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Rates and Products of the Reaction of a β,β-Dichlorobenzylic Alcohol and Its Derivatives in CF_3CO_2H–H_2SO_4. A 1,2-Chlorine Shift Giving an α-Chloro Ketone

Bruce L. Jensen* and Paul E. Peterson*

Department of Chemistry, University of Maine, Orono, Maine 04473, and Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

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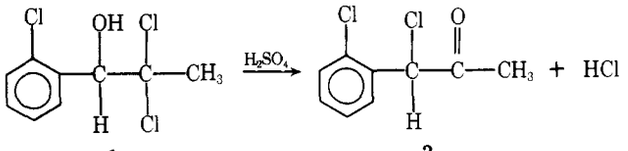
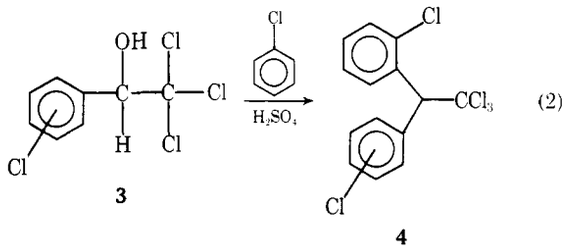
The *p*-toluenesulfonate and *p*-bromobenzenesulfonate of 1-(*o*-chlorophenyl)-2,2-dichloro-1-propanol (**1**) reacted at a conveniently measurable rate in 25 mL of CF_3CO_2H containing 1.127 g of 96% H_2SO_4. 1-(*o*-Chlorophenyl)-1-chloro-2-propanone and the trifluoroacetate of **1** were formed. The ketone, previously obtained from reaction of **1** in H_2SO_4, appears to be formed via a chloronium ion intermediate. The absence of rate effects of substituents in the leaving group is connected with acid catalysis.

Recently it was found[1] that the chlorine-containing alcohol **1** was converted exclusively to the α-chloro ketone **2** upon reaction with concentrated (96%) sulfuric acid. The formation



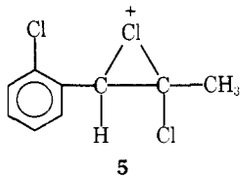
1 **2** (1)

of **2**, the apparent product of a 1,2-chlorine shift, was so facile that **1** formed no condensation product with chlorobenzene in the presence of H_2SO_4. Various alcohols related to **1** do undergo such condensation (e.g., that of eq 2) to give the



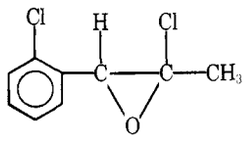
3 **4** (2)

pesticide DDT or related compounds.[2] Accordingly, we were prompted to further define the mechanism of the reaction of eq 1 and related processes. At the outset of our study, two main types of mechanism were considered. In one, mentioned previously,[1] the reaction of eq 1 is initiated by breaking the C–O bond, possibly with simultaneous chlorine participation to give a chloronium ion intermediate **5**. Another mechanism



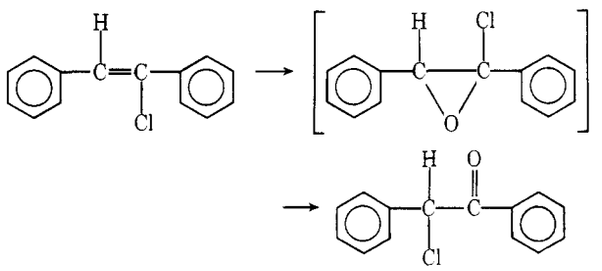
5

involves breaking of a C–Cl bond, presumably facilitated by electrophilic acid catalysis, with possible simultaneous hydroxyl participation to form a chloro epoxide intermediate, **6**. McDonald and co-workers have shown that chloro epoxides



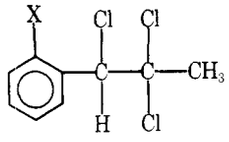
6

may rearrange with chlorine shift, to chloro ketones, probably via ketocarbonium ion intermediates.[3] The example[3a] of eq 3 is particularly relevant (cf. eq 1). The McDonald reaction typically occurs in neat liquid. Lewis acid catalysis may occur, but protonic acids tend to favor alternative reaction paths.[3b] Although the reaction of this paper occurs in protonic solvents, it appears that the McDonald mechanism should not be ruled out of consideration. A third type of mechanism for formation



(3)

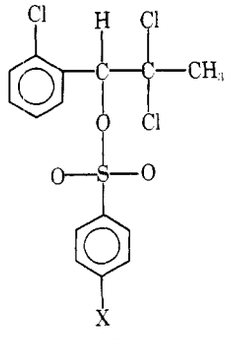
of **2** involves the intermediacy of chloride **7a**, formed in an intermolecular reaction from HCl evolved into the sulfuric acid solvent via side reactions or, after reaction has begun, via eq 1. Although reaction via **7** would involve no chlorine shift, hydrolysis of geminal halides is known to yield ketones. Furthermore, the reported isolation of **7b** from an experiment in H_2SO_4[1] suggested that the sequence involving **7** must be considered!



