt effects to consider: a normal salt effect[4] and a special salt effect.[5] As mentioned earlier, typical b values for normal salt effects

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(4) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 167.

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(6) A. Diaz, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, 88, 3133 (1966).

(7) G. W. Nachtigall, Ph.D. Thesis, University of Colorado, 1968.

Table II. Rate Constants for Acetolysis of 1-Cl as a Function of Lithium Perchlorate Concentration in Acetic Acid

Run no.	[1-Cl], M	Temp, °C	[$LiClO_4$], 10^4 M	10^5 k, sec^{-1}	No. of points	Correlation coeff
1	0.0277	81.5	0.125	3.0 ± 0.2[a]	5	0.987
2	0.0277	81.5	1.25	3.0 ± 0.1	6	0.995
3	0.0277	81.5	12.5	5.6 ± 0.2	6	0.998
4	0.0277	81.5	75.0	19.0 ± 0.8	5	0.997
5	0.0277	81.5	250	52.0 ± 1	5	0.999
				10^7 k, sec^{-1}		
6	0.0277	51.8	0.125	8.5 ± 0.8	5	1.000
7	0.0277	51.8	1.25	10.2 ± 0.3	6	0.999
8	0.20	51.8	10	22 ± 1	3	
9	0.20	51.8	10[c]	10.0 ± 0.5	3	
10	0.0277	51.8	12.5	25 ± 1	5	0.989
11	0.0277	51.8	250	230 ± 20[b]	5	0.988
12	0.0277	51.8	500	398 ± 8[b]	5	0.999
13	0.0277	51.8	1000	600 ± 30	5	0.989

[a] Error is determined as the standard deviation of the slope. [b] Verified by pmr technique. [c] This sample also contained 0.010 M LiCl.

in acetolysis fall in the range of 0–40, with lithium perchlorate giving the largest b values. The data for the acetolysis of 1-Cl using $LiClO_4$ as the added salt would require a b value of 700 (see curve 1 of Figure 1). The possibility of a special salt effect was then examined. Low concentrations of special salts cause abnormally large increases in overall acetolysis rate. This effect is observed with relatively stable ions[5] so one might anticipate that 1-Cl would show this effect and 2-Cl would not. The mechanism of the special salt effect[5e] has been interpreted as involving the prevention of ion-pair return from the solvent-separated ion-pair state ($R^+||X^-$ in Scheme I). Added salt M^+Y^- in-

Scheme I

$$R{-}X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+X^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R^+||X^- \xrightarrow{k_3} \text{products}$$

$$M^+||Y^- \rightleftharpoons M^+||X^-$$

$$R^+||Y^- \xrightarrow{k_4} \text{products}$$

teracts with the original solvent-separated ion-pair to form a new solvent-separated pair ($R^+||Y^-$) which goes on to products. This explanation would be particularly attractive in the present case since MY is KOAc and the salt would be depleted as the reaction proceeded. Thus the observed diminishing rate would be predicted. In addition, potassium acetate is replaced by potassium chloride as the reaction proceeds and the rate could be further slowed by induced common-ion rate depression.[5d] In Scheme I, it is evident that if a common-ion salt M^+X^- is present, the original solvent-separated ion-pair is regenerated, and the rate acceleration due to the special salt effect may be suppressed.

In a typical treatment of a special salt effect,[5] the observed first-order rate constants are plotted *vs.* salt concentration. The curve shows an initial steep rise characteristic of the special salt effect. The slope of the linear portion of the curve at higher salt concentration represents the normal salt effect. Extrapolation of the linear portion of the special salt curve gives k_{ext}^0, which is the rate constant including the special salt effect, but exclusive of the normal salt effect. In the cases reported by Winstein and his collaborators, the special effect has been realized at rather low salt concentrations (usually below 10^{-2} M) regardless of the salt employed.[5b,d] Winstein's data, available for comparison, are for *p*-bromobenzenesulfonates and *p*-toluenesulfonates, and acetolyses involving these leaving groups show values of k_{ext}^0/k_t^0 from 1 to 3.5.

Figure 1 shows the plot of the data for acetolysis of 1-Cl at 82° at various $LiClO_4$ and KOAc concentrations.

