Electrochemical Fluorination of *S*-Methylthioglycollic Acid Chloride[1]

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Perfluoroalkyl sulfur pentafluorides, R_fSF_5, react with unsaturated fluorocarbon derivatives to add $R_F\cdot$ and $F\cdot$ across the double bond,[2,3] as shown in Equations 1 and 2.

$$CF_3SF_5 + CF_3CF{=}CF_2 \longrightarrow C_4F_{10} \text{ isomers} \qquad (1)$$

$$CF_3SF_5 + CF_3N{=}CF_2 \longrightarrow (CF_3)_3N \qquad (2)$$

In hopes of extending the scope of this reaction to more useful R_F groups, it was decided to investigate the reaction of SF_5CF_2COF under similar conditions. Haszeldine[4] has shown that electrochemical fluorination of thioglycollic acid gives an extremely low yield of SF_5CF_2COF; however, since dialkyl sulfides have been found to cleave during this process to give good yields of R_FSF_5,[5,6] it was thought that the desired compound might be obtained by electrochemical fluorination of CH_3SCH_2COCl. The absence of active hydrogens such as —COOH and —SH in this compound would be expected to improve cell performance over that shown by thioglycollic acid. The results of the fluorination of CH_3SCH_2COCl are reported in this paper.

Identification of the materials obtained by fractionation of the crude cell product after conclusion of the run showed that although considerable cleavage had occurred, loss of the methyl group alone had not taken place. The two products found in greatest abundance were CF_3SF_5 and $(CF_3)_2SF_4$. A large fraction was obtained which had values (b.p. 14–20°, mol. wt. 211–228) near those reported for SF_5CF_2COF (b.p. 22°, mol. wt. 224), but by chromatographic separation it was found that this material was merely a mixture containing $(CF_3)_2SF_4$ and smaller amounts of unidentified incompletely fluorinated substances.

Two compounds were isolated which largely retained the original structure. These were $CF_3SF_4CF_2CF_3$ and $CF_3SF_4CF_2COF$, each representing about 7% of the total cell product. These were identified by infrared and nuclear magnetic resonance (NMR) spectra, and by analysis of the methyl ester of the latter. Retention of the entire structure in $CF_3SF_4CF_2COF$ is rather surprising, and indicates that fluorocarbon acids containing sulfur as well as those containing nitrogen[7] can be made by this method, although the yields in both cases are quite poor.

The most novel compound was a liquid (b.p. 88°, m.w. 352) whose analysis corresponded to $C_2F_{14}S_2$, mol. wt. 354. The three possible structures for this formula are $CF_3SF_4CF_2SF_5$ (I), $SF_5CF_2CF_2SF_5$ (II), and $CF_3SF_4SF_4CF_3$ (III). The first can be eliminated on the basis of the NMR spectrum, which showed all the fluorines on carbon and 6 or 8 of those on sulfur to be identical. The δ-value for the single C-F peak (a triplet) was -5.5 (ref. CF_3COOH). This is in the normal region for CF_3 attached to SF_4 ($CF_3SF_4CF_2CF_3$ -9.8) and considerably removed from that for CF_2 between CF_3 and SF_4 or SF_5. Chemical shifts for the latter configuration run roughly from +15 to +25, on the basis of information obtained in this laboratory or from the literature,[8] concerning half a dozen compounds of this type. The resonance of the fluorine on sulfur was quite complex, two of the peaks being split into five or seven, but the δ-values of -95.5 and -116 correspond better with SF_4 (-94.8, -123 in $O(CF_2CF_2)_2SF_4$)[8] than with SF_5 (-118.7 to 137.5).[8] Because of the symmetry, presence of CF_3 and SF_5 in the same molecule is prohibited, and structure III, $CF_3SF_4SF_4CF_3$, is therefore the most probable. This is the first reported instance of two vicinal SF_4 groups in a fluorocarbon derivative, and this compound cannot be made by electrochemical fluorination of dimethyl disulfide.[6]

EXPERIMENTAL

The apparatus and procedures for the electrochemical fluorination process have been previously described.[5,6] From 615 g. of CH_3SCH_2COCl, made by methylation of thioglycollic acid with methyl sulfate and conversion to the acid chloride by means of either PCl_3 or $SOCl_2$,[9] a total of 436 g. product boiling above −80° was obtained, including 30 g. recovered as a second phase when the cell was drained after the run. The concentration of solute during the operation was roughly 2 mole %. Fractionation was performed in columns appropriate for the temperatures involved and packed with nickel helices. Although the five principal fractions described below were the only ones identified, forerun and intercuts were relatively large, and small amounts of material boiling as high as 35°/2 mm. were obtained.

Fraction A. Boiling point −23 to −18°, 64 g., mol. wt. 195, chromatographic purity 93%. The infrared spectrum of a center cut was identical with that of CF_3SF_5, b.p. −20°, mol. wt. 196.