7
a, X = Cl
b, X = H

Description and Results

For mechanistic studies it was highly desirable to find conditions suitable for rate determinations. Presuming that a path involving initial C–O bond breaking was the most likely alternative, we elected to study the reactions of **8a**, the tosylate of **1**. Since trifluoroacetic acid was used by one of us as the



8
a, X = CH_3
b, X = Br

solvent in many previous studies of halogen participation in solvolysis,[4] we decided to add as much trifluoroacetic acid as possible to the sulfuric acid reaction medium. Encouragingly, in CF_3CO_2H–H_2SO_4 the tosylate **8a** gave ketone **2** and the trifluoroacetate ester of **1** in an approximate 1:1 ratio. Reaction occurred at a measurable rate at 35 °C in CF_3CO_2H containing 96% H_2SO_4 (see footnote, Table I, for concentrations). Hydrogen NMR at 90 MHz proved to be a sensitive, convenient method for following the course of reaction. With conditions suitable for kinetic studies at hand, we prepared the *p*-bromobenzenesulfonate of **1** and determined the reaction rates of both the tosylate and brosylate. Remarkably, the rates were almost identical, whereas we had expected to observe a substituent rate enhancement for the brosylate relative to the tosylate leaving group, $k_{Bs}/k_{Ts} = \sim 2$.[5] We obtained a similar result for the tosylate and brosylate of isopropyl alcohol. The rate constants, to be discussed later, are given in Table I. It was noted that in the absence of H_2SO_4 the tosylate and brosylate solvolyzed in trifluoroacetic acid at a higher temperature (65 °C) with approximate half-lives of 180 and 85 min, respectively. However, little ketone **2** was formed, and several unidentified NMR peaks appeared instead. Unpublished observations in the laboratory of one of the authors indicate that the addition of strong acids to CF_3CO_2H lowers its nucleophilicity. Evidently a low nucleophilicity is required to obtain the product whose formation was the object of the present study.

Since the alcohol **1** forms ketone **2** in 96% H_2SO_4, it seemed likely that alcohol **1** would exhibit a similar reaction in the mixture of CF_3CO_2H and H_2SO_4 used for tosylate solvolysis. Actually, a new compound, presumably the bisulfate of **1**, formed rapidly (22% after 10 min), along with the trifluoroacetate of **1** (5% after 10 min). After 5 h, the composition was trifluoroacetate (63%), bisulfate (8%), and ketone **2** (6%). The ketone may have been derived from trifluoroacetate, since mixtures of trifluoroacetate and ketone derived from tosylate solvolysis were gradually converted to ketone upon prolonged reaction at 65 °C (76% ketone after 7.5 h). One might suppose

Table I. Rates of Solvolysis in CF_3CO_2H–H_2SO_4[a]

	Registry no.	$10^4 k$, 35 °C, s^{-1}	Concn, mol L^{-1}
1-OTs	37610-59-6	1.9	0.125
1-OBs	63641-56-5	1.6	0.125
		$10^4 k$, 20 °C, s^{-1}	Concn, mol L^{-1}
i-PrOTs	2307-69-9	6.2	0.19
i-PrOBs	24767-70-2	6.4	0.14

[a] 1.127 g of 96% H_2SO_4 in 25 mL of CF_3CO_2H; molarity of H_2SO_4 = 0.446.

