TABLE IV

OXIDATION OF 2-METHYL-2-PENTANOL WITH NIS[a]

Conditions (Solvent, irradiation, time)	Yield of products, % Acetone	*n*-Propyl iodide
Benzene, $h\nu$, 2 hr	40	52
Benzene, $h\nu$, 1.5 hr	52	58

[a] Only trace amounts of methyl iodide and 2-pentanone could be found. An unknown glc peak, 10–20% of the starting NIS, appeared between the benzene and *n*-propyl iodide peaks and was believed to be 2,2-dimethyltetrahydrofuran. No identification of the peak was attempted.

Oxidation of 3-Ethyl-3-pentanol with NIS.—Five milliliters of a solution of 0.516 *M* 3-ethyl-3-pentanol (2.58 mmol) and 0.596 *M* chlorobenzene (2.88 mmol) in dry benzene were added to 302 mg (1.34 mmol) of NIS. The mixtue was irradiated and heated to reflux for 1 hr. Glc analysis indicated yields of 101% ethyl iodide and 99% 3-pentanone. Water extractions of the reaction mixture produced 97 mg (0.98 mmol) of succinimide. Identification was made by mixture melting point and ir comparison with known succinimide. The results of all reactions of NIS with 3-ethyl-3-pentanol are given in Table I.

Registry No.—NIS, 516-12-1; *tert*-butyl alcohol, 75-65-0; 3-ethyl-3-pentanol, 597-49-9; 3-methyl-3-pentanol, 77-74-7; 2-methyl-2-pentanol, 590-36-3.

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The Solvolysis and Rearrangement of 2-Phenylethyl Tosylate in Trifluoroethanol[1]

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2,2,2-Trifluoroethanol (TFE) was first introduced as a solvent for the study of solvolytic reactions by Scott.[3] Subsequently, Trahanovsky and Doyle[4] pointed out that the low nucleophilicity of TFE promotes the formation of cyclized products from 5-hexenyl arenesulfonates. In a comprehensive study, Shiner, *et al.*,[5] have evaluated many of the desirable properties and characteristics of TFE for solvolysis studies. Bentley and Lacadie[6] have shown that TFE accentuates differences in reactivity of diverse benzyl chlorides more than does ethanol, aqueous dioxane, or acetic acid.

We have investigated the utility of TFE for the study of the solvolytic rearrangement of β-arylethyl tosylates. Our results indicate that TFE has considerable potential in this regard.

Solvolysis of 2-phenylethyl tosylate (**1**) in TFE is substantially *more rapid* than that for a model compound, ethyl tosylate (**2**). Electron-donating substituents in the aromatic moiety cause a marked further increase in the observed rates (Table I). From 2-(*p*-methylphenyl)ethyl tosylate (**3**) and 2-(*p*-methoxyphenyl)ethyl tosylate (**4**) a ρ of -2.5 (using σ^+) is obtained. This value is comparable to that observed for similar solvolytic rearrangements in acetic acid.[7]

TABLE I

RATE CONSTANTS FOR THE SOLVOLYSIS OF ARYLETHYL TOSYLATES IN TRIFLUOROETHANOL

Compound solvolyzed[a]	T, °C	$k_t \times 10^6$, sec^{-1}	Added salt
1	75.0	4.83 ± 0.05	
	100.0	37.5 ± 0.6	
	75.0	5.35 ± 0.1	NaOAc[b]
	74.8	64.9[c]	
	75.0	67.7[c]	NaOAc[b]
2	75.0	3.87 ± 0.04[c]	
	90.0	12.5 ± 0.2[c]	
	109.6	5.38 ± 0.06	
	109.6	...[d]	NaOAc[b]
3	75.0	53.1 ± 1	
4	75.0	339 ± 5	
5	75.0	3.98 ± 0.05	
6	75.0	...[e]	
	75.0	13.1	NaOAc[b]

[a] Kinetic solutions were 0.02 *M* in sulfonate. [b] Sodium acetate, 0.03 *M*. [c] *p*-Nitrobenzenesulfonate rather than tolysate solvolyzed. [d] Non-first-order kinetics; apparent "first-order rate constant" from initial rate data, 26.6 × 10^{-6} sec^{-1}. [e] Decomposition occurs.

Isotopically substituted **1**, 2-phenyl-*1,1*-d_2-ethyl tosylate (**5**) shows essentially complete scrambling in the products of solvolysis. Furthermore, the secondary deuterium isotope effect upon the rate is large, $k_H/k_D = 1.21$, which is apparently near maximum, and is as large as the ratios observed in the formolysis of activated β-arylethyl systems.[8] This high k_H/k_D is evidence for the dominance of the participating pathway, k_Δ, over the k_s pathway in the trifluoroethanolysis of **1** and supports an unsymmetrical partially bridged transition state.

A final point of interest, which is germane to present mechanistic discussions regarding the role of the phenonium ion in these solvolyses is the sharp *qualitative* difference in behavior between **1** and **2** when solvolyses are carried out in TFE with the addition of sodium acetate. The rate constant for **1** increases, and the magnitude of the increase is typical of normal salt effects. **2**, on the other hand, gives non-first-order behavior under these conditions, suggestive of bimolecular reaction between **2** and acetate ion.

A further study had been carried out examining the solvolysis of 2-(2-furyl)ethyl tosylate (**6**) in TFE buffered with sodium acetate.[9] This reaction is clean kinetically, in contrast to preliminary results with **6** in formic acid and sodium formate. In formic acid **6** shows appreciable extraneous decomposition and severe darkening of the kinetic solution before the apparent first half-period is complete.

