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SHORT COMMUNICATION

The Reaction of 2,2,2-Trifluoroethyl Iodide with Sodium Phenolate. A Novel Competition Between Substitution and Elimination Reactions

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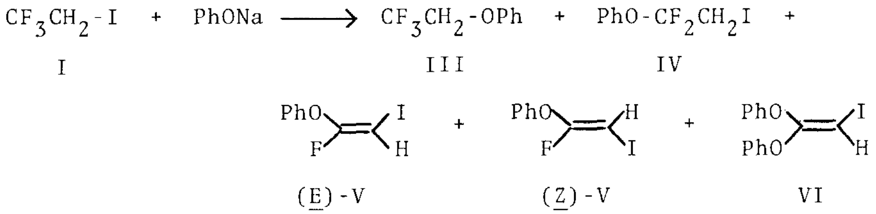
It is well-known [1] that, in the reaction of an alkyl halide with nucleophiles, the nucleophilic substitution (S_N) reaction competes with the beta-elimination (E_B) reaction, in both of which the halide ion acts as the common leaving group. We now report that, in the reaction of 2,2,2-trifluoroethyl iodide (I) with sodium phenolate, the S_N reaction with removal of I^- competes with the E_B reaction with removal of F^-, providing an example of unusual competitions between S_N and E_B reactions involving different leaving groups.

Hine [2] reported the S_N2-reactivities of various 2-fluorinated ethyl iodides including I toward PhS^-, indicating that I is less reactive than ethyl iodide by a factor of 1.7×10^4; however, no further information has been available on the S_N reaction of I. Thus the reaction of I with sodium benzenethiolate was first undertaken in this work. The reaction of I with PhS^- in DMF at room temperature gave only the S_N-product, (2,2,2-trifluoroethylthio)benzene (II) in 71% yield.

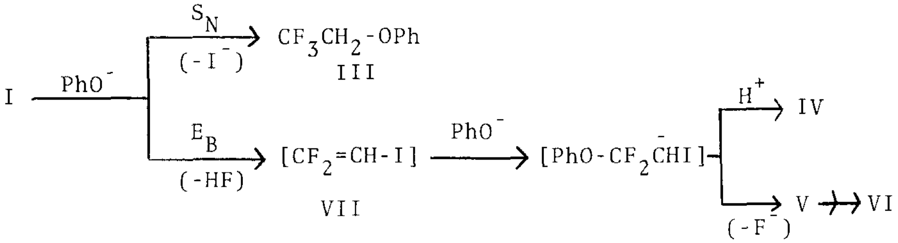
In contrast to this easy reaction with the thiolate, sodium phenolate did not react with I under the similar conditions. Then the reaction of I with 1.5 equiv. of sodium phenolate was carried out in DMF at 80°C for 20 h, and the resulting mixture was found to consist of I (20%), (2,2,2-trifluoroethoxy)benzene(III)(37%), (1,1-difluoro-2-iodoethoxy)-

benzene (IV) (7%), (E)-1-fluoro-2-iodo-1-phenoxyethene (V) (9%), and its Z-isomer (2%), and 2-iodo-1,1-diphenoxyethene (VI) (13%).



All the products were separated and identified by the spectral data (see Experimental). The geometrical assignments of (E)- and (Z)-V were made on the basis of the fact that the vicinal coupling constants (J_{HF}) for (Z)-V was larger than that for (E)-V [3].

Examination of the structures of the products unequivocally reveals that the reaction of I with PhO^- affords not only the S_N-product (III) formed via removal of I^- but also the several E_B-products (IV-VI) containing the iodine atom; the formations of these products can be most rationally explained as shown in the following scheme.



The E_B sequence is initiated by elimination of HF from I presumably via the E1cB mechanism [4] yielding the difluoroiodoethene (VII) which was not isolated under those reaction conditions. Addition of PhO^- to VII followed by protonation and by loss of F^- gives IV* and V (E and Z), respectively [6]

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* The direct displacement of the fluorine atom of I by phenolate ion is very unlikely because of the great difficulty of carbon-fluorine stretching in the displacement reaction [5].

Further addition of PhO^- to V followed by loss of F^- affords the diphenoxylated product (VI) [6].

On the greatest interest is the fact that the reaction of I with PhO^- simultaneously undergoes both the S_N and E_B reactions involving the different leaving groups, the ratio of S_N/E_B being 1.2. The observed competition between the S_N and E_B reactions suggests that the reaction of I with PhO^- is intermediate between the reaction of I with PhS^- (solely S_N reaction) and the reactions of 1,1-difluoro-1,2-dihaloethanes including 2,2,2-trifluoroethyl bromide with sodium alcoholates (solely E_B reactions) [7].