Table II. Rates of Trifluoroacetolysis of Tosylates, Brosylates, and a *p*-Nitrobenzenesulfonate

Compound	$10^5 k$, 25 °C, s^{-1}
Cyclohexyl brosylate	44.5[a]
Cyclohexyl tosylate	25.2[b]
Isopropyl nosylate	22[c]
Isopropyl brosylate	5.55 (est)[d]
Isopropyl tosylate	2.49[e]

[a] J. E. Duddey and P. E. Peterson, unpublished work. [b] D. M. Chevli and P. E. Peterson, unpublished work. [c] P. E. Peterson and J. F. Coffey, *J. Am. Chem. Soc.*, **93**, 5208 (1971). [d] Estimated using the Hammett equation, $\log k_x/k_y = \rho\Delta\sigma^n$. The σ^n value for *p*-NO_2 was incremented by 0.18 (to 0.96) to allow for the hydrogen-bonding effect of CF_3CO_2H. See P. E. Peterson, D. M. Chevli, and K. A. Sipp, *J. Org. Chem.*, **33**, 972 (1968) for further references. [e] P. E. Peterson, R. E. Kelley, and K. A. Sipp, *J. Am. Chem. Soc.*, **87**, 5169 (1965).

that a bisulfate intermediate would give a ratio of ketone to trifluoroacetate comparable to that obtained from the tosylate. That it did not may be due to the lower nucleophilicity of the solvent in the reaction of alcohol **1** owing to an acid–base reaction between the alcohol and sulfuric acid.

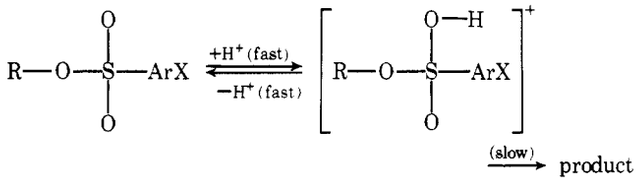
Discussion

The finding that the tosylate **8a** and brosylate **8b** yield 50% ketone **2** in CF_3CO_2H–H_2SO_4 and that reaction is faster than that of the presumed bisulfate or the alcohol provides further indication that neither the bisulfate or the epoxide **6** is an intermediate. The literature contains no indication that generation of a cationic center β to a tosyloxy group (e.g., in reactions of ditosylates) leads to epoxide intermediates. Under our conditions the chloride **7a** is also not an intermediate, since it was not observed by NMR, and a control experiment using 2-chloropentane showed that chlorides are, as expected, less reactive than tosylates of similar structure. Accordingly, the formation of ketone **2** from sulfonates **8a** and **8b** does seem to be initiated by breaking of the benzylic C–O bond. It may be argued that alcohol **1** may react in H_2SO_4 via an epoxide even if **8a** and **8b** in CF_3CO_2H–H_2SO_4 react by another mechanism. However, our study implies that a mechanism involving C–O bond breaking in alcohol **1** or its bisulfate should be readily accessible.

Initially, we expected the brosylate **8b** to react faster than the tosylate **8a**, based on other solvolytic data in the literature which suggested that the better leaving group (brosylate) would give evidence of rate determining C–O bond breaking by reacting faster.[5] Data gathered in part from unpublished results (Table II) show that trifluoroacetolyses do show a brosylate/tosylate rate ratio of 1.8 (for cyclohexyl) or 2.2 (estimated for isopropyl).

In sharp contrast, the results reported in Table I for the trifluoroacetolysis of isopropyl tosylate and brosylate (and for

Scheme I



8a and 8b) in CF_3CO_2H–H_2SO_4 show that the *sulfuric acid promoted* trifluoroacetolyses of our study are *insensitive to substituents in the leaving group.* It seems likely that substituted arylsulfonate is protonated in a rapid equilibrium prior to solvolysis (eq 1) (Scheme I). Opposing substituent effects in the two steps would explain the overall absence of substantial effects. A similar situation could occur if the intermediate is hydrogen bonded to H_2SO_4 instead of protonated. The situation is reminiscent of that which is found in acid-catalyzed ester hydrolyses,[6] in which substituent effects are small, presumably because of a comparable compensation of effects.

In retrospect, a decline in substituent effects as the solvent becomes more acidic (and presumably a stronger hydrogen-bonding solvent) is already evident from available brosylate/tosylate rate ratios. For the cyclohexyl compounds, the ratios are: acetolysis,[5] 3.5; formolysis,[5] 2.7; trifluoroacetolysis (Table II), 1.8.

The acid-catalyzed solvolysis of tosylates in pure sulfuric acid has received some study, particularly in Myhre's laboratory,[7] but the CF_3CO_2H–H_2SO_4 system used here is a promising alternative system for future work. It readily dissolves reactants, gives readily isolated trifluoroacetate or other products (ketone in the present instance), and is subject to control of acidity without addition of water through variation in the sulfuric acid concentration. At the concentration level of H_2SO_4 used here, the isopropyl tosylate rate at 35 °C is 27 times that found at 25 °C in the absence of H_2SO_4.

