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KINETIC STUDIES AND IMPROVED REACTION CONDITIONS FOR THE HALOGEN SHIFT REARRANGEMENTS OF ARYLDIHALOPROPANOLS[1]

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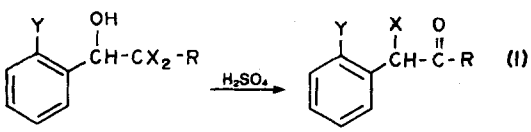
Abstract—Solvolytic data were obtained from the acid catalyzed trifluoroacetolysis of 1-(*o*-chlorophenyl)-2,2-dichloro-1-propyl trifluoroacetate (**1a**-TFA) and the analogous 2,2-dibromo trifluoroacetate **1b**-TFA which implicate a halonium ion intermediate in the rearrangement to an α-haloketone. Employing the conditions used to achieve kinetic control, substantial increases in yield were realized for those compounds which reacted too rapidly in and were unstable to concentrated sulfuric acid (i.e. **1b** and **1c**).

A preliminary publication[3] reported that 1-(*o*-chlorophenyl)-2,2-dichloro-1-propanol (**1a**) is smoothly converted to 1-(*o*-chlorophenyl)-1-chloro-2-propanone (**2a**) upon treatment with concentrated sulfuric acid (eqn 1).



(1)

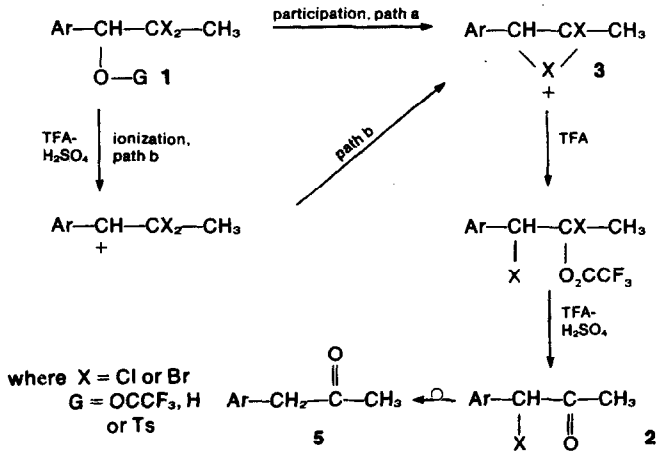
1a: Y = Cl, X = Cl, R = CH_3 **2a**: Y = Cl, X = Cl, R = CH_3
b: Y = Cl, X = Br, R = CH_3 **b**: Y = Cl, X = Br, R = CH_3
c: Y = CH_3, X = Cl, R = CH_3 **c**: Y = CH_3, X = Cl, R = CH_3

The reaction was found to be extremely facile while affording the α-chloroketone **2a** in excellent yield; 74% isolated and 90% by GLC analysis.

Following this discovery, an extensive investigation[4] was made into the scope and limitations of this novel rearrangement. A number of substituted 2,2-dihaloethanols were prepared and subjected to variations in reaction conditions. Optimum results for rearrangement were obtained for 1-aryl-2-methyl-2,2-dihaloethanols in cold concentrated sulfuric acid affording the α-haloketones **2** in generally rather good yields (*ca.* 60–90%). However, several compounds with Me side chains rearranged with less than expected yields. For example, while **2a** could be isolated in better than 74% yield, the corresponding α-bromoketone **2b** could be obtained in only 15% yield. Similarly, **1c** afforded **2c** in only 20% yield. These low yields represented a major problem for the use of this rearrangement as a general method for ketone transposition (conversion **1** → **5**).

