the solid thus obtained from 95% ethanol gave a picrate, m.p. 135–136°, as the major fraction. This picrate was subsequently shown to be the derivative of 6-methyl-6,7-dihydro-1,5-pyrindine (IIb).

Anal. Calcd. for $C_{15}H_{14}N_4O_7$: C, 49.72; H, 3.86. Found: C, 49.73; H, 3.93.

Two grams of this picrate was converted to the free base (IIb) by treatment with concd. ammonium hydroxide. The free base (IIb) was dried over sodium hydroxide and distilled giving a colorless liquid, b.p. 208° (751 mm.), n_D^{23} 1.5239, d_{20}^{20} 1.0007.

Anal. Calcd. for $C_9H_{11}N$: neut. equiv. 133.2. Found: neut. equiv. 132.1.

A *styphnate* derivative of the amine (IIb) was made m.p. 156–157°.

Anal. Calcd. for $C_{15}H_{14}N_4O_8$: C, 47.62; H, 3.70. Found: C, 47.79; H, 3.72.

Another picrate, m.p. 147–149°, was obtained in smaller amounts during the fractional recrystallization mentioned above. This picrate was subsequently shown to be the derivative of 5-methyl-6,7-dihydro-1,5-pyrindine (IIa). A mixed melting point with the petroleum base picrate previously isolated,[1] m.p. 147–149°, showed no depression. The infrared spectra of the petroleum base picrate (m.p. 147–149°) and the synthetic base picrate were identical.

Anal. Calcd. for $C_{15}H_{14}N_4O_7$: C, 49.72; H, 3.86; N, 15.46. Found: C, 49.88; H, 4.08; N, 15.40.

Conversion of 100 mg. of this picrate to the free base (IIa) by treatment with ammonium hydroxide yielded a liquid which, after drying and distillation, boiled at 207–208° (746 mm.).

A *styphnate* derivative of IIa was prepared by adding about 30 mg. of the amine (IIa) to about 1 cc. of a saturated solution of styphnic acid in 95% ethanol. Recrystallization from 95% ethanol yielded small yellow needles, m.p. 172–173.5°.

Anal. Calcd. for $C_{15}H_{14}N_4O_8$: C, 47.6; H, 3.7. Found: C, 47.5; H, 3.8.

6,7-Dihydro-1,5-pyrindine (X) *from 4a-carbethoxyoctahydro-1,5-pyrindine* (IX). One-half gram of the aminoester (IX), prepared according to Albertson,[7] was slowly distilled through 30% palladium-on-charcoal which was held between 350–360°. As before, hydrogen was used as a carrier gas for the vapors. The reaction was complete in 48 hr. The product was converted to a picrate derivative and after two recrystallizations from 95% ethanol gave 0.28 g. (31%) of picrate, m.p. 180–181°. This picrate showed no melting point depression on admixture with an authentic sample of the picrate derivative of X.

Alternate synthesis of 5- and 6-methyl-6,7-dihydro-1,5-pyrindine (IIa *and* IIb). Dieckmann condensation of diethyl β-methyladipate afforded the β-ketoester mixture (III and VI) b.p. 117–119° (16 mm.); (lit.,[2] m.p. 107–108°, 11–12 mm.). This mixture was monocyanoethylated by adding 17 g. of acrylonitrile (0.32 mole) slowly with stirring to 52 g. of the mixture of β-ketoesters (III and VI) (0.30 mole) in 60 g. of 1,4-dioxane containing 4.2 g. of Triton B. The temperature of the reaction mixture was maintained between 30–40° by external cooling during the addition. After 45 min. the addition was complete and the reaction mixture was stirred an additional hour. After adding about 40 cc. of diethyl ether to the reaction mixture it was washed briefly with 5% hydrochloric acid, then once with water. After drying over sodium sulfate, the solvents were removed *in vacuo* and the residue distilled giving 48 g. of colorless material (73%), b.p. 136° (0.5–1 mm.), n_D^{20} 1.4642.

