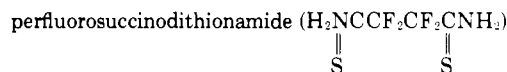


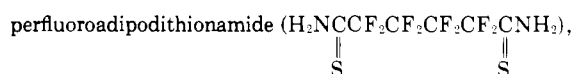
Synthesis of Perfluorosuccinodithionamide and Perfluoroadipodithionamide

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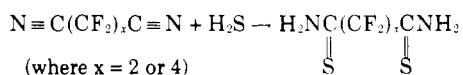
AS PART OF A PROJECT designed to provide certain monomers for the Air Force materials program, two previously unreported fluorine-containing dithionamides have been synthesized. These compounds,



and



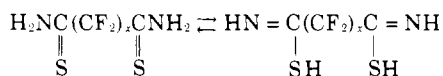
were prepared by reaction of the nitrile with hydrogen sulfide using published methods (1, 2).



Maximum yields were 40 and 39%, respectively.

The attempted preparation of perfluoroglutardithionamide was unsuccessful. The reaction was run in a stainless steel autoclave at 25° to 40° C. both undiluted and in benzene-diethylamine. The reaction was also carried out in glass at 0° in both triethylamine-pyridine and methanol-picoline-diethylaminoethanol.

An infrared spectrum (Nujol mull) of perfluorosuccinodithionamide showed absorption peaks at 3.03 and 3.18 μ , probably due to N-H stretching. Absorption in the Amide II region was observed at 6.08 and 6.14 μ . Absorption between 8 and 9 μ was also observed and was probably due to C-F stretching. In general, the infrared spectrum of perfluoroadipodithionamide showed similar peaks in the amide regions. Absorption was observed at 3.02-3.08 (doublet), 3.20 and 6.15 μ . Peaks due to C-F stretching again occurred in the 8-9 micron region. No peaks were found in the S-H region, indicating that the tautomeric equilibrium:



is displaced to the left, favoring the thioketo form.

EXPERIMENTAL

Melting points were taken on a Mel-temp capillary melting point apparatus. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Perfluorosuccinodithionamide. Picoline (1.9 grams, 0.020 moles), diethylaminoethanol (0.9 grams, 0.0008 moles), methanol (25 ml.) and perfluorosuccinonitrile (5.0 grams, 0.032 moles) were placed in a 3-neck, 200-ml. flask fitted with a stirrer, gas inlet, and outlet tube. The flask contents were cooled in an ice-salt bath and hydrogen sulfide was bubbled into solution. After 30 minutes the formation of solid material was observed, but addition of hydrogen sulfide was continued for three hours. Light yellow crystals (1.6 grams) were removed by filtration. The reaction was continued an additional three hours and another batch of crystals (0.6 grams) was collected. The filtrate was acidified (pH 1) and 0.6 grams material precipitated. The total yield was 2.8 grams (40%), m.p. 112-114°. After one recrystallization white crystals were obtained.

Anal. Calcd. for $\text{C}_4\text{H}_4\text{F}_4\text{N}_2\text{S}_2$ (m. wt. calcd. 222.22): C, 21.82; H, 1.83; F, 34.52; N, 12.73; S, 29.10. Found: C, 21.57; H, 2.03; F, 34.37; N, 12.49; S, 29.30.

Perfluoroadipodithionamide. Triethylamine (1.5 grams, 0.014 moles), pyridine (30 ml.) and perfluoroadiponitrile (3.0 grams, 0.012 moles) were reacted at room temperature with hydrogen sulfide according to the method described by Fairfull, Lowe, and Peak (1). The equipment used was identical to that described above. Addition of hydrogen sulfide was maintained for 19 hours, after which the reaction mixture was poured over ice, precipitating a light yellow solid. The solid was filtered and dried, giving 1.5 grams (39%) of crude material which was recrystallized from ethanol-water to give pure perfluoroadipodithionamide, m.p. (dec.) 174-179°.

Anal. Calcd. for $\text{C}_6\text{H}_4\text{F}_8\text{N}_2\text{S}_2$ (m. wt. calcd. 322.24): C, 22.50; H, 1.26; F, 47.47; N, 8.72; S, 20.02. Found: C, 22.32; H, 1.13; F, 47.20; N, 8.75; S, 19.96.

LITERATURE CITED

- (1) Fairfull, A., Lowe, J., Peak, D., *J. Chem. Soc.* (1952), p. 742.
- (2) Schmidt, U., *Ber.* **92**, 1171 (1959).

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