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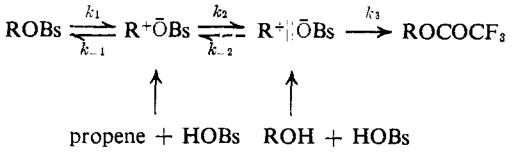
The Addition of Undissociated Strong Acids to Alkenes. "Hidden Return" Revealed

Sir:

We wish to report observations which shed new light on the behavior of the ion pairs which are involved in the trifluoroacetolysis of secondary arenesulfonate esters.[1,2] Isopropyl *p*-bromobenzenesulfonate (ROBs) reacts in trifluoroacetic acid (TFA) at 25° to give, within the limits of nmr detection, a quantitative yield of isopropyl trifluoroacetate ($ROCOCF_3$). The half-life based on the rate of disappearance of the nmr signal is 182 min. Neither the product yield nor the half-life is significantly different if the reaction is carried out in the presence of excess sodium trifluoroacetate. Propene is converted to $ROCOCF_3$ relatively slowly by TFA either alone or buffered (half-life ~300 min). However, *in trifluoroacetic acid, propene (0.2 M) and p-bromobenzenesulfonic acid (HOBs, 0.1 M) react within less than 1 min to produce isopropyl p-bromobenzenesulfonate apparently quantitatively.* We interpret this to mean that propene and undissociated HOBs react directly to produce a "tight" ion–pair ($R^+\bar{O}Bs$) which covalently combines at a rate much faster than it dissociates. Dewar and Fahey[3] have argued that the *cis* addition of HBr to acenaphthylene in acetic acid involves formation and rapid combination of ion pairs. It is obvious that in these reactions ion-pair combination is faster than solvolysis.[4]

Isopropyl alcohol (ROH, 0.1 *M*) on the other hand is converted by HOBs (0.12 *M*) in TFA exclusively to $ROCOCF_3$ with a half-life of 7 min; no intermediate formation of ROBs is detected even though its solvolytic half-life is much longer. This is interpreted as indicating that HOBs reacts with ROH to form isopropyloxonium brosylate ($R^+OH_2O^-Bs$) ion pairs which are converted in the rate-determining step to isopropyl cation and brosylate ion *separated* by a molecule of water ($R^+OH_2{}^-OBs$);[6] this molecule-separated ion pair solvolyzes rapidly and does not undergo kinetically significant internal return to ROBs. Thus, we conclude that the trifluoroacetolysis of ROBs must involve rate-determining dissociation of the tight ion pair



$$\mathrm{ROBs} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+\bar{O}Bs \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R^+\|\bar{O}Bs \xrightarrow{k_3} ROCOCF_3$$
$$\uparrow \text{ propene + HOBs} \qquad \uparrow \text{ ROH + HOBs}$$

The formation of ROBs from propene and HOBs shows that $k_{-1} > k_2$; the lack of formation of ROBs from ROH and HOBs indicates that the *water*-separated ion pair does not return; it seems reasonable that *solvent*-separated ion pairs would not return either so that $k_3 > k_{-2}$.[9]

Streitwieser and Dafforn[10] have reported that in trifluoroacetolysis isopropyl toluenesulfonate shows an α-deuterium rate effect (k_H/k_D) of 1.22 ± 0.02 and a β-d_6 effect of 2.12 ± 0.1. It has previously been suggested[11] that the α-*d* effect on a limiting reaction of an alkyl arenesulfonate should be about 1.22 and that the lower effects observed in other solvents indicate some nucleophilic character, probably nucleophilic attack on the tight ion pair.[12] The idea that *many reactions classified as limiting*[11-13] *involve rate-determining dissociation of tight ion pairs*[12] is thus further reinforced. It is important to note that the β-d_3 effect of 1.46 (or $\sqrt{2.12}$) reported for the limiting solvolytic formation of a simple secondary carbonium ion is significantly larger than that for a simple tertiary system,[14] *e.g.*, 1.3304 for the solvolysis of *t*-butyl-d_3 chloride in 60% aqueous ethanol.[15]

Experiments with other alkene–alcohol–alkyl ester systems in TFA and in other solvents which do not ionize the conjugate acids of the usual leaving groups are currently underway to determine the generality of the pattern of results reported here. Preliminary observations indicate a similar pattern with styrene–1-phenylethanol–1-phenylethyl chloride in trifluoroethanol and with isobutylene–*t*-butyl alcohol–*t*-butyl chloride in trifluoroethanol. These two cases show, however, a lower ratio (*ca.* 6:1 and 2:1, respectively) of rates of covalent recombination to solvolysis for the ion pairs produced

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[1] For a recent discussion of the evidence relating to the importance of ion pairs in solvolysis see S. Winstein, B. Appel, R. Baker, and A. Diaz, "Organic Reaction Mechanism," Special Publication No. 19, The Chemical Society, London, 1965, p 109.

