Table II. Products from the Reaction of Trifluoroacetic Acid and Hydrogen Bromide with 1-Phenylpropyne (**3**) at 25°

Exptl condn[a]	Product ratio
CF_3CO_2H, isopentane	**2a**:**2b** = 1.53
CF_3CO_2H, CH_2Cl_2	1.48
CF_3CO_2H, CH_2Cl_2, $(C_2H_5)_4N^+\,O^-COCF_3$	1.13
HBr,[b] CH_2Cl_2	**1a**:**1b** = 2.8
HBr,[b] CH_2Cl_2, $(C_2H_5)_4N^+Br^-$	0.65

[a] 0.9 *M* 1-phenylpropyne, CF_3CO_2H, and tetraethylammonium salts being used. [b] 50 ml of solvent saturated with HBr.

fortunately, experiments in solvent dioxane, which is even more nucleophilic, were not successful owing to formation of a complex with the silver salt.

It is interesting to note that the steric consequence of SN1 displacement of the cis isomer **1a** and of the electrophilic addition of trifluoroacetic acid to **3** (*cf.* Table II) is nearly the same, the ratio **2a**:**2b** being 1.3 and 1.5, respectively. Such a result is reasonable if a vinylic cation–trifluoroacetate pair of similar configuration is involved in both reactions. As expected[9] added trifluoroacetate ion (and added bromide ion even more so) leads to an increase in trans addition product, undoubtedly *via* nucleophilic intervention during the ion-pair stage of the reaction.

Our results can also be compared with those of Rappoport[1a] and Bergman[1b] who not only used solvents of high ionizing power such as 80% ethanol, acetic acid, and dimethylformamide, but also vinylic halides which reacted readily with silver acetate in acetic acid. Since these conditions do not suffice to ionize the 1-phenylpropen-1-yl bromides **1a** and **1b**, it becomes clear that the vinylic cations produced in the earlier studies were more stable than ours and in the polar solvents used had an excellent chance of forming cis and trans isomers in the same ratio from reactant of either geometry. To our knowledge, the reactions reported here represent the first examples of a stereoselective heterolysis of vinyl halides and we conclude that vinyl halides like saturated alkyl halides and tosylates are subject to similar environmental influences in SN1 reactions.

Acknowledgment. We are grateful to the Ministry of Education for Northern Ireland and to The Queen's University of Belfast for the award of a Postgraduate Studentship and a Foundation Scholarship, respectively, to G. F. P. K.

has suggested that a tight ion pair might be involved, since even a single inversion had not been observed previously for displacements on vinyl carbon. However, the large amount of retention of configuration leads us to prefer our suggestion.

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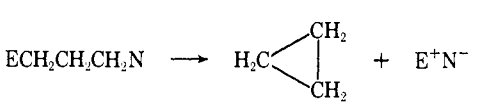
Received July 25, 1970

Kinetics of Acetolysis of ω-Tosyloxyalkyltrimethyltins. Evidence for σ Participation in Cyclopropane Formation from 3-Tosyloxypropyltrimethyltin

Sir:

Many cyclization reactions can be formally represented as α,ω eliminations. For example, methods for preparing cyclopropanes include dehydrotosylation,[1] dehydrobromination,[2–4] dechloroboronation,[5–7] and debromosilylation.[8] If the overall elimination reaction is envisioned as shown in eq 1, the product-forming



(1)

step can result from one of at least four processes: (a) intramolecular nucleophilic displacement by the carbanion formed by ionization of the E–C bond; (b) intramolecular electrophilic displacement by the carbonium ion formed by ionization of the C–N bond; (c) an intramolecular free-radical displacement by a radical formed by homolysis of either the C–N or C–E bond; (d) a concerted process in which ring formation and elimination occur simultaneously. Mechanism a might be observed in the base-induced eliminations and mechanism b may be involved in the aluminum chloride catalyzed dechlorosilylation[8] of 3-chloropropyltrimethylsilane. We wish to report kinetic evidence for mechanism d.

We have prepared four ω-tosyloxyalkyltrimethyltins, $(CH_3)_3Sn(CH_2)_nOTs$, with $n = 3$–6, by addition of trimethyltin hydride to the appropriate unsaturated alcohols,[9] followed by reaction with *p*-toluenesulfonyl chloride. Each had the expected elemental analysis, nmr spectrum, and infrared spectrum.

When 3-tosyloxypropyltrimethyltin was heated in biphenyl solution it decomposed at about 125° yielding 82% cyclopropane and 77% trimethyltin tosylate, along with small amounts of tetramethyltin and dimethyltin ditosylate formed, presumably, by disproportionation of trimethyltin tosylate. The other three tosyloxyalkyltrimethyltins required temperatures around 230° for decomposition. In each case alkenes were the major products.

5-Tosyloxypentyltrimethyltin yielded 10% cyclopentane in the hydrocarbon product. *n*-Propyl tosylate also decomposed at 230° yielding a substantial amount of propylene.

Solvolysis of 3-tosyloxypropyltrimethyltin in anhydrous acetic acid containing sodium acetate at 65° yielded cyclopropane as the only volatile product, and trimethyltin acetate isolated in 80% yield. The other three homologs were solvolyzed in the same system at 120°. From the butyl, pentyl, and hexyl analog, respectively, there was obtained 0.46, 0.52, and 0.51 mol of methane and 0.53, 0.48, and 0.50 mol of ω-acetoxyalkyltrimethyltin.