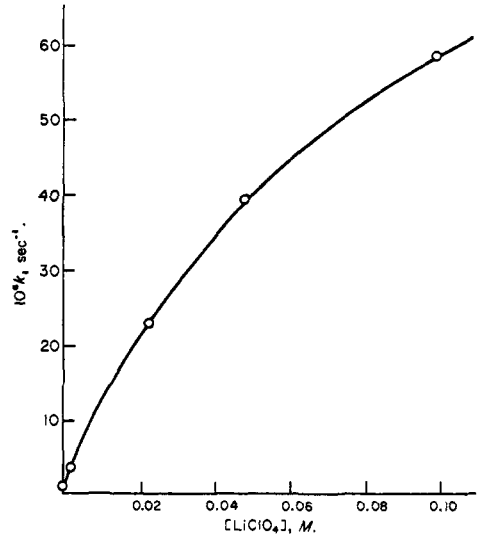

Figure 2. The effect of lithium perchlorate concentration on acetolysis rates of 1-Cl at 51.8°.

Clearly a special salt effect is not observed in its normal manifestation. A reasonable explanation for these results is that the termination of the initial steep rise of the special salt effect has not yet been realized.

The obvious test of this hypothesis was to plot points at higher lithium perchlorate concentrations, but this was impossible at 82°(the reaction was too fast). Thus, further study was made at 52°. The results are recorded in Table II and plotted in Figure 2. Curvature is now evident. Further rate study at increased concentration was not made owing to lack of reliability.[8] To verify this unusual special salt effect, tests for induced common-ion rate depression[5d] were made (runs 8 and 9, Table II). Thus the rate enhancement caused by 10^{-3} M $LiClO_4$ was almost completely suppressed by addition of 10^{-2} M LiCl.

(8) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 78, 2763 (1956).

Our inability to carry out experiments at higher salt concentrations beyond those plotted in Figure 2 keeps us from knowing whether or not we have observed the limit of the special salt effect. For this reason we are unable to determine k_{ext}^0 with any confidence. However, it seems clear that a value of k_{ext}^0/k_t^0 of about 50 is probably minimal, compared with values of 1–3.5 found for arenesulfonates.[5]

This appears unusual, but the following rationalization appears reasonable. Ion-pair return is known[5e,9] to be more important in halides than in arenesulfonates, when measured by a comparison of polarimetric (k_α) and titrimetric (k_t^0) rate constants in optically active systems. It seems reasonable that if ion-pair return (from tight ion pairs) is more effective with halides than with arenesulfonates, as measured by k_α/k_t^0, then this might be anticipated to be true also for ion-pair return from solvent-separated ion pairs, as measured by k_{ext}^0/k_t^0.

It is now apparent that the reactivity ratio for **1**-Cl *vs.* **2**-Cl for acetolysis of 10^3 reported earlier[2] must be increased by a factor of about 100 in order to get a correct measure of relative rates of formation of solvent-separated ion pairs and hopefully to get a more correct measure of relative ionization rates and of the relative stabilization of the isomeric carbonium ions which are formed in the solvolytic reactions.

Experimental Section

anti-7-Chlorobenzonorbornadiene (**2**-Cl) has previously been reported.[10] *syn*-7-Chlorobenzonorbornadiene (**1**-Cl) was obtained, as outlined previously,[2] from *exo*-5-acetoxy-*syn*-7-chlorobenzonorbornene (**4**).[10] A solution of 11.98 g (50.5 mmol) of **4** in a mixture of 70 ml of concentrated hydrochloric acid with 360 ml of methanol (reagent grade) was heated at reflux for 23 hr. Addition of 600 ml of H_2O and extraction with ether yielded 9.55 g (97%) of *syn*-7-chloro-*exo*-5-benzonorbornenol (**5**), white crystals, mp 113–114° after recrystallization from carbon tetrachloride.

Anal. Calcd for $C_{11}H_{11}OCl$: C, 67.87; H, 5.70. Found: C, 67.52; H, 5.72.

5 was converted to its *p*-bromobenzenesulfonate (**6**) by treatment with 1 equiv of *p*-bromobenzenesulfonyl chloride in a solution in dry pyridine (90 hr at room temperature). The product was isolated by addition of the solution to ice water and extraction with ether, affording, after recrystallization from *n*-heptane (to remove unreacted starting materials), yields of up to 72% of pure **6**, mp 123–124.5°.