In the recent paper from Myhre's laboratory[7] it was found that the solvolysis of $CF_3CHOTsCH_3$ in H_2SO_4 occurs with probable cleavage at sulfur (and retention of configuration at the C–O bond). Since the effect of substituents in the leaving group is unknown for this new type of reaction, the possibility that our unusual substituent effects arise from this type of cleavage must be considered. However, in our system this cleavage should give alcohol 1, which reacts only slowly under the conditions used. The alcohol 1 (or its bisulfate) was not observed in our tosylate or brosylate solvolyses. Accordingly, our reaction is not initiated by reaction at sulfur.

Based on the considerations mentioned above, a mechanism for chlorine shift (for 8 and possibly for 1) involving the chloronium ion intermediate 5 is in the best accord with our observations. However, chlorine participation could occur in the rate-determining step (path a, Scheme II) or in a product-forming step which follows the initial heterolysis (path b, Scheme II).

Scheme II

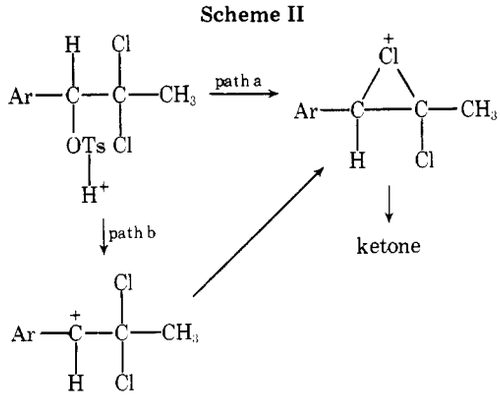


Table III. Chemical Shifts of Alcohol 1, Ketone 2, and Related Compounds

Functional group	Registry no.	δ, CH[a]	δ, CH_3[a]
OH (1)	35996-56-6	5.91	2.09
OTs		6.31	2.04, 2.33
OBs		6.28	2.08
OSO_3H	63641-57-6	6.48	2.13
O_2CCF_3	63641-58-7	6.89	2.12
Ketone (2)	37610-57-4	6.01	2.38

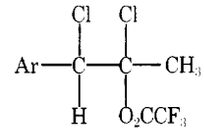
[a] Relative to a capillary of tetramethylsilane.

Neighboring group participation, including chlorine participation, has been detected by rate acceleration, compared to the expected rate for carbonium ion formation,[4,8] and by the net retention of configuration.[9] Accordingly, either path in Scheme II is compatible with our data, although we note that other halogen shifts in halotosylate solvolyses have invariably shown evidence for halogen participation in the rate-determining step.[4] An investigation into the halogen participation and steric course of this reaction is presently underway in our laboratories.[10]

The initial product of halogen shift in our system is presumably the chlorotrifluoroacetate. It is presumed that ionization of the chlorine on the potential ketone carbon occurs rapidly in CF_3CO_2H–H_2SO_4. Further transformations would afford ketone and trifluoroacetic anhydride.

Conclusion

By the use of the solvent CF_3CO_2H–H_2SO_4, the chlorine shift of alcohol 1 and its sulfonates has been brought under kinetic control. This solvent system has potential use for elucidation of the effect of structural modifications of structure 1, and for other studies of neighboring group participation.[10]



Experimental Section

Rate Determination. Products were identified by comparison of their 90-MHz NMR spectra with those of authentic materials previously prepared,[1] except for the presumed bisulfate of alcohol 1. The high signal to noise ratio of the Perkin-Elmer R-32 NMR instrument facilitated rate determinations based on relative peak heights or areas of the sharp singlets (Table III) of the side chain in 1, 2, and related compounds. The quality of rate plots was comparable to that of earlier methods. Since rates may be a sensitive function of the water content of the solvent, all rates in Table I were determined using a single batch of CF_3CO_2H–H_2SO_4. First-order rate constants were determined as the negative of the slope of plots of ln $(1 - A_p/A_t)$ vs. time. Here A_p and A_t are areas of NMR peaks of the product and the total area (products plus reactant), respectively. Areas of the CH_3 singlets were used in the calculation. In the case of isopropyl derivatives, peak heights of the best-separated peaks of the CH_3 doublets were used instead of areas, since the heights were free from contributions of the tail of the adjacent peak.

