out employing Eastman Kodak precoated silica gel chromatogram sheets. The benzene used in the LTA reactions was Baker spectrograde, dried over sodium and redistilled prior to use. All aryl halides used were freshly distilled prior to use. Lead tetraacetate, 10% moist with acetic acid, was obtained from Arapahoe. All other reagents were of the highest purity commercially available. All LTA reactions were run under nitrogen.

(24) Gas chromatographic analyses were performed on an F&M Scientific Model 720 dual column temperature programmed gas chromatograph. Quantitative analysis of the reaction products in a given mixture was performed by internal standardization method with relative percentages being assessed *via* cutting and weighing or triangulation methods. These methods generally gave answers within 5% of one another. The columns employed were as follows. (a) Column A: 4 ft × 0.25 in Apiezon L on Chromosorb P (60–80 mesh); 40 psi of He (60 ml/min); 230–245°; temperature programmed to 280° in order to elute *p*-methoxybenzophenone with minimum tailing. (b) Column B: 2 ft × 0.25 in. 19% Silicone gum rubber (UC-bw98) on Chromosorb P (60–90 mesh); 40 psi of He (60 ml/min); 200°. (c) Column C: 4 ft × 0.25 in. 20% Silicone gum rubber (SE-30) on Chromosorb W; 40 psi of He (60 ml/min); 210°.

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Notes

Trifluoroacetic Acid as a Medium for Aromatic Nitration Using Sodium Nitrate

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The nitration of aromatic systems is one of the most thoroughly studied of all organic reactions, and the central role of the nitronium ion, NO_2^+, in these processes has been well established.[2] Trifluoroacetic acid (TFA) has occasionally been used as a medium for electrophilic aromatic substitutions[3] and, in particular, Brown and Wirkkala used neat TFA and anhydrous nitric acid to nitrate benzene and toluene.[4] Some of our work on the use of TFA as a medium for the permanganate oxidation of hydrocarbons[5] involved cryoscopic measurements in TFA and these results indicated that nitronium and nitrosonium ions could be conveniently generated in TFA using sodium nitrate and sodium nitrite, respectively. We report herein the results obtained for nitration of benzene, toluene, and phenol, using these reagents.

The data presented in Table I show that nitration is almost quantitative after 4 hr of reaction with sodium nitrate. The mixture of isomers resulting from the nitration of toluene is similar to that reported by Brown and Wirkkala (ortho, meta, para = 61.6%, 2.6%, 35.8%).[4]

Trace amounts of phenolic substances were detected in the reaction products.[6] Such products may result either from oxygen attack by the ambident nitronium ion, followed by solvolysis and rapid nitration to produce nitrophenols, or by an addition–elimination mechanism[7] to give phenyl trifluoroacetate which then undergoes solvolysis and nitration.[8]

Attempts to use this medium for nitrosations were unsuccessful, as the data in Table I illustrate, even though cryoscopic and spectroscopic measurements indicated that up to 50% of the nitrite salt was converted to nitrosonium ion. Complex formation between nitrosonium ion and the arene was observed, as had been previously reported.[9] The small amount of nitration that occurs under these conditions is presumably the result of disproportionation[10] or oxidation[11] of nitrogen(III).

Table I

Reactants	Products	% yield[a]	% Conversion[b]
Benzene and $NaNO_3$	Nitrobenzene	99.9	100
	Phenolic products[c]	~0.05	
Toluene and $NaNO_3$	*p*-Nitrotoluene[d]	30.0	95
	o-Nitrotoluene	63.7	
	m-Nitrotoluene	1.2	
Phenol and $NaNO_3$	Tar[e]		
Benzene and $NaNO_2$	Nitrobenzene	3	3
Toluene and $NaNO_2$	Nitrotoluene mixture	~2	~2

[a] Based on quantities of starting materials used. [b] Based on quantities of starting materials consumed. [c] Indicated by the reversible changes in spectra of the product mixture produced by acidification and basification: λ_{max} 415, 366 nm in base and 320 nm (sh) in acid; a 1:1 mixture of *o*- and *p*-nitrophenols has λ_{max} at 415 nm in base and 330 nm in acid. [d] The mixture of nitrotoluenes was analyzed by vpc on a 10% silicon GS-SF-96 firebrick 60/80, 0.25-in. × 10-ft column at 162° and with 40 cm³/min of helium; it was then matched against known samples. Retention times were as follows: *o*-nitrotoluene, 8.5 min; *p*-nitrotoluene, 11.1 min., *m*-nitrotoluene, 10.5 min; toluene, 1.5 min. [e] Rapid, exothermic reaction occurred; could be hazardous.