Anal. Calcd. for $C_{12}H_{17}O_3N$: C, 64.57; H, 7.62. Found: C, 64.58; H, 7.73.

The monocyanoethylated product (IV and VII) obtained above was then reductively cyclized as in the preparation of octahydro-1,5-pyrindine.[1] After removal of Raney nickel and ethanol, the product was distilled giving a colorless liquid, b.p. 151° (35 mm.).

(7) N. F. Albertson, *J. Am. Chem. Soc.*, 72, 2594 (1950).

Anal. Calcd. for $C_{12}H_{21}NO_2$: neut. equiv. 211.3. Found: neut. equiv. 212.7.

The aminoester mixture (V and VIII) was dehydrogenated and decarbethoxylated in the manner described in the preparation of X. The product obtained by this procedure was chromatographed on a preparative gas chromatographic unit[8] and the amines (IIa and IIb), which occurred as a single peak, were collected. This material was treated with equimolar quantities of picric acid in 95% ethanol. The melting point of the crude picrate mixture which resulted was 121.5–127.5°. This corresponds to an 80:20% mixture of 135–136:147–149° melting picrates according to a previously prepared melting point mixture diagram of the two isomers. After four recrystallizations of a portion of this crude picrate mixture 146 mg. of picrate, m.p. 135–136°, was obtained which did not depress the melting point of the 135–136° melting picrate obtained by the enamine route. The filtrates from the recrystallizations were combined and solvent removed under reduced pressure. After twelve recrystallizations of the crude picrate residue which remained, 24.3 mg. of picrate, m.p. 147–149°, was obtained. This picrate, m.p. 147–149°, showed no melting point depression on admixture with the picrate, m.p. 147–149°, obtained by the enamine route. The filtrates from the last recrystallizations were combined and solvent removed under reduced pressure. The residual crude picrate, after drying, consisted of 106 mg. and melted at 113–117°. According to the melting point mixture diagram of the two isomeric picrates this residue corresponded to a 45:55% mixture of 135–136°:147–149° melting picrates.

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(8) See ref. 1 for a description of the gas chromatographic apparatus.

Six and Twelve Carbon Fluorocarbon Derivatives of Sulfur Hexafluoride

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Electrochemical reactions of organic sulfides in anhydrous hydrogen fluoride have received some attention in recent years.[1] This work extends these investigations to include hexyl and phenyl sulfide. As in previous work, the compounds R_fSF_4, $(R_f)_2SF_4$, R_fF and R_f-R_f (where R_f is C_6F_{13} or cyclo C_6F_{11}) were isolated or detected. The yields of isolable product were low for phenyl sulfide. Many of the above products that were liquids at 25° were purified by preparative scale chromatog-

(1) (a) A. F. Clifford, H. K. El-Shamy, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.* 2372 (1953). (b) W. A. Severson, T. J. Brice, and R. I. Coon, 128th Meeting ACS, Minneapolis, Minn., Sept. 11–16, 1955. (c) R. Dresdner, *J. Am. Chem. Soc.* 79, 69 (1957). (d) F. W. Hoffman, T. C. Simmons, R. B. Beck, H. V. Holler, T. Katz, R. J. Koshar, E. R. Larsen, J. E. Mulvaney, F. E. Rogers, B. Singleton, and R. S. Sparks, *J. Am. Chem. Soc.* 79, 2424 (1957). (e) R. D. Dresdner and J. A. Young, *J. Am. Chem. Soc.* 81, 574 (1959). (f) J. A. Young and R. D. Dresdner, *J. Org. Chem.* 24, 1021 (1959). (g) R. N. Haszeldine and F. Nyman, *J. Chem. Soc.* 2684 (1956).

raphy in one-inch columns packed with hexadecane on an inert support.[2] The products that were solids at 25° were further purified by the method of Tatlow[3] using hot heptane for the recrystallizations.