Finally, the striking difference in the course of reaction of I between PhS^- and PhO^- is accounted for by the difference in softness between the nucleophiles; the more polarizable thiolate ion tends to undergo the S_N reaction while the more basic phenolate ion tends to abstract the proton leading to the E_B reaction.

Experimental

All the NMR spectra were recorded in tetrachloromethane. The chemical shifts for ^1H and ^{19}F NMR are given in δ ppm downfield from tetramethylsilane and upfield from 1,2-difluorotetrachloroethane, respectively.

Reaction of Trifluoroethyl Iodide (I) with Sodium Benzenethiolate

The reaction was carried out in the dark. Benzenethiol (3.96 g, 0.036 mol) was added to a stirred suspension of sodium hydride (0.86 g, 0.036 mol) in DMF (30 ml). After the addition, the mixture was stirred at room temperature for 30 min. A solution of iodide I [8] (6.30 g, 0.030 mol) in DMF (10 ml) was then added to the thiolate solution over a 30-min period. After an additional 2 h at room temperature, the mixture was poured into water, and the aqueous mixture was extracted twice with ether. The combined ether extracts were washed with a 5% aq. NaOH and dried ($MgSO_4$). The ether was evaporated and the residue was distilled to give II (4.09 g, 71%) b.p. 79-80°C/20 mmHg (cited [2] b.p. 62-63°C/5.5 mmHg);

^{1}H NMR, δ 3.35 (q, J=9 Hz, 2H), 7.1-7.6 (m, 5H); ^{19}F NMR, δ -0.8 (t, J=9 Hz). Analysis: Found: F, 29.7%, $C_8H_7F_3S$ requires F, 29.7%.

Reaction of Trifluoroethyl Iodide (I) with Sodium Phenolate

The reaction was carried out in a sealed tube. Phenol (4.23 g, 0.045 mol) was added to a stirred suspension of sodium hydride (1.08 g, 0.045 mol) in DMF (45 ml). After an additional 30 min at room temperature, iodide I (6.30 g, 0.030 mol) was added and the tube was sealed. The mixture was stirred at 80°C for 20 h and then cooled. The mixture was poured into water and the aqueous mixture was extracted twice with ether. The combined ether extracts were washed with a 5% aq. NaOH and dried ($MgSO_4$). The amount of remaining iodide I was determined by analytical GC (20% PEG 20 M, 7 ft.X 1/6 in.) using benzene as the internal standard. Evaporation of the ether gave an oily residue. Yield of each component in the residue described above was determined by ^{19}F NMR using $(CFCl_2)_2$ as the reference for IV and V and by ^{1}H NMR using diethyl maleate as the reference for VI.

Each component was then separated by a combination of fractional distillation and column chromatography as follows. Fractional distillation of the oily residue afforded the three fractions (A, B, and C).

Fraction A, b.p. 85-87°C/60 mmHg; Product III; ^{1}H NMR,δ 4.21 (q, J=8.3 Hz, 2H), 6.7-7.4 (m, 5H); ^{19}F NMR δ 6.47 (t, J=8.3 Hz). Analysis: Found: F, 32.4%. $C_8H_7F_3O$ requires F, 32.4%.

Fraction B, b.p. 62-66°C/3 mmHg. The ^{1}H NMR spectrum showed that this fraction consisted of IV and V (*E* and *Z*). Thus the fraction was subjected to column chromatography on silica gel using hexane as an eluent giving pure IV and a mixture of (*E*)- and (*Z*)-V successively; Product IV: MS, M^+ (m/e) 284 (IV requires 284); ^{1}H NMR,δ3.64 (t, J=9.6 Hz, 2H), 7.0-7.6 (m, 5H), ^{19}F NMR,δ1.07 (t, J=9.6 Hz); (*E*)- and (*Z*)-V: GC-MS, 264 for the *E*-isomer and 264 for the *Z*-isomer (both isomers require 264); IR (film), 1680 cm^{-1} (C=C-F); (*E*)-V: ^{1}H NMR δ 5.23 (d, J=1.9 Hz, 1H), 7.0-7.6 (m, 5H); ^{19}F NMR, δ 2.13 (d, J=1.9 Hz); (Z)-V: ^{1}H NMR, δ 4.73 (d, J=26.3 Hz, 1H), 7.0-7.6 (m, 5H); ^{19}F NMR, δ 4.94 (d, J=26.3 Hz).

Fraction C, b.p. 122-130°C/0.14 mmHg; Product VI: MS, M^{+} (m/e) 338 (VI requires 338); IR (film), 1645 cm^{-1} (C=C-H); ^{1}H NMR, δ5.00 (s, 1H), 6.8-7.4 (m, 10H).

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