Despite the apparent complexity of the reactions of the higher homologs, the kinetics of the acetolysis of the four tosylates were measured spectrophotometrically[10,11] in the presence of sodium acetate. First-order

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rate plots were found to be linear over at least two half-lives. Rate constants for these compounds and for ethyl tosylate, representing the mean values obtained from two runs in each case, are given in Table I.

Table I. Kinetic Data from Solvolysis of Tosyloxyalkyltrimethyltins, $(CH_3)_3Sn(CH_2)_nOTs$, in Acetic Acid–Acetate

n	T, °C	$k_1 \times 10^5$, sec^{-1}	Rel k_1 at 120°	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
3	25.0	0.388 ± 0.005			
3	45.1	4.73 ± 0.10			
3	65.2	31.0 ± 1.5		21.3	−7.8
3	120.3	3100[a]	585		
4	120.3	3.17 ± 0.15	0.595		
5	120.3	3.41 ± 0.17	0.642		
6	120.3	4.16 ± 0.10	0.783		
EtOTs	120.3	5.31 ± 0.08	1.00	24.4[b]	−16.7[b]

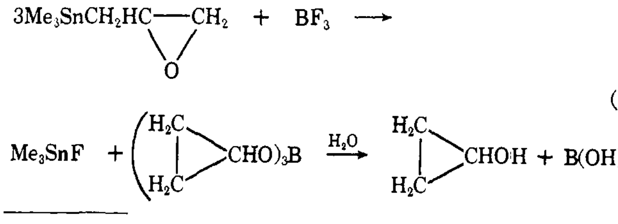
[a] Extrapolated. [b] Reference 12.

A calibration of our data is provided by comparison of our value of 5.31×10^{-5} sec^{-1} at 120.3° for ethyl tosylate with that obtained by extrapolation from the data of Winstein and Marshall[12] of 4.75×10^{-5} sec^{-1}. The rate constant for solvolysis of 3-tosyloxypropyltrimethyltin in trifluoroethanol at 25.0° was $36.0 \pm 0.7 \times 10^{-5}$, nearly a hundred times the value in acetic acid.

3-Tosyloxypropyltrimethyltin solvolyzes faster than ethyl tosylate by a factor of 585 and faster than the other tosyloxyalkyltrimethyltins by factors approaching a thousand. Since the last four entries in the table probably do not represent limiting unimolecular solvolyses, but have substantial S_N2 character,[13] these rate coefficient ratios would be even larger in a less nucleophilic polar solvent. The high reactivity of 3-tosyloxypropyltrimethyltin and the formation of cyclopropane provide strong evidence for σ participation by the electrons of the tin–carbon bond in facilitating departure of the tosylate ion in a concerted 1,3-elimination reaction.

2-Ferrocenylethyl tosylate solvolyzes about 500 times as fast as 2-phenylethyl tosylate.[14] Participation, analogous to that proposed above, involving a pair of electrons of the iron–cyclopentadienide bond has been suggested by Traylor and Ware.[15] Indeed, these authors suggested carbon–metal σ participation as a general phenomenon for the formation of cyclopropanes from γ-metalloalkyl halides.

The use of organotin derivatives has synthetic potential which we are examining. For example, 3,4-epoxybutyltrimethyltin reacts rapidly with boron trifluoride etherate to form cyclopropylcarbinyl borate, which hydrolyzes in moist air to provide a high yield of cyclopropylcarbinol (eq 2).



(2)

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work, and to M & T Chemicals, Inc., for gifts of organotins through the courtesy of Bernard Kushlevsky.

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Mechanisms of Photochemical Reactions in Solution. LXV.[1] Quenching of Excited Singlet States of Electron-Rich Aromatic Compounds by Methyl Chloroacetate

Sir:

For several years this laboratory has been investigating singlet quenching of aromatic compounds by quenchers having no low-lying singlet states.[2–5] We visualize this phenomenon as involving an interaction between the excited state of the aromatic molecule and the quencher, forming a loosely bound exciplex; the net result of this interaction is an increase of the rates of nonradiative decay processes. A general model of this interaction has been formulated as the following

$$\psi_{\text{exciplex}} = a\psi_{\text{A*Q}} + b\psi_{\text{AQ*}} + c\psi_{\text{A}^+\text{Q}^-} + d\psi_{\text{A}^-\text{Q}^+}$$

where A = aromatic compound, Q = quencher, and * denotes the excited state.

Clearly the importance of each of the terms would be expected to vary depending upon the structure of A or Q. For example, the exciplex involved in singlet quenching of aromatic hydrocarbons by amines seems to approach a true charge-transfer state in which the excited hydrocarbon acts as an electron acceptor.[2,3] Quenching of fluorescence of aromatic compounds by conjugated dienes, however, most likely involves several if not all of the above interactions.[4,5] We were intrigued by the possibility that the intramolecular photocyclizations observed by Witkop and coworkers[6] might be initiated by partial electron transfer in which the excited state of the aromatic compound acted as an electron *donor* to the chlorinated amide. That is, the third term in the above equation would have significant weight. This complex could then undergo rapid radiationless decay to either new products or to the original compounds.

We have found that the fluorescence of many electron-rich aromatics is quenched efficiently by methyl chloroacetate and chloroacetamide.[7] The absorption

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(7) Recent experiments have indicated that quenchers are not limited to chloro-substituted derivatives of acetic acid. For example, benzyl chloride and allyl chloride quench the fluorescence of 1,4-dimethoxybenzene with high efficiency.