Freon 112, 1,2-difluoro-1,1,2,2-tetrachloroethane, was an excellent solvent for the solid products and molecular weights were determined by the freezing point depression method in this medium. The molal freezing point constant was determined using perfluorodicyclohexyl as the standard. Raoult's law was observed at concentrations up to 0.06 molal. Semi-quantitative purity estimations of all the products reported were determined by vapor phase chromatography using in all cases for the liquids both a polar substrate such as the ethyl ester of Kel-F acid 8114 and a nonpolar substrate such as hexadecane. These were run at various flows of nitrogen carrier gas and at temperatures between 80 and 100°. Very significant changes in purity (as determined by the integrated areas under the various chromatographic peaks) were noted before and after preparative scale purifications on narrow boiling fractions obtained by fractionation. In all cases only minor impurity components, 1–2%, were observed in the purified materials.

Both compounds, hexyl and phenyl sulfide, yielded some extremely high boiling (210–240° at 0.1 mm.) resinous products. One such sample was used to prepare a chromatographic column on which the purity of the purified solid products could be estimated. These products were dissolved in Freon 113 and injected into the unit operated at 200°.

The electrochemical cell and operation procedures were very similar to those described previously[1d,e] although minor alterations were made in the overhead reflux condenser to prevent the perfluorocyclohexane from clogging. Products accumulated at two points: in the cold traps at the end of the gas train and as the less volatile fluorocarbon layer that accumulated at the bottom of the cell. In each operation the cell-retained products were siphoned from the cell into a polyethylene separatory funnel and separated from a small layer of hydrogen fluoride. This fluorocarbon material was neutralized with dilute aqueous sodium bicarbonate, dried, filtered, and fractionated in appropriate equipment.

EXPERIMENTAL

Results from hexyl sulfide. Four hundred and seventy grams of $(C_6H_{13})_2S$ (2.3 moles) was electrolysed at 4.6 volts and at about 10 amperes and yielded 1041 g. of products during 340 hr. of operation. The main product by weight, 411 g., was a mixture of C_6F_{14} isomers, b.p. 57.2–58.0°,

m.w. 338, $n_D^{25°}$ 1.2501; reported[4] for n-C_6F_{14}, b.p. 57.32° $n_D^{22°}$ 1.2515. This material was analysed by chromatography using a 40-foot column with hexadecane on inert, acid washed Celite; the main component appeared to present as 75% by weight while another peak representing 20% seemed to be isomeric and about 5% was probably nonisomeric impurity. An aliquot of the material was subjected to preparative scale chromatographic purification in which all but a small amount of the apparent isomeric impurity was removed. The refractive index at 25° of this purified material was 1.2498.

The second largest fraction by weight amounted to 234 g. and boiled between 117.8 and 118.5°. On chromatographic analysis this material demonstrated a main peak of about 74% by weight and seven other impurity peaks. An aliquot of this was purified chromatographically until all but about 1% of the impurities were removed. It had the correct analysis for perfluorohexylsulfur pentafluoride, $C_6F_{13}SF_5$, calcd. MR_D 41.28, mol. wt. 448; observed values: MRp 41.77, n_D^{25} 1.2829, d_D^{25} 1.8910, b.p. 118.2°, m.p. −31.5 to −30.5°, mol. wt. 446.

Anal. Calcd. for $C_6F_{13}SF_5$: F, 76.60; S, 7.18. Found: F, 76.7; S, 6.99.

A fractionation flat was encountered in the vacuum fractionation of the higher boiling materials which condensed to a slush. This occurred at 65° and about 1 mm. The fraction amounted to 100 g. It was filtered at 0°. The residues began to melt at 50°. After several recrystallizations from hot heptane the white crystals reached a constant melting point of 71–72°. A purified sample was analysed chromatographically using a stationary phase of the highest boiling resin recovered from the cell residues. Only about a 2% impurity was detected under the conditions of the tests. Molecular weights of the compounds were determined. About 50 g. of the material, which analysed correctly for perfluorodihexylsulphur tetrafluoride, was recovered, calcd. mol. wt. 746; found mol. wt. 725, 730, m.p. 71–72°.