Experimental Section

In a typical experiment 0.01 mol of sodium nitrate or sodium nitrite was added to 25 ml of neat TFA and then 0.01 mol of the arene was added while the mixture was stirred magnetically. The reaction was allowed to continue for 4 hr at room temperature, after which it was quenched by the addition of 20 ml water and by the addition of enough sodium hydroxide (either as 6 *M* solution or as pellets) to achieve a pH ≥10. The resulting solution was saturated with sodium chloride and successively extracted with three 50-ml portions of ether. The ether extracts were combined and dried over anhydrous magnesium sulfate and then reduced to 50 ml by flash evaporation. The concentrates were weighed and analyzed by vpc.

If TFA recovery is important, the sodium chloride saturation step can be omitted; then, after the ether extraction, the aqueous solution is slowly acidified by the addition of concentrated sulfuric acid until 5 parts per volume of aqueous solution have been added. This mixture is distilled to remove TFA, which will distil along with some water. The fraction between 71 and 105° is collected, treated again with sulfuric acid, and redistilled. Anhydrous TFA results; bp 71.2°.

All compounds used were of reagent grade. The arenes were purified by distillation or recrystallization; the TFA was distilled prior to use.

Registry No.—TFA, 76-05-1; $NaNO_3$, 7631-99-4; $NaNO_2$, 7632-00-0; toluene, 108-88-3; phenol, 108-95-2; benzene, 71-43-2.

References and Notes

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Study of the Trifluoroethanolysis of Cyclobutylcarbinyl and Related *p*-Bromobenzenesulfonates

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Our previous investigation[2] of the solvolytic behavior of cyclobutylcarbinyl brosylate (4-OBs) and related compounds revealed the kinetic and product distribution data were accommodated by Scheme I where solvent capture of a carbon-bridged species accounts for at least 99% of the acetolysis product. Justification for the intermediacy of a carbon-bridged species was based upon (1) the presence of 99% ring-expanded product, (2) the absence of a significant 1-ring substituent effect upon solvolytic reactivity, (3) the absence of cyclopentene product, and (4) the establishment of a good correlation between log k_t for 4-OBs and log k_t for neophyl tosylate.

Prompted by these findings, we extended our investigation to include a product distribution study in 2,2,2-trifluoroethanol (TFE) of the following cycloalkylcarbinyl brosylates. This paper reports the analysis of the product distribution data according to Scheme I in an effort to gain insight into the role of the solvent in the product partitioning process.

$$(CH_2)_nCHCH_2OBs$$

$$n + 1 = 4,\ \text{4-OBs}$$

$$n + 1 = 5,\ \text{5-OBs}$$

$$n + 1 = 6,\ \text{6-OBs}$$

The product data are summarized in Table I. The vapor-phase chromatographic separations and characterizations of products were carried out on a Carbowax 20M–silver nitrate column. Urea was used as a buffer and product studies were conducted at the same temperature as the kinetic investigations.[2] Previously reported[3] stability studies have established that the reported products are indeed the initially formed products and not those of subsequent reactions.

On the basis[2] that solvolysis occurs by one or more of the discrete pathways outlined in Scheme I, the data in Table II are readily obtained. It is interesting to note that the solvent change from acetic acid to TFE is characteried by a decrease in the per cent k_s reaction product for all three substrates, most dramatically for 6-OBs, which confirms the unique ability of TFE to accentuate neighboring group participation under nonacidic conditions.[3d,4-6] This result is readily accommodated by the interesting solvent properties of TFE,[7-10] particularly its enhanced ionizing ability relative to acetic acid without any significant change in solvent nucleophilicity,[10,11] for a substantial body of information[12-14] has accumulated in support of increasing anchimeric assistance (relative to solvent assistance) with increasing ionizing strength of the solvent in solvolysis reactions.

Focusing our attention on the product data summarized in Table I, we observe that the change from acetic acid to TFE results in a considerable increase in the amount of ring-expanded olefin obtained from the solvolysis of 4-OBs and 5-OBs. Thus the trifluoroethanolysis of 4-OBs yields

Scheme I