Following this study, we were prompted to further delineate the mechanism of this rearrangement process.[5] Solvolytic data were obtained from the acid catalyzed trifluoroacetolysis of the *p*-toluenesulfonate and *p*-bromobenzenesulfonate of **1a** and was advanced as evidence for the formation of the α-chloroketone **2a** by rate determining C–O bond cleavage. Accordingly, the chloroepoxide, geminal-dihalide, and alcohol were eliminated as possible intermediates in the rearrangement process. Based on these considerations, as well as others, a mechanism for 1,2-halogen shift involving a halonium ion intermediate was adduced which was in best accord with our data. However, it was not shown whether halogen participation occurred in the rate determining step (path a) or in a product forming step which follows the initial heterolysis (path b).

We wish to report, herein, evidence for halogen participation during the solvolysis of 1-(*o*-chlorophenyl)-2,2-dichloro-1-propyl trifluoroacetate (**1a**-TFA) and the



Scheme 1.

analogous 2,2-dibromo trifluoroacetate **1b**-TFA in TFA-H_2SO_4. We have extended the study to include determinations of reaction rates of 1-(*o*-methylphenyl)-2,2-dichloro-1-propyl trifluoroacetate (**1c**-TFA) and additional 1,2-halogen shift reactions. The results reported here uphold the evidence in our previous studies and further implicate the existence of a halonium ion intermediate during rearrangement. Making use of the conditions employed to achieve kinetic control, we were able to increase substantially the yields of some α-haloketones. By doing so the use of this rearrangement becomes more attractive for synthetic purposes.

DESCRIPTION AND RESULTS

For mechanistic studies it was highly desirable to find a leaving group suitable for rate determinations. Anticipating that halogen participation was extremely possible in the rearrangement process and knowing the tremendous rate enhancement afforded by our solvent system,[5] we first chose to study the reaction rates of 1-(*o*-chlorophenyl)-2,2-dichloro-1-propyl *p*-toluenesulfonate and trifluoroacetate. Both compounds were prepared subsequently and subjected to acid catalyzed solvolysis at 57° in trifluoroacetic acid containing concentrated sulfuric acid (see footnote, Table 1, for concentrations). Kinetic studies for these and all other compounds were carried out conveniently by following the course of reaction with proton magnetic resonance spectroscopy. Rate constants were determined as the negative slope of plots of $\ln(1-A_p/A_t)$ versus time, where A_p and A_t are areas of NMR Me-singlets of the product and the total area (product plus reactant). Excellent first-order plots were obtained for all compounds up to 2–4 half-lives. Solvolysis products were identified by comparison of their NMR spectra with those of authentic materials previously prepared. The tosylate/trifluoroacetate rate ratio, determined by this technique, was calculated to be 46. Thus, the trifluoroacetate leaving group was chosen for our studies since kinetic control could be more easily achieved for the reasons cited above. Surprisingly, this appears to be the first reported rate comparison of these groups. The rate constants are recorded in Table 1.

With conditions at hand suitable for measurement of 1,2-halogen participation, 2,2-dichloro- and 2,2-dibromo-1-(*o*-chlorophenyl)-1-propyl trifluoroacetates were prepared and their rates of reaction measured. We noted that at 57° the 2,2-dichloro trifluoroacetate **1a**-TFA solvolyzed with an approximate half-life of 690 min while the 2,2-dibromo trifluoroacetate **1b**-TFA displayed a 48 min half-life. At the higher temperature of 67°, the half-lives of **1a**-TFA and **1b**-TFA were 276 min and 23 min, respectively. All kinetic runs afforded easily interpretable spectra with little decomposition evident.

A comparison was then made of the rate effect of an electron-donating *ortho*-Me substituent with the electron-withdrawing properties of the *ortho*-Cl. By doing so we hoped to arrive at a reasonable explanation for the low yield of α-chloroketone **2c** when **1c** was treated with concentrated sulfuric acid. 2,2-Dichloro-1-(*o*-methylphenyl)-1-propyl trifluoroacetate (**1c**-TFA) proved to solvolyze very rapidly with an approximate half-life of 8–9 min at 67°. A summary of the rate data is presented in Table 1.

