Five cycles of TBC–BC–TBC interconversions are required to average the three different proton chemical shifts of the TBC form to one chemical shift, whereas only two cycles are required to average the two ^{13}C chemical shifts.

In 1,1-dimethyl- and 1,1,4,4-tetramethylcyclononane the changes observed are racemization of chiral conformations. Here, three cycles of TBC–BC–TBC interconversions are required and the itinerary goes through BC's and TBC's with sterically hindered methyl groups. Very large transannular methyl–methyl repulsions are found in these intermediate forms for the tetramethyl compound in agreement with a barrier which is 14 kcal/mol greater than that of cyclononane. The smaller transannular methyl–hydrogen repulsions for the dimethyl case lead to an increase in barrier of only 3 kcal/mol. Thus, the pathway described above rationalizes the conformational barriers in a satisfactory way.

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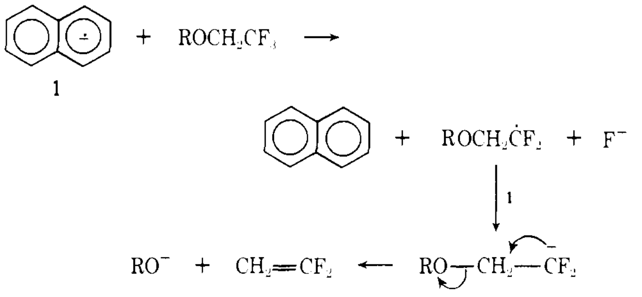
The Sodium Naphthalene Promoted Cleavage of Trifluoroethyl Ethers

Sir:

Several recent investigations have established that solvolysis of simple secondary derivatives, even in acetic and formic acids, is strongly assisted by nucleophilic solvent participation.[1] These investigations serve to reinforce an awareness that solvolysis of primary systems must also be so assisted.[2] This awareness has important consequences for the investigation of neighboring group participation, since strong solvent assistance to solvolysis may well mask the potential intervention of less potent internal nucleophiles. Anchimeric assistance by such neighboring groups can be made manifest by employing solvents of low intrinsic nucleophilicity. Considerable success in this direction has been achieved utilizing trifluoroacetic acid as a solvolysis medium,[3] but this approach is limited by the high relative acidity of trifluoroacetic acid and the consequent instability of many substrates and products in this solvent. 2,2,2-Trifluoroethanol (TFE) appears to be a solvent which combines the advantages of acceptably low acidity ($pK_a = 12.37$)[4] and low intrinsic nucleophilicity.[5] Given these features it is at first glance surprising how little attention this solvent has received as a solvolysis medium. A principal reason for this disinterest may well be the difficulty encountered to date in identifying and assaying the products of solvolysis in trifluoroethanol. Few authentic trifluoroethyl ethers are known, and synthesis of compounds of this type is not trivial in many cases.

Prompted by the requirement for a solvolysis medium of low intrinsic nucleophilicity and minimal acidity in which quantitative correlation of rates and products of reaction could be achieved, we have sought to develop an efficient stereospecific method for converting trifluoroethyl ethers to the corresponding alcohols. We are now pleased to describe such a technique and to exemplify its application.

All alkyl halides react with 1,2-dimethoxyethane (DME) solutions of sodium naphthalene by initial dissociative electron transfer to yield alkyl radicals and halide ion.[6] The radicals thus produced can undergo a variety of reactions, one of which is rapid reduction by a second molecule of radical anion to the alkyl anion.[7,8] Alkyl fluorides represent no exception to this generalization, although the rate of the initial dissociative electron transfer is much slower than for other halides.[8] These considerations suggest the following scheme for cleaving 2,2,2-trifluoroethyl ethers.



Since the initially formed radical is kinetically much more susceptible to further reduction than is a second fluoro substituent, and since β-alkoxide should prove a superior leaving group to α-fluoride in the subsequently formed anion, the possibility of carbene formation resulting from the second reduction step—a reaction which does, indeed, occur with alkyl *gem*-dichlorides and the polychloromethanes[9]—appears unlikely.

Hexyl 2,2,2-trifluoroethyl ether was synthesized by

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refluxing hexyl *p*-nitrobenzenesulfonate in trifluoroethanol for 72 hr, purified by bulb-to-bulb distillation, characterized by microanalysis and its nmr and mass spectra, and shown to be at least 99% pure by gas–liquid chromatography. A solution approximately 1 *M* in naphthalene radical anion was prepared by magnetically stirring for 4 hr stoichiometric quantities of sodium and naphthalene in 25 ml of DME in a 50-ml flask protected from atmospheric moisture and oxygen by means of a serum cap. Utilizing a hypodermic syringe, 5 ml of this solution was transferred to a similarly protected flask containing 1 ml of DME solution 0.01 *M* in hexyl trifluoroethyl ether and 0.01 *M* in dodecane (an internal standard). This solution was stirred for several days at room temperature and analyzed periodically for loss of ether and generation of hexanol.