Anal. Calcd. for $C_{12}F_{30}S$: F, 76.4; S, 4.30. Found: F, 76.8; S, 4.41.

At 85°, 51 mm., a fraction amounting to 51 g. was obtained that by analogy with other work should have been $C_{12}F_{26}$. It had a wide melting range beginning at 10° and showed three equal peaks when it was analysed on the fluorocarbon resin.

Results from phenyl sulfide. Four hundred grams of phenyl sulfide (2.1 moles) electrolysed at 5.1 volts and about 10 amperes yielded 925 g. of products during 267 hr. of operation. The effluent gas product was mainly perfluorocyclohexane, which amounted to 375 g. of crude product, purified by sublimation. The crude material was placed in a large stoppered glass filter funnel. As perfluorocyclohexane condensed on the walls of the funnel the trapped liquid impurities passed through the filter and were removed *via* a stopcock. The process was repeated until no more liquid was collected. The vapor above the subliming solid had a composition of 99.3% of one component, as analysed chromatographically. The purified material had a molecular weight of 300. Three hundred grams was recovered.

A fraction amounting to 30 g. was recovered in the fraction that boiled between 109.5 and 110.5°. Chromatographic purification yielded a product in which the main component was 98.9%. Analysis showed this material to be perfluorocyclohexylsulphur pentafluoride, c-$C_6F_{11}SF_5$, calcd., mol. wt. 408, MR_D 39.08; observed mol. wt. 404, n_D^{25} 1.3041, d_4^{25} 1.9530, MR_D 39.67, b.p. (micro) 110.5°, m.p. glass.

Anal. Calcd. for $C_6F_{16}S$: F, 74.40; S, 7.83. Found: F, 74.00; S, 7.87.

A second fraction was isolated at 88° and 35 mm. which amounted to 117 g. of a slush. The slush was filtered, washed with water and acetone, and dried. The crude material

(2) T. M. Reed, J. F. Walter, R. Cecil, and R. D. Dresdner, *Ind. and Eng. Chem.* **51**, 271 (1959).

(3) G. B. Barlow and J. C. Tatlow, *J. Chem. Soc.* 4695 (1952).

(4) A. M. Lovelace, W. Postelnek, and D. A. Rausch, *Aliphatic Fluorine Compounds*, Reinhold Publishing Corp., New York, 1958, page 74.

melted at 65.2–67.2°. Chemical analysis showed only a trace of sulfur. The material was recrystallized from boiling heptane several times to a constant melting point of 75.5–76.0°. This agrees with the reported[3] value for perfluorodicyclohexyl. This compound was analysed by vapor phase chromatography using the fluorocarbon resin column and appeared to be 99% one component. The infrared spectrum of a melt agreed exactly with that for perfluorodicyclohexyl as determined by Tatlow.[3] The carbon and fluorine analyses of the compound were within 0.3% of the calculated values.

A final fraction was isolated at 126° and 37 mm. This was a slush amounting to only 12 g. Six grams of crude filtration residue melted at 65–67.5°. It decomposed at 180 to 200° and accordingly could not be analysed by vapor phase chromatography. At lower temperatures the development time was so long that only one broad low peak was obtained. Consequently, the material was recrystallized from hot heptane to a constant melting point of 90–91°. Analysis and molecular weight by the cryoscopic method in Freon 112 indicated that the purified material was the perfluorodicyclohexylsulphur tetrafluoride, $(C_6F_{11})_2SF_4$, mol. wt. 670; observed mol. wt. 660, m.p. 90–91°.

Anal. Calcd. for $C_{12}F_{26}S$: F, 73.73; S, 4.77. Found: F, 73.38; S, 4.81.