Seizing upon the opportunity to utilize our solvolysis conditions in a synthetic capacity, we next reacted preparative amounts of **1b**-TFA and **1c**-TFA in trifluoroacetic acid-sulfuric acid and closely monitored the reaction progress by NMR. By this method, yields of 60% and 55% for the α-haloketones **2b** and **2c**, respectively, were realized. These yields represented a 3–4 fold improvement over the use of concentrated sulfuric acid with unesterified starting materials. Furthermore, less discoloration and decomposition during reaction were evident, leading to a highly pure product.

DISCUSSION

Among the methods used in appropriate systems to detect neighboring group participation, rearrangement[6,7]

Table 1. Rates of solvolysis in TFA-H_2SO_4*

	10^5k, 57°, sec^{-1}	Concentration, mole l^{-1}
1a-OTs	8.3	0.14
1a-TFA	0.18	0.14
1b-TFA	2.3	0.13
	10^5k, 67°, sec^{-1}	Concentration, mole l^{-1}
1a-TFA	4.8	0.19
1b-TFA	80.0	0.15
1c-TFA	123.0	0.13

*1.167 g 96–98% H_2SO_4 diluted to a total volume of 25 ml with CF_3CO_2H; concentration of H_2SO_4 = 0.46 molar

and rate acceleration studies[7,8] have been very informative. For example, in a classic paper Winstein and coworkers[8a] invoked halogen participation and the concomitant 3-membered-ring halonium ion to explain the rates of solvolysis of *cis*- and *trans*-2-halocyclohexyl esters. This investigation; as well as others,[8,9] demonstrated that the relative participation tendency for bromine is much greater than that of chlorine. Furthermore, the reaction would have been retarded by the inductive effect of halogen if halogen participation had not contributed to the overall rate enhancement. Amplifying this point, rate decelerations by factors of ~10,000 have been determined[10] for *cis*-2-halocyclohexyl brosylates since only inductive halogen destabilization is operational and geometry precludes halogen participation. Additionally, Peterson *et al.*[9] have shown that a weakly nucleophilic solvent constitutes the most favorable medium for the observation of halogen participation.[11]

Turning to an examination of the rate data in Table 1 it is gratifying to note that our solvolysis of trifluoroacetates exhibit marked rate accelerations owing to halogen participation when Br-containing compounds are compared with the analogous Cl-compounds. Although the 10–16 fold effect[12] is less than that found in the *trans*-2-halocyclohexyl sulfonate solvolysis, halogen participation in the rate determining step appears to be the best explanation for the effect of replacing Cl by Br. Accordingly, this mechanistic pathway (path a, Scheme 1) seems preferable to the alternative one involving ionization and subsequent halogen shift (path b, Scheme 1).

A rate comparison of 1-(*o*-methylphenyl)-2,2-dichloro-1-propl trifluoroacetate (**1c**-TFA) with the corresponding *o*-chlorophenyl ester **1a**-TFA revealed two things. First, as expected, the electron-donating methyl substituent stabilized the partial positive charge on the C atom bearing the leaving group during the transition state of the rate-determining step relative to the *ortho*-Cl substituent. As a result of this added stabilization, the rate of solvolysis increased. A 25–32 fold rate enhancement was noted when **1c**-TFA solvolysis was compared to that of **1a**-TFA. Such data suggested, secondly, that when the unesterified compound **1c** is treated with concentrated sulfuric acid kinetic control of the reaction is lost completely. Consequently, product is exposed to large amounts of concentrated acid for unnecessary time periods resulting in considerable decomposition and proportionally lower yields. This argument can also be applied to the dibromo compounds **1b** and **1b**-TFA. Accordingly, when the solvolyses of **1b**-TFA and **1c**-TFA were carried out on synthetically useful amounts of material in TFA-H_2SO_4(0.46 M) at 65–70°C under carefully monitored conditions, 3–4 fold improvements of yields were obtained. These results seem to uphold the promise shown in the kinetic studies.