Samples for analysis were obtained by withdrawing an aliquot of the reaction mixture into a small test tube. After the rapid air quenching of excess radical anion was complete, a drop or two of saturated NH_4Cl solution was added to hydrolyze the alkoxide salts, and the solution was dried by addition of a few crystals of anhydrous sodium sulfate. Direct glc analysis of samples thus prepared gave the following results. (1) After 5 days the yield of hexanol was greater than 90%. (2) The rate of disappearance of trifluoroethyl ether and the rate of formation of hexanol were in good agreement, and, under these pseudo-first-order conditions, the half-life was on the order of 24 hr. (3) Other than hexanol, the only products of reaction more volatile than naphthalene were found to have extremely short glc retention times. There are at least two such products, one of which has a retention time identical with that of an authentic sample of ethylene. Ethylene would be expected to result from further reduction of fluoroethylene which, in turn, is the expected product of reduction of 1,1-difluoroethylene. These results all suggest that the postulated cleavage of trifluoroethyl ethers to difluoroethylene and alkoxide anion is realized in practice.

The utility of this procedure for the identification and quantitative analysis of the products of trifluoroethanolysis is illustrated by the following example. Formolysis of *trans,trans*-5,9-decadienyl *p*-nitrobenzenesulfonate (**2**) yields a complex mixture of products including a total of six acyclic, monocyclic, and bicyclic formates.[10] In order to investigate the possibility that a bicyclic cation is generated directly by cooperative anchimeric assistance of both double bonds in the transition state for ionization, it is important to minimize competitive solvent assistance to ionization. The reaction mixture derived from solvolysis of **2** in TFE was poured into sufficient 40% NaOH solution to neutralize all the TFE. After dilution with water, the resulting aqueous suspension was extracted with pentane, the pentane extracts were concentrated, and the concentrate was analyzed by glc and then treated as described above for hexyl trifluoroethyl ether. In this manner it was clearly established that both the olefinic products of the initial solvolysis reaction and the alkoxides generated in the early stages of the reaction of the mixture of trifluoroethyl ethers with **1** are stable under the conditions required for the cleavage reaction. It was further demonstrated that the rate of cleavage of trifluoroethyl ethers is independent of the structure of the alkoxide formed. The simplicity of this assay procedure permitted a ready examination of the effect of the presence of competing nucleophiles in the solvolysis mixture on the distribution of mono- and bicyclic products. The details of this investigation[11] and the mechanistic conclusions derived therefrom will be presented elsewhere.

Although a full and precise definition of the scope and limitations of this technique must await the completion of further experimentation currently in progress, a few brief comments on this point may be of value. Despite the fact that several days are required for complete reaction of a mixture of trifluoroethyl ethers with sodium naphthalene, glc analysis can be carried out readily at relatively low levels of conversion of ether to alkoxide, since in our experience even mixtures of isomeric primary, secondary, and tertiary trifluoroethyl ethers yield alcohols with universally longer glc retention times. Furthermore, since the rate of cleavage is independent of the structure of the alkoxide produced, the relative yield of alcohols produced at low conversion is identical both with that at high conversion and with the relative yield of the trifluoroethyl ethers. Coupling of the initially produced difluoroalkyl radical with sodium naphthalene[6] appears to be minimal (<10%), and, again, its extent is independent of the structure of the alkyl fragment of the trifluoroethyl ether. An occasional complication to glc analysis, namely the coincidental overlapping of product peaks with the large naphthalene peak, can be easily overcome by employing as reducing agent the radical anion derived from either biphenyl or phenanthrene, which have progressively longer glc retention times. The presence of other easily reduced substituents in the product trifluoroethyl ethers will, of course, lead to complications on treatment with sodium naphthalene. In our experience, however, unsubstituted or alkyl-substituted arenes, alkenes, and cyclopropane derivatives are stable under the conditions required to effect cleavage. To date we have not yet attempted to conduct this reaction on a preparative scale. The only apparent difficulty in doing so would be the necessity to develop efficient methods for separating the product alcohols from the massive amounts of naphthalene generated in the reaction; chromatographic techniques would appear best suited for this purpose.

In summary, we believe that the sodium naphthalene promoted cleavage of trifluoroethyl ethers described above should facilitate use of TFE as a solvolysis medium for the investigation of anchimeric assistance by weakly nucleophilic neighboring groups.

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