[2] For references to the use of trifluoroacetic acid as a solvolysis medium see P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Amer. Chem. Soc.*, **89**, 5902 (1967).

[3] M. J. S. Dewar and R. C. Fahey, *Angew. Chem. Intern. Ed. Engl.*, **3**, 245 (1964).

[4] The reaction of diazoneopentane with carboxylic acids in ether[5] which leads to 99% rearranged products probably involves the production of tight ion pairs in which the rearrangement is faster than recombination, despite the low dielectric constant of the solvent and the fairly high nucleophilicity of the counter ion.

[5] D. Y. Curtin and S. M. Gerber, *J. Amer. Chem. Soc.*, **74**, 4052 (1952).

[6] If the $R^+OH_2{}^-OBs$ ion pairs dissociate before the C–O bond of $ROH_2{}^+$ ionizes then the free carbonium ion rather than the water-separated ion pair would be produced in the rate-determining step. We believe that the dissociation does not precede C–O bond cleavage because the low dielectric constant (8.42, 20°)[7] of the TFA solvent does not support extensive ion dissociation.[8] In any event, the results are *consistent* with return from the water-separated ion pair being slow.

[7] W. Dannhauser and R. H. Cole, *J. Amer. Chem. Soc.*, **74**, 6105 (1952).

[8] J. H. Simons and K. E. Lorentzen, *ibid.*, **74**, 4746 (1952).

[9] We do not mean to indicate that $R^+OH_2{}^-OBs$ is identically the same species as $R^+HO_2CCF_3{}^-OBs$ but both can be represented by the general notation $R^+\|\bar{O}Bs$ and their relative rates of dissociation and recombination in the same solvent should be similar. Also, $R^+\bar{O}Bs$ may not be *exactly* the same species (in terms of conformation and solvation especially) when formed by proton transfer from HOBs to propene as when produced by ionization of ROBs; the differences are probably slight, however, and $R^+\bar{O}Bs$ from the latter source should not be any *less* likely to recombine than that from the former.

[10] A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969).

[11] V. J. Shiner, Jr., M. W. Rapp, E. A. Halevi, and M. Wolfsberg, *J. Amer. Chem. Soc.*, **90**, 7171 (1968).

[12] V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *ibid.*, **91**, 4838 (1969).

[13] V. J. Shiner, Jr., W. L. Buddenbaum, B. L. Murr, and G. Lamaty, *ibid.*, **90**, 418 (1968).

[14] T. Koenig and R. Wolf, *ibid.*, **91**, 2569 (1969).

[15] V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *ibid.*, **85**, 2413 (1963).

from the alkene and HCl. We believe that the tight ion pairs produced from the alkyl halides probably show relatively more recombination and that the rate-determining steps in the trifluoroethanolyses of *t*-butyl chloride and 1-phenylethyl chloride are also dissociation of the tight ion pairs.

Because of the absence of a technique to evaluate the importance of "hidden return" it has not heretofore generally been possible to make a distinction between two fundamentally different kinds of participation: namely (1) participation in the initial bond ionization and (2) participation in the process of further reaction of an initially formed ion pair.[16] The latter explanation is especially attractive for those examples where ion-pair return is known to be dominant in the reference compound and where the compound which appears to react *via* participation would give a carbonium ion which is subject to facile rearrangement to a more stable classical ion. Thus, since our experiments indicate that return of isopropyl cation–brosylate ion pairs in TFA is fast relative to solvolysis it is obvious that 3,3-dimethyl-2-butyl brosylate might ionize only slightly faster than isopropyl brosylate but have its solvolysis rate in TFA, relative to isopropyl, much accelerated if the Wagner–Meerwein rearrangement took place rapidly in the tight ion-pair stage; after rearrangement, return to the very reactive tertiary brosylate would not slow the rate and reverse rearrangement with return would be prohibited by the much higher energy of the secondary ion relative to the tertiary ion. Until the importance of tight ion-pair return can be evaluated it is unwarranted to accept rate acceleration as conclusive evidence for participation *in the first ionization step in reactions where facile rearrangement to a more stable classical ion is possible.*[17] An isotope effect in the migrating group only shows participation in the rate-determining step and does not serve to distinguish between the two types of participation.[18] Further, rate-determining proton loss from the tight ion pair could show a deuterium isotope effect similar to that associated with hydrogen participation.[19]

The reactions reported here were followed using a Varian HA-100 magnetic resonance instrument; characteristic peak positions in TFA solvent were as follows: isopropyl brosylate, δ 1.07 doublet, J = 7 Hz; isopropyl trifluoroacetate, δ 1.14 doublet, J = 7 Hz; isopropyl alcohol, δ 1.10 doublet, J = 7 Hz; propylene, δ 1.42, J = 1.7 and 7 Hz. The internal standard for these reactions was 1,4-dioxane. The chemical shift of dioxane is somewhat dependent on acid concentration.