In view of the evidence implicating a halonium ion during solvolysis, the most obvious precursor of the α-haloketone appears to be a halotrifluoroacetate **4**. Attack by trifluoroacetic acid on the halonium ion would serve as a direct precursor for the rearrangement product. Yet, during the course of our NMR kinetic studies no evidence could be found which would support such a structure. It is likely, however, that the α-haloketone is not distinguished from the halotrifluoroacetate **4** by proton NMR, since Peterson *et al.*[13,14] have found that the chlorotrifluoroacetate derived from 2-chloropropene is indistinguishable from acetone by ^1H NMR in trifluoroacetic acid.

EXPERIMENTAL

M.ps were obtained with a Thomas–Hoover apparatus. Distillations were performed on a Büchi/Brinkman Kugelrohrofen micro-distillation oven or with a short-path distillation apparatus and b.ps were uncorrected. The NMR spectra were recorded on a Hitachi Perkin–Elmer R20-B spectrometer in $CDCl_3$ with TMS as an internal standard or in trifluoroacetic acid soln with a capillary of TMS. IR spectra were determined on a Perkin–Elmer model 457 spectrophotometer. Microanalyses were performed by Galbriath Laboratories, Knoxville, Tenn.[17]

Preparation of 1-aryl-2,2-dihalo-1-propanols

General procedure. The reaction sequence used for the preparation of 1-(*o*-chlorophenyl)-2,2-dibromo-1-propanol and its derivatives was that employed for synthesis of the other analogues.

A soln of EtI (296 g, 1.9 mol) in anhyd ether (500 ml) and dry benezene (50 ml) was added dropwise to a mixture of Mg (48.6 g, 2.0 mol), dry ether (50 ml) and a crystal of I_2. The addition was carried out as to maintain reflux and took 30–45 min. After the soln was added, the mixture was refluxed for 30 min and cooled to room temp. A soln of *o*-chlorobenzonitrile (131 g, 0.95 mol) in dry benzene (500 ml) was added dropwise over a period of 30 min. After the addition, dry benzene (100 ml) was added and the mixture was refluxed for 6 hr and then stirred at room temp. over night. The reaction flask was cooled in an ice bath while 10% H_2SO_4aq (250 ml) was added dropwise. The aqueous layer was extracted once with benzene (100 ml) and the combined organic layers washed with dil. H_2SO_4aq, water, dil. $NaHCO_3$aq and water before drying over Na_2SO_4. Evaporation of the solvent left a residue which was distilled to afford 1-(*o*-chlorophenyl)-1-propanone: 110 g (69%); b.p. 82–87° (1.5 mm); lit.[15] b.p. 85° (4.0 mm); IR (film) 2990, 2950, 1700, 1590, 1470, 1430, 1350, 1215, 1060, 950, 735 cm^{-1}; NMR ($CDCl_3$) δ 7.36 (m, 4, ArH), 2.97 (q, 2, CH_2), 1.22 (t, 3, CH_3).

At room temp., to a soln of 1-(*o*-chlorophenyl)-1-propanone (50.6 g, 0.3 mol) in CCl_4 (300 ml) was added a soln of Br_2 (96 g, 0.6 mol) in CCl_4 (100 ml) with stirring. The Br_2 was initially taken up rapidly but the red color persisted after about half of the addition. The soln was stirred for 48 hr. The mixture was washed with water, dil. $NaHCO_3$aq, dil. $NaHSO_3$aq and water before drying over Na_2SO_4. (Note: This compound is a powerful lachrymator and must be handled with care!) Concentration and distillation gave 1-(*o*-chlorophenyl)-2,2-dibromo-1-propanone as a light yellow liquid: 64 g (65%); b.p. 115–118°C (0.6 nm); NMR (CCl_4) δ 7.25 (m, 4, ArH), 2.60 (s, 3, CH_3).