In both of the reported operations considerable material boiling well above the highest boiling products reported was obtained. This is not uncommon in low voltage electrolyses in hydrogen fluoride.

Better yields of the cyclic derivatives would probably have been obtained if the starting sulfide had been the cyclohexyl sulfide instead of the phenyl derivative. Further evidence for this statement is apparent from the fact that, in general, unsaturated compounds even though resonance stabilized tend to run poorly in the cells and frequently cause corrosion of the electrodes. Although the corrosion in this case was not as severe as that generally encountered with unsaturated materials, nickel bearing compounds were found in the cell in some quantity. Furthermore, they were observed to react with water quite violently with the evolution of heat and sparks.

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The Interaction of Some Arylamines with Dowex-50 in 1,2-Dimethoxyethane

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The use of ion exchange resins has been largely limited to aqueous solutions or polar solvents. To a certain extent this is because of the generally higher degree of resin swelling than that which occurs in nonpolar solvents. It is not necessary for a resin to swell in order to exhibit an appreciable ion exchange capacity. However, swelling helps to accommodate larger exchanging particles (molecules or ions).[1] Many organic compounds show limited solubilities in polar solvents or react with them. Studies show that Dowex-50 is effective in removing various aromatic amines from a solution of the amine in anhydrous 1,2-dimethoxyethane.[2] The degree of swelling of the ion exchange resin is, as might be expected, a function not only of the solvent but also of the extent to which the resin is crosslinked. The rate of adsorption of the amine is a function of the steric requirements of the amine as well as the degree of swelling and hence the porosity of the resin. By selectively swelling the ion exchange resin it is possible to get a "molecular sieve" effect where the rate and extent of adsorption is sharply dependent upon the steric requirements of the amine. The use of Dowex-50 in 1,2-dimethoxyethane was decided upon as a result of an investigation of the degree of swelling of Dowex-50 in a number of anhydrous ethers.

As can be seen from an examination of Table I, the resin is not only swollen to a rather high degree in 1,2-dimethoxyethane, but there is also a strong variation of the degree of swelling with the extent of divinylbenzene crosslinkage.

TABLE I

SWELLING OF DRY DOWEX-50 IN THE HYDROGEN FORM

Cross linkage (% Divinyl-benzene)	Solvent	Max. Swelling, % vol.	Time, hr.
4	Water	215	0.25
4	$CH_3OCH_2CH_2OCH_3$	110	0.5
4	$CH_3(OCH_2CH_2)_2OCH_3$	92	1
4	1,4-Dioxane	100	24
8	Water	115	0.25
8	$CH_3OCH_2CH_2OCH_3$	93	2
8	$CH_3(OCH_2CH_2)_2OCH_3$	80	2
8	1,4-Dioxane	75	24
12	Water	85	0.25
12	$CH_3OCH_2CH_2OCH_3$	60	2
12	$CH_3(OCH_2CH_2)_2OCH_3$	55	2
12	1,4-Dioxane	35	48

It is seen that the degree of swelling decreases with increasing crosslinkage in each case. The rate of swelling in dioxane is slow, requiring forty-eight hours for maximum swelling in the case of the 12% crosslinked resin. The degree of swelling for 1,2-dimethoxyethane and also dimethyl ether of diethylene glycol is appreciable and differs markedly for resins of different crosslinkage. Moreover the time required for attainment of maximum swelling is reasonable.

Table II summarizes the results of the batchwise extraction of some arylamines by Dowex-50 preswollen in 1,2-dimethoxyethane. The amine uptake is stated as milliequivalents of amine adsorbed per gram of resin (dry basis).

(1) R. Kunin, G. W. Bodamer, *Ind. Eng. Chem.*, **45**, 2577 (1953).

(2) Ansul Ether-121. All glycol ethers were supplied by Ansul Chemical Co., Marinette, Wis.