Thus TFE shows promise for the study of β-arylethyl sulfonates. It accentuates the participating

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pathway and gives large rate increases over nonassisted solvolysis. For acid-sensitive substrates it holds advantages over formic acid (or trifluoroacetic acid).

Experimental Section

Materials.—The sulfonates were prepared by standard procedures and had properties in accordance with literature values: **1**, mp 37–38° (lit.[10] mp 37.5–38.2°); **2**, mp 31–32° (lit.[11] mp 33.5–34.2°); **3**, mp 65.7–66.5° (lit.[12] mp 68.6–69.2°); **4**, mp 57.0–57.5° (lit.[13] mp 57–58°); 2-phenylethyl *p*-nitrobenzenesulfonate, mp 97–98° (lit.[14] mp 101.5–102°); ethyl *p*-nitrobenzenesulfonate, mp 90.2–91.0° (lit.[15] mp 91°).

2-(2-Furyl)ethanol was prepared by lithium aluminum hydride reduction of 2-furylacetic acid.[16] After work-up in the usual fashion, the furylethanol was characterized by nmr, and converted directly into the rather unstable tosylate (**6**), mp 29–30° (from hexane), characterized by nmr.

2,2,2-Trifluoroethanol was purchased from Halocarbon Products Corp., Hackensack, N. J., dried over molecular sieves (Union Carbide Corp. 4A),[17] and distilled prior to initial use. Shiner, *et al.*,[5] outline efficacious recovery procedures.

Kinetic Methods.—The usual sealed ampoule technique was used. Titrations were carried out with standardized 0.01 *N* potassium hydroxide in TFE, using a Metrohn Model E-336-A potentiograph with an EA 120 U electrode. The midpoint of the derivative titration curve was used as the end point. For the solutions buffered with sodium acetate, the titrant was a standardized solution of perchloric acid (0.03 *N*) in TFE. The same electrode was used with the potentiograph.

Rate constants were generally determined from 16 to 18 points, which were treated by the least-squares program LSKIN 1.[18]

Registry No.—**1**, 4455-09-8; **2**, 80-40-0; **3**, 14503-40-3; **4**, 5107-52-8; **5**, 36809-05-9; **6**, 36809-06-0; trifluoroethanol, 75-89-8.

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The Reaction of Nitrous Acid with Oximes

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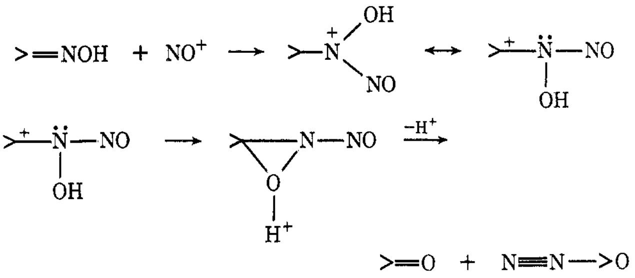
The oxidation of oximes with nitrous acid is a known procedure for the recovery of aldehydes and ketones from the parent oximes. Although this method has been widely utilized, little has appeared in the literature concerning the mechanism of the reaction. Kainz and Huber[1] have studied the reaction of nitrous acid with the oximes of cyclohexanone, benzoin, and acetone. They found that N_2O predominated as the off-gas with N_2 being formed in lesser amount. They hypothesized the intermediacy of both a nitrimine and nitramide from which N_2O could be derived. No mechanistic explanation was offered, however, for N_2 formation. Furthermore, Horner *et al.*, have reported that aldoximes react with "nitrous gases" to give azine bisoxides, and that these azine bisoxides give either N_2O and carbonyl compound or a nitrimine.[2]

More recently Wieland and Grim[3] reported that treatment of butanedione monooxime with ^{18}O-enriched nitrous acid under N_2 resulted in an 89% enrichment of nitrous oxide ($N_2{}^{18}O$), the oxygen of which came only from the nitrous acid and not from the oxime. They therefore proposed the following mechanism.



In this report, we shall deal with the ^{15}N nitrous acid catalyzed decomposition of oximes and the probable modes of formation of N_2O, N_2, and NO therefrom.

Experimental Section[4]

In a typical experiment equimolar amounts of oxime and ^{15}N sodium nitrite was dissolved in a solution containing 45 ml of H_2O and 125 ml of dioxane. Helium was passed through the reaction system and the attached gas sampling tubes. When a helium atmosphere had been obtained, an amount of 50% aqueous sulfuric acid was introduced equivalent to either the amount of sodium nitrite or to a twofold excess. Gas samples were taken at predetermined times, and the reaction mixture was analyzed for aldehyde and other organic products by standard quantitative methods.[5] The gas samples were analyzed by mass spectroscopy and compared to an assay on the ^{15}N sodium nitrite, which was decomposed by aqueous acid under helium. A quantitative estimate of the contribution by oxime and nitrous acid to the various products could then be made by comparing the amount of ^{15}N products in the assay to the ^{15}N products from the reactions.

Results

The results of our experiments are given in Table I. In the reaction of butyraldoxime, the presence of excess mineral acid has a pronounced effect on both the yield of butyraldehyde and on the distribution of gas between N_2O and NO. While the difference in yield between that reaction and the one with only nitrous acid can be attributed partially to a difference in rate of reaction, the difference in gas distribution is too great to allow for this simple explanation. It should also be noted that the nitrogen in N_2O and N_2 comes almost equally from the oxime and nitrous acid, while the nitrogen in NO comes exclusively from

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