At −20°, $NaBH_4$ (7.6 g, 0.2 mol) was added portionwise to a stirred soln of 1-(*o*-chlorophenyl)-2,2-dibromo-1-propanone (63.5 g, 0.195 mol) in MeOH (300 ml). The addition took 30 min and stirring was continued for 1.5 hr. The mixture was poured into NH_4Claq (10%, 1.5 l.) at 0° and extracted into CH_2Cl_2. The combined extracts were washed with water and sat. NaCl aq before drying over $NaSO_4$. The residue,[16] after evaporation of the solvent, was fractionally distilled to give **1b** as a colorless oil: 10 g (16%); b.p. 116–123° (0.3 mm); IR (film) 3460, 3080, 2990, 2940, 1600, 1580, 1480, 1440, 1380, 1060, 1030, 755 cm^{-1}; NMR ($CDCl_3$) δ 7.30 (m, 4, ArH), 5.50 (s, 1, CH), 3.20 (s, 3, CH_3), 2.46 (s, 3, CH_3).

To a soln of **1b** (7.9 g, 24 mmol) in anhyd ether (50 ml) was added trifluoroacetic anhydride (10 ml) in ether (10 ml). The soln stirred at room temp. for 18 hr and then cooled to 0°. Ice water (100 ml) was added dropwise and the aqueous layer separated. The ethereal layer was washed with water, dil. $NaHCO_3$aq and water before drying over Na_2SO_4. Evaporation afforded **1b**-TFA as a colorless heat sensitive liquid: 10 g (99%); IR (film) 2980, 1800, 1605, 1445, 1380, 1350, 1230, 1150, 1070, 760 cm^{-1};NMR (TFA-H_2SO_4) δ 7.30 (m, 4, ArH), 6.83 (s, 1, CH), 2.47 (s, 3, CH_3).

A soln of **1b** (0.5 g, 1.5 mmol) in Ac_2O (5 ml) containing a crystal of *p*-toluenesulfonic acid was refluxed for 2 hr. Stirring at room temp. was continued over night before the mixture was

poured into ice water (25 ml) and extracted with CH_2Cl_2. The extracts were dried over Na_2SO_4 and concentrated *in vacuo* to leave a white residue. Recrystallization from hexane afforded the acetate of **1b** as colorless crystals: 0.3 g (54%); m.p. 104–105°; IR ($CHCl_3$) 2960, 1750, 1600, 1440, 1380, 1065, 1035, 610, 575 cm^{-1}; NMR ($CDCl_3$) δ 7.32 (m, 4, ArH), 6.60 (s, 1, CH), 2.46 (s, 3, CH_3), 2.13 (s, 3, CH_3). (Found: C, 35.75; H, 2.84 Calc. for $C_{11}H_{11}O_2ClBr_2$: C, 35.66; H, 2.99%).

A soln of **1b** (0.5 g, 1.5 mmol) and *p*-toluenesulfonyl chloride (0.72 g, 3.7 mmol) in pyridine (25 ml) was stirred for 5 days at room temp. Work-up in the usual manner gave **1b**-OTs as colorless crystals: 0.4 g (22%); m.p. 86–87° (hexane); NMR (TFA) δ 7.3 (m, 4, ArH), 6.23 (s, 1, CH), 2.4 (s, 3, $ArCH_3$), 2.4 (s, 3, CH_3).

1-(o-*Chlorophenyl*)-2,2-*dichloro*-1-*propanone*.[3] b.p. 58–50° (0.75 mm); NMR ($CDCl_3$) δ 7.50 (m, 4, ArH), 2.33 (s, 3, CH_3).

1-(-o-*Chlorophenyl*)-2,2-*dichloro*-1-*propanol*.[3] b.p. 79–81° (0.2 mm); mp 68–69° (hexane-carbon tetrachloride); NMR ($CDCl_3$) δ 7.55 (m, 4, ArH), 5.66 (d, 1, CH), 3.13 (d, 1, OH), 2.13 (s, 3, CH_3).

1-(o-*Chlorophenyl*)-2,2-*dichloro*-1-*propyl trifluoroacetate*. b.p. 85–90° (0.1 mm) dec; NMR (TFA-H_2SO_4) δ 7.2 (m, 4, ArH), 6.89 (s, 1, CG), 2.12 (s, 3, CH_3).

