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SHORT COMMUNICATION

The Thiolate Anion as a Nucleophile
Part V*. Reactions of Ethanedithiol

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It has recently been reported that a polymer was formed in the reaction of ethanedithiol with hexafluorobenzene, using N,N-dimethyl-formamide as solvent [2]. As a continuation of the previous studies in this series on the reactions of thiolate anions with various halogenated benzene derivatives, the reactions of ethanedithiol with hexafluorobenzene were examined. The reaction conditions have been described previously [1]. The solvent used was a mixture of varying proportions of pyridine and ethylene glycol.

Although a polymer was isolated in most reactions, it has been possible to optimize the conditions to give a relatively small yield of a monomeric product, which could not be increased by using a more dilute solution.

$$C_6F_6 + 2HSCH_2CH_2SH \longrightarrow C_6F_4(SCH_2CH_2SH)_2 + 2HF$$

It was not possible to isolate the compound $C_6F_5SCH_2CH_2SH$, although this has recently been prepared from pentafluorothiophenol and ethylene sulfide [3]. Compounds of the type C_6F_5SR readily reacted with a mole of the RS^- anion to form p-$(RS)_2C_6F_4$, and in some cases the reaction of the RS^- anion with hexafluorobenzene gave only $C_6F_4(SR)_2$ [4]. Similarly 2-mercaptoethanol reacted with hexafluorobenzene to form the sulfur bonded analog p-$(HOCH_2CH_2S)_2C_6F_4$ [5].

The mass spectrum of the monomer showed a weak peak corresponding to the molecular ion at m/e 334. The most abundant peak corresponded to $C_2H_5S^+$ (m/e 61). Initial fragmentation corresponded to loss of SC_2H_4 from the molecular ion.

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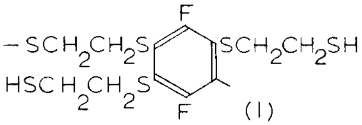
*For Part IV, see ref. 1.

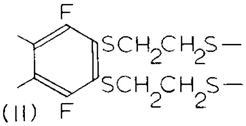
$$C_6F_4(SCH_2CH_2SH)_2^{+\cdot} \longrightarrow C_8F_4S_3H_6^{+\cdot} + SC_2H_4$$

$$C_8F_4S_3H_6^{+\cdot} \longrightarrow C_6F_4S_2H_2^{+\cdot} + SC_2H_4$$

The infrared spectrum showed an S-H band at 256w cm^{-1} and C-S bands at 684m and 620m cm^{-1} ($\nu S\text{-}CH_2$) and 510vw cm^{-1} (ν C-S ring), similar assignments have been made in analogous compounds [6]. In the fluorine NMR spectrum a singlet, half peak width 1.2 Hz, was observed at 134.7 p.p.m. (D_6 acetone solvent, $FCCl_3$ external standard). The fluorine NMR spectra of the compounds p-$(RS)_2C_6F_4$, R=Me, Ph, showed only a singlet at 130-135 p.p.m.[4], so it can be concluded that the structure is p-$(HSCH_2CH_2S)_2C_6F_4$. Two distinct methylene groups of equal intensity and an SH group (2.90 p.p.m.) were found in the proton NMR spectrum. One methylene group was observed as a triplet at 3.20 p.p.m., J(H-H) 7.5 Hz.. Superficially two triplets were observed for the other methylene group at 2.74 p.p.m., J(H-H) 8.0 Hz., and 2.70 p.p.m., J(H-H) 8.9 Hz.. These may be part of a second order spectrum. The methylene protons in $C_6F_5SCH_2CH_2SH$ were observed as an A_2B_2 spectrum [3].

The simplest "polymer", $C_6F_5SCH_2CH_2SC_6F_5$, which has been prepared from $(C_6F_5S)_2Pb$ and ethylene dichloride [7], should be obtained when both SH groups of the dithiol reacted with separate molecules of hexafluorobenzene. Chemical analysis of the polymeric product obtained corresponded to the unit I. The two fluorine atoms remaining on the benzene nucleus are probably <u>para</u> to each other, consistent with previous observations [1,4]. The chemical analysis of the previously reported polymer corresponded to a unit such as II [2]. The highest relatively intense peak in the mass spectrum of the polymer occurred at m/e 480, corresponding to a structural unit such as III.


(I)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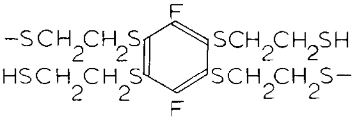
(III)

Differential thermal analysis of the monomer showed a sharp endotherm at its melting point, followed by thermal decomposition starting at 225°. The polymer showed two endotherms at 144° and 152°, but did not melt under 300°.

EXPERIMENTAL

The basic details of the experimental method have been described [1]. Maximum yield of the monomeric product was obtained using 10 mmoles C_6F_6 in 2 ml pyridine, to which 10 mmoles $HSCH_2CH_2SH$ and 11.2 mmoles NaOH in 10 ml ethylene glycol were added at 0°C and kept at 0° for 45 min. before quenching. Only polymeric product was obtained under the same conditions either by using 20 mmoles NaOH (0°C) or 2.5 mmoles NaOH (room temp.). Yield of monomer extracted from the crude product by sublimation, approx. 6%, m.p. 93-95° (Found: C, 35.7; H, 3.08; S, 38.2. $C_{10}H_{10}F_4S_4$ requires C, 35.9; H, 3.01; S, 38.3%). Chemical analysis of the polymeric residue corresponded to the unit I (Found: C, 37.1; H, 2.4. $C_{12}H_{14}F_2S_6$ requires C, 37.1; H, 3.6%) Similar analyses were obtained for other polymeric products.

Infrared spectra were recorded as KBr discs on a Perkin Elmer 457. Proton NMR spectra were obtained on a Varian HR 220, fluorine NMR spectra on a Varian XL 100, and the mass spectra using a Varian MAT-CH7. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, W.Germany and Frau E. Ullrich (Universität Würzburg). DTA data were obtained using a DuPont Thermal Analyser 990.

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