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Fraction B. Boiling point 16–20°, 85 g., mol. wt. 219–228; reported[4] for SF_5CF_2COF, b.p. 22°, mol. wt. 224. Since a gas chromatograph showed four to six components over this boiling range a 2 g. sample was quantitatively chromatographed, using a stationary phase of the ethyl ester of Kel-F acid 8114, on Celite. About 75% of this amount, representing approximately 63 g. of the whole fraction, was recovered as one peak, mol. wt. 250, and was identified as $(CF_3)_2SF_4$ by comparison of its infrared spectrum with that of known $(CF_3)_2SF_4$, b.p. 20°, mol. wt. 246. The remainder of the chromatographed material had an average mol. wt. of only 148.

Fraction C. Boiling point 47.5°, 24 g., mol. wt. 297, purity 99%. An infrared spectrum showed all peaks found in the spectrum of $CF_3SF_4CF_2CF_3$, b.p. 47.1°, mol. wt. 296, but also additional lines at 10.80–10.85 and 12.25, and an elemental analysis was therefore made.

Anal. Calcd. for $C_3F_{12}S$: C, 12.2; F, 77.1; S, 10.8. Found: C, 12.4; F, 76.8; S, 11.0.

Fraction D. Boiling point 55°, 39 g., mol. wt. 279 (calcd. for $CF_2SF_4CF_2COF$ 274), purity 83%. An infrared spectrum showed a sharp peak for −COF at 5.27. Because of the impurities present, this compound was converted for analysis to the methyl ester (67% yield) by refluxing with methanol. The ester had b.p. 123°, n_D^{30} 1.3259.

Anal. Calcd. for $C_4H_9H_3O_2$: C, 16.8; F, 59.7; H, 1.1; S, 11.2. Found: C, 17.1; F, 59.0; H, 1.1; S, 10.9.

Principal infrared lines for these two new compounds are: $CF_3SF_4CF_2COF$ 5.27, 7.80, 7.90–7.95, 8.06, 9.70, 10.12 (w), 10.83, 11.32 (w), 11.65–11.80, 12.50, 14.00–14.05, 14.85–14.95; $CF_3SF_4CF_2COOCH_3$ (in CCl_4) 5.60, 6.95, 7.62, 8.00–8.05, 8.17, 8.63–8.73, 9.95, 11.90–12.00, 12.18, 14.50.

Fraction E. Boiling point 87–88°, 10 g., mol. wt. 352, n_D^{28} 1.2964, purity 95%. Refluxing with 30% aqueous KOH did not change the mol. wt. and no sign of reaction was observed. Identified by NMR, as discussed above. Principle infrared lines for this compound are 7.95, 8.63, 10.85–11.05, 11.65–11.75, 12.75, 14.25–14.50.

Anal. Calcd. for $C_2F_{14}S_2$: F, 75.2; S, 18.0; mol. wt. 354. Found: F, 75.1; S, 18.0; mol. wt. 352.

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Structure of the Reaction Product of Phenyl Vinyl Ketone and Hydroxylamine

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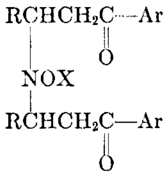
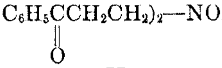
Under the proper conditions, the reaction of certain α,β-unsaturated aryl ketones (or a precursor of the unsaturated ketone) with methoxyamine, substituted hydroxylamines, or hydroxylamine has been reported to yield bisketoamines analogous to structure I.[2]



X = H or CH_3

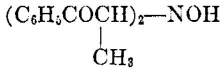
I

In line with this, Auwers and Müller[3] have described a compound melting at 140° to which they assigned the structure bis(β-benzoylethyl)hydroxylamine (II). This material was prepared from the corresponding dioxime, which in turn resulted from the treatment of β-chloropropiophenone with free hydroxylamine and excess alkali. Shortly before this, Danilowa and Danilow[4] had reported a compound melting at 122.5° (obtained from the reaction of a 1:1 ratio of phenyl vinyl ketone and free hydroxylamine) to which they assigned structure III. Both groups reported a compound melting at 153–154° which they described as the dioxime of the respective dicarbonyl compounds (II and III).



$(C_6H_5\underset{\underset{O}{\|}}{C}CH_2CH_2)_2\text{—}NOH$

II



$(C_6H_5CO\underset{\underset{CH_3}{|}}{C}H)_2\text{—}NOH$

III

In the present work, the reaction of phenyl vinyl ketone with hydroxylamine hydrochloride in the presence of sodium acetate produced compounds which were demonstrated to be bis(β-benzoylethyl)-hydroxylamine (II), m.p. 120.5–121°, or the dioxime (m.p. 148–149°) of this compound. With hydroxylamine hydrochloride and sodium acetate the dicarbonyl compound could be readily converted into the dioxime, but repeated recrystallizations from three different solvents failed to raise the melting point of the dioxime (148–149°) to the value reported by Auwers[3] and Danilowa.[4] In order to clarify the structure of these compounds two similar compounds were prepared for a comparative nuclear magnetic resonance study; bis(β-benzoylethyl)methoxyamine (IV) was produced in 53% yield from phenyl vinyl ketone and methoxyamine hydrochloride and bis[β-(p-methoxybenzoyl)ethyl]-

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