1-(o-*Methylphenyl*)-1-*propanone*. b.p. 56–58° (0.25 mm); NMR ($CDCl_3$) δ 7.20 (m, 4, ArH), 2.82 (q, 2, CH_2) 2.42 (s, 3, CH_3), 1.14 (t, 3, CH_3).

1-(o-*Methylphenyl*)-2,2-*dichloro*-1-*propanone*. b.p. 67–69° (0.04 mm); NMR ($CDCl_3$) δ 7.13 (m, 4, ArH), 2.28 (s, 3, CH_3), 2.22 (s, 3, CH_3).

1-(o-*Methylphenyl*)-2,2-*dichloro*-1-*propanol*. b.p. 87–89° (0.2 mm); NMR ($CDCl_3$) δ 7.20 (m, 4, ArH), 5.16 (s, 1, CH), 3.42(s, 1, OH), 2.30 (s, 3, $ArCH_3$), 1.97 (s, 3, CH_3).

1-(o-*Methylphenyl*)-2,2-*dichloro*-1-*propyl trifluoroacetate*. Liquid unstable to heat; NMR (TFA-H_2SO_4) δ 7.20 (m, 4, ArH), 6.55 (s, 1, CH), 2.51 (s, 3, $ArCH_3$) 2.03 (s, 3, CH_3).

1-(o-*Methylphenyl*)-2,2-*dichloro*-1-*propyl acetate*. m.p. 74–76° (hexane); NMR ($CDCl_3$) δ 7.40 (m, 4, ArH), 6.38 (s, 1, CH), 2.52 (s, 3, CH_3), 2.10 (s, 3, CH_3), 2.08 (s, 3, CH_3). (Found: C, 55.24; H, 5.40. Calc. for $C_{12}H_{14}Cl_2O_2$: C, 55.19; H, 5.40%).

Rearrangement of dihalopropanols—General procedure

1-(o-*Chlorophenyl*)-1-*bromo*-2-*propanone* (**2b**). To a stirred soln of **1b**-TFA (4.0 g, 9.4 mmol) was added H_2SO_4 (1.167 g, 98%) in trifluoroacetic acid (25 ml) heated to 65–70° in a water-bath. The soln turned cloudy and then dark colored. The reaction, monitored by NMR spectroscopy, was allowed to proceed exactly 1 hr. It was then poured into ice water and extracted into CH_2Cl_2. The combined extracts were washed with water and $NaHCO_3$aq before drying over Na_2SO_4. The mixture was filtered and evaporated to give a residue which was vacuum distilled affording **2b** as a near colorless oil: 1.4 g (60%); IR ($CHCl_3$) 3007, 1732, 1598, 1578, 1473, 1449, 1362, 1149, 1055, 1040, 692, 578 cm^{-1}; NMR (TFA) δ 7.30 (m, 4, ArH), 6.00 (s, 1, CH), 2.41 (s, 3, CH_3); NMR ($CDCl_3$) δ 7.29 (m, 4, ArH), 5.93 (s, 1, CH), 2.30 (s, 3, CH_3).

1-(o-*Methylphenyl*)-1-*chloro*-2-*propanone* (**2c**). b.p. 110–115° (0.25 mm); IR (film) 3030, 1735, 1495, 1465, 1360, 1160, 750 cm^{-1}; NMR (TFA-H_2SO_4) δ 7.30 (m, 4, ArH), 5.70 (s, 1, CH), 2.35 (s, 3, CH_3), 2.28 (s, 3, CH_3); NMR ($CDCl_3$) δ 7.20 (m, 4, ArH), 5.53 (s, 1, CH), 2.37 (s, 3, $ArCH_3$), 2.17 (s, 3, CH_3).