Anal. Calcd for $C_{17}H_{14}O_3BrClS$: C, 49.35; H, 3.41. Found: C, 49.62; H, 3.39.

The conditions and procedure employed in the conversion of **6** to **1**-Cl were found to be critical. Best results were obtained when 167 ml of a 1.2 *M* solution of potassium *tert*-butoxide (MSA Corp.) (0.20 mol) in hexamethylphosphoramide (Aldrich; purified by drying over CaH_2 and distillation at reduced pressure, using a center cut) was added dropwise over a period of 50 min to a solution of 41.4 g (0.10 mol) of **6** in 166 ml of hexamethylphosphoramide, which was being stirred under a nitrogen atmosphere and maintained at a temperature between 0 and 5° (ice bath). The mixture assumed a deep purple, ink-like appearance. The addition complete, the reaction mixture was stored in the tightly stoppered reaction flask at 0° for 12 hr. The black mixture was then poured into a separatory funnel already containing 1200 ml of 0.5 *N* hydrochloric acid (ice cold) and 400 ml of ether and shaken immediately. The dark brown ether extract was collected and combined with two additional (250- and 200-ml) extracts of the aqueous layer. The combined extracts were washed twice with ice-cold mixtures of 500 ml of water and 200 ml of 0.5 *N* hydrochloric acid, treated for 1.5 hr with 1 teaspoonful of activated charcoal (in the cold), dried over magnesium sulfate, and evaporated under reduced pressure, yielding a residue of 16.7 g (94%) of a yellow-brown crystalline mass of crude **1**-Cl. Purification by sublimation at 50° and 0.1 Torr yielded pure **1**-Cl, mp 59–59.5°.

Anal. Calcd for $C_{11}H_9Cl$: C, 74.79; H, 5.15. Found: C, 74.63; H, 5.21.

Kinetic Experiments. The usual sealed ampoule technique was employed. The rates of acetolysis of **1**-Cl and **2**-Cl were followed by titration for acetate ion.[11] The solvent was glacial acetic acid containing 1% of acetic anhydride. Standard lithium perchlorate was prepared (0.50 *M*) and diluted to appropriate concentrations.[8] For the runs in the absence of potassium acetate, 1 equiv of standard potassium acetate (in solution) was added to the aliquots prior to titration. The rate of acetolysis of **1**-Cl was determined in the absence of potassium acetate from a rate plot indicative of approach of equilibrium. The equilibrium constant between **1**-Cl and **1**-OAc and hydrogen chloride was found to be 0.025 mol/l. and was identical when reached from either direction. With an initial **1**-Cl concentration of 0.026 *M*, the equilibrium mixture contained 40% **1**-Cl and 60% **1**-OAc. The first 30% of the reaction (per cent based on total conversion to **1**-OAc) was assumed to reflect only the forward reaction. This assumption was verified by calculating the forward rate from the exact equation[12] and the pertinent data at 30% reaction. The results were within the experimental error of the observed rate.

Pmr Analysis of Induced Common-Ion Rate Depression. The buffering effect of lithium chloride would not permit accurate titration so the reaction was followed by pmr. This method was also used at higher lithium perchlorate concentrations to verify the titration results. A solution in acetic acid 0.20 *M* in **1**-Cl and 10^{-3} *M* in $LiClO_4$ (total volume 0.5 ml) was prepared in an nmr tube. A second tube was prepared 0.01 *M* in LiCl, 10^{-3} *M* in $LiClO_4$, and 0.20 *M* in **1**-Cl. The tubes were immersed in a 52° bath and withdrawn at appropriate times for analysis. The C-7 protons in **1**-Cl and **1**-OAc are separated by 0.47 ppm (**1**-Cl τ 5.64 (t), **1**-OAc τ 5.17 (t)). The per cent reaction was determined by integration. Only the first 15% of the reaction was followed.

Acknowledgments. The authors are indebted to the National Science Foundation for support of this work. G. W. N. also wishes to acknowledge support by a Public Health Fellowship (1-F1-GM-33,790) from the National Institute of General Medical Sciences.

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