1-(*o*-Chlorophenyl)-1-tosyloxy-2,2-dichloropropane. The compound was prepared according to the procedure of Jensen and Counsell.[1]

1-(*o*-Chlorophenyl)-1-brosyloxy-2,2-dichloropropane. The compound was prepared from 1-(*o*-chlorophenyl)-2,2-dichloro-1-propanol (1.2 g) by reaction with *p*-bromobenzenesulfonyl chloride (1.9 g) in pyridine (35 mL) at 45 °C for 3 days. The pyridine solution was quenched in cold 6 N hydrochloric acid and extracted with ether. The combined extracts were washed with dilute hydrochloric acid and water before drying over magnesium sulfate. Recrystallization from

hexane afforded colorless crystals, mp 109–111 °C.

Anal. Calcd for $C_{15}H_{12}BrCl_3O_3S$: C, 39.28; H, 2.63. Found: C, 39.20; H, 2.80.

Isopropyl Tosylate. The compound was prepared as previously described.[11]

Isopropyl Brosylate. The compound was prepared by the usual method.[12]

Acknowledgments. We thank the Summer Faculty Research Fund, University of Maine at Orono, for financial support of this work, and the University of South Carolina for providing its facilities.

Registry No.—CF_3CO_2H, 76-05-1; H_2SO_4, 7664-93-9; 1-(*o*-chlorophenyl)-2,2-dichloro-1-propanol, 355996-56-6.

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Equilibria in Reactions of Fluorocarbon Olefins, Imines, and Ketones with Fluoride Ion

John A. Young*

Universidad Autonoma de Guadalajara, Guadalajara, Mexico

Margaret H. Bennett

Florida Department of Citrus, Lake Alfred, Florida

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Rate and enthalpy measurements indicate that fluoride ion adds more easily to the C=O bond in $H(CF_2)_6COCF_3$ than to the C=C bond in $H(CF_2)_7OCF=CF_2$, at near ambient temperatures in a polar aprotic solvent. When both are present, however, there can be rapid fluoride exchange from the kinetically more favored to the less favored anion; the initial composition thus has little importance. In fluoride-catalyzed dimerization of C=C, C=O, and C=N compounds at 170–180 °C under equilibrium conditions, the final product will be the most thermodynamically stable one and can be predicted on the basis of relative acidities. The codimerization reaction is highly product specific.

Fluoride ion adds to highly fluorinated olefins and carbonyl compounds to form respectively carbanions and alkoxide ions which undergo many of the characteristic reactions of their nonfluorinated analogues.[1]

$$R_FCF=CF_2 + F^- \rightarrow R_FC^-FCF_3 \quad (1)$$

$$(R_F)_2C=O + F^- \rightarrow (R_F)_2CFO^- \quad (2)$$

In a mixed system containing olefin, carbonyl compound, and fluoride ion, two reaction possibilities exist: alkylation of the carbonyl compound or alkoxylation of the olefin

$$R_F'CF=CF_2 \xrightarrow{F^-} R_F'CF^- \xrightarrow{(R_F)_2C=O} R_F'CFC(R_F)_2 \quad (3)$$

$$(R_F)_2C=O \xrightarrow{F^-} (R_F)_2CFO^- \xrightarrow{R_FCF=CF_2}$$

$$(R_F)_2CFOCF_2C^-FR_F' \quad (4)$$

The first of these reactions has often been reported and the second never. Broadly speaking the question somewhat resembles the addition of an enolate ion to C=O in classical base-catalyzed carbonyl condensations, in which the new bond formed is C–C rather than C–O. The fluorinated carbanion and alkoxide ions are not ambident, as is the enolate ion, but it has heretofore been assumed that they are in some way interconvertible. The present work shows that this interconvertibility is real, that the overall reaction is apt to be thermodynamically rather than kinetically controlled, and that the product can be predicted in terms of relative acidities.

In order to study the C=O/C=C system shown in eq 3 and 4, two compounds of medium chain length, $H(CF_2)_6COCF_3$ (1) and $H(CF_2)_7OCF=CF_2$ (2), were prepared. A vinyl ether rather than an α-olefin was chosen since a terminal *F*-olefin[2] undergoes very facile double-bond migration in the presence of fluoride ion and this reaction would have interfered with the kinetic studies. A schematic diagram of the two syntheses is shown in Scheme I. No unusual difficulties were encountered. During identification of the vinyl iodide, an unexpected fragmentation pattern in the mass spectrum of the compound

Scheme I