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[16] S. Winstein and G. C. Robinson, *J. Amer. Chem. Soc.*, **80**, 169 (1958). See footnote 34 especially.

[17] W. G. Dauben and J. L. Chitwood, *ibid.*, **90**, 6876 (1968).

[18] S. Winstein and J. Takohashi, *Tetrahedron*, **2**, 316 (1958).

[19] V. J. Shiner, Jr., and J. G. Jewett, *J. Amer. Chem. Soc.*, **87**, 1382 (1965).

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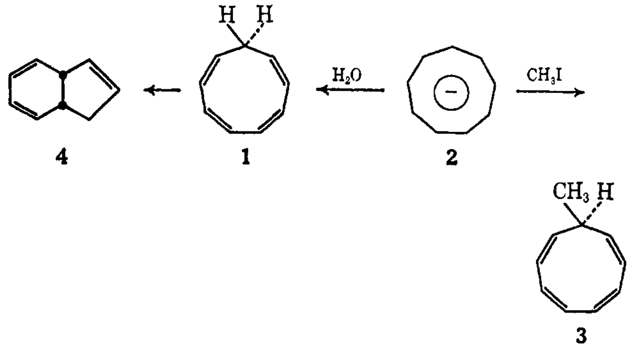
The Preparation and Isolation of *cis,cis,cis,cis*-1,3,5,7-Cyclononatetraene

Sir:

cis,cis,cis,cis-1,3,5,7-Cyclononatetraene (**1**) has been the object of much discussion in the literature but primarily since the successful preparation of cyclononatetraenide ion (**2**).[1-9] While the primary emphasis has been with regard to the intermediacy of **1** in thermal and photochemical transformations of other C_9H_{10} compounds, questions with regard to the stability, acidity, and general structural nature of **1** have also been raised. Despite the fact that there is some evidence[8] that it might be possible to isolate this very important C_9H_{10} olefin, there has been to date no report of its preparation and direct observation. It is the purpose of this communication to remedy this situation and preliminarily report the isolation of **1** and its 9-methyl derivative (**3**).



In a typical procedure a solution of **2** (20 mmoles) in tetrahydrofuran[7,8] (7 ml) at *ca.* 0° was quenched with ice water (20 ml) and was rapidly extracted into cold CCl_4 (9 ml). The cold CCl_4 extract was washed rapidly with ice-cold 1 *N* HCl followed by ice water. The cold extract was filtered through anhydrous $MgSO_4$, and an aliquot was used to obtain the nmr spectrum of **1** shown in Figure 1. The procedure for the 9-methyl derivative **3** was essentially the same except that CH_3I (20 mmoles) was added to the tetrahydrofuran solution of **2** at 0° and was allowed to react for 2.5 hr before the aqueous quench and work-up. Using this technique one can obtain solutions of **1** in the organic solvent of choice depending upon one's needs.

Solutions of **1** and **3** in ether were reduced at 0° with hydrogen and Raney nickel for *ca.* 6 hr. In the case of **1** about 60% cyclononane was obtained along with *cis*-hydrindan and in the case of **3** about 50% methylcyclononane[10] was produced along with the corresponding methyl-*cis*-hydrindans.[11]

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[1] E. Vogel and H. Kiefer, *Angew. Chem.*, **73**, 548 (1961).

[2] E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963).

[3] E. Vogel, W. Wiedeman, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963).

[4] W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

[5] K. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, **86**, 905 (1964).

[6] G. Fonken and W. Moran, *Chem. Ind.* (London), 1841 (1963).

[7] T. Katz and P. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964).

[8] E. LaLancette and R. Benson, *ibid.*, **87**, 1941 (1965).

[9] H. Simmons, D. Chesnut, and E. LaLancette, *ibid.*, **87**, 982 (1965).

[10] Methylcyclononane was prepared independently by the sequence cyclononanone → 1-methylcyclononan-1-ol → 1-methylcyclononene → methylcyclononane.

[11] P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969).