Kinetic procedures. Reactions rates were followed by NMR spectroscopy. Solutions (0.13–0.19 M) were prepared using a single batch of trifluoroacetic acid–sulfuric acid. Rate determinations were based on relative peak heights which were free from contributions of the tail of the adjacent peak or areas of the Me-singlets. First-order rate constants were determined as the negative slope of plots of $\ln(1 - A_p/A_t)$ versus time. Here A_p and A_t are areas of NMR peaks of the product and the total area (product plus reactant). Excellent first-order rate plots were obtained to 75–90% reaction and are comparable in quality to that of earlier methods. Products were identified by comparison of their NMR spectra with those of authentic materials previously isolated.[4,5] A list of chemical shift values for all compounds is presented in Table 2.

Acknowledgement—We wish to thank Prof. Paul E. Peterson for informing us of his results and for helpful discussions of this problem.

Table 2. Chemical shifts of aryldihalopropanols and derivatives

Compound	δ, CH*	δ, CH_3*
1a	5.91	2.09
1a-TFA	6.89	2.12
1a-OTs	6.31	2.04, 2.33
2a	6.01	2.38
1b	5.78	2.44
1b-TFA	6.83	2.47
2b	6.00	2.41
1c	5.55	2.03, 2.42
1c-TFA	6.54	2.12, 2.51
2c	5.70	2.28, 2.35

*Determined in a TFA-H_2SO_4 solution relative to a capillary of tetramethylsilane.

REFERENCES

[1]Presented, in part, at the 7th *Northeast Regional Meeting of the American Chemical Society, Albany, New York*, Abstract No. 219 (Aug. 1976).

[2]Taken, in part, from a thesis by S. E. Burke and S. E. Thomas in partial fulfillment of the requirements for the Honors Program, University of Maine at Orono, Orono, ME 04473, U.S.A.

[3]B. L. Jensen and R. E. Counsell, *J. Org. Chem.* **38**, 835 (1973).

[4]B. L. Jensen, S. E. Burke, S. E. Thomas and W. H. Klausmeier, *Tetrahedron Letts* 2639 (1977).

[5]B. L. Jensen and P. E. Peterson, *J. Org. Chem.* **42**, 4052 (1977).

[6]J. M. Harris, *Progr. Phys. Org. Chem.* **11**, 90 (1974).

[7]P. E. Peterson, *Accts. Chem. Res.* **4**, 407 (1971).

[8a]S. Winstein, E. Grunwald and L. L. Ingraham, *J. Am. Chem. Soc.* **70**, 821 (1948); [b]E. Grunwald, *Ibid.* **73**, 5458 (1951); [c]B. Capon, *Quart. Rev., Chem. Soc.* **18**, 21 (1964); [d]For a reinterpretation of these original data, see Refs. 7, 10.

[9]P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard and R. J. Kamat, *J. Am. Chem. Soc.* **89**, 5902 (1967).

[10]A. Streitwieser, *Ibid.* **78**, 4935 (1956).

[11]It should be emphasized that the magnitude of the rate constant for any solvolysis is a composite of reactions involving participation, induction, solvent influence and the way the carbonium ion center is generated; see Ref. 9 for a discussion of these effects.

[12]The amount of rearrangement product isolated in our system is also dictated by the acidity (non-nucleophilicity) of the solvolysis medium. When trifluoroacetic acid is employed at 67°C little α-haloketone (*ca.* < 5%) is formed. However, in sulfuric acid rearrangement is complete with isolated yields of 60–74%.

[13]P. E. Peterson R. J. Bopp and M. A. Ajo, *J. Am. Chem. Soc.* **92**, 2834 (1970).

[14]P. E. Peterson, *J. Org. Chem.* **31**, 439 (1966).

[15]V. L. Szotyory and E. Hambrug, *J. Prakt. Chem.* **23**, 208 (1963).

[16]Reduction of this ketone results in a mixture (1:1) of **1b** and 1-(*o*-chlorophenyl)-2-bromo-1-propanol, b.p. 105–115° (0.5 mm).

[17]During the course of the investigation numerous unstable compounds were encountered. When such compounds were obtained they were converted to their solid acetate derivatives prior to microanalysis.