cess of ammonia maintained at −80°. After 1 hour, the excess of ammonia was evaporated and the remainder extracted with ether and subsequently with absolute ethanol. Evaporation of the solvents yielded 12.2 g. of XI; white needles from acetone. No melting was observed when a sample was heated under the usual conditions at the Fisher-Johns plate, since the product was converted by heat with loss of ammonia into a higher molecular weight condensation product.

Anal. Calcd. for $C_4H_3F_4N_3$: C, 28.35; H, 1.78; F, 44.94; N, 24.84. Found: C, 29.28; H, 2.50; F, 43.63; N, 24.22.

2,2,3,3-Tetrafluoro-3-*N'*-phenylamidinopropionanilide (XVII).—To a solution of 5.9 g. (0.064 mole) of aniline in 80 ml. of dry ether, 3 g. (0.012 mole) of VIII was added dropwise, with stirring, at 0°. After stirring for several hours, the aniline hydrochloride was removed. Evaporation of the ether yielded a solid reaction product contaminated with aniline. This material was dissolved in ether and washed with 2 *N* hydrochloric acid. Upon evaporation of the ether, 1.5 g. of solid material was obtained which, after extraction with boiling ligroin, melted at 166–168°. Recrystallization from ethanol–water (1:1) yielded XVII, white needles, m.p. 168°.

Anal. Calcd. for $C_{16}H_{13}F_4N_3O$: N, 12.38. Found: N, 12.07, 11.94.

Cooling of the ligroin extract resulted in the precipitation of white crystals, m.p. 130–132°, presumably 2-*N*-phenylamino-5-*N*-phenylimino-3,3,4,4-tetrafluoro-1-pyrroline (XVI).

3,4-Dichloro-2,2,5-trifluoropyrrolenine (XXV).—Pentachloropyrrolenine[16] (112 g.) was allowed to react with excess silver fluoride (300 g.) at 135° for 2 hr. The reaction product was distilled in a moderate vacuum to yield, in addition to 16.5 g. of a liquid fraction, 39.6 g. (44%) of XXV. Recrystallization of the latter from petroleum ether (b.p. 90–97°) gave white needles, m.p. 107.5–108.5°.

Anal. Calcd. for $C_4Cl_2F_3N$: C, 25.32; Cl, 37.27; F, 29.98; N, 7.43. Found: C, 25.38; Cl, 37.19; F, 28.57; N, 8.39.

The liquid material boiled under atmospheric pressure at 123–125°. Analytical values indicate that this material is *dichloromaleoyl fluoride.*

Anal. Calcd. for $C_4Cl_2F_2O_2$: C, 25.37; F, 20.16. Found: C, 24.96; F, 21.92; N, none.

Acknowledgment.—We are very much indebted to the Olin Mathieson Chemical Corp. for their generous support of this work.

(16) R. Anschütz and G. Schroeter, *Ann.*, **295**, 82 (1896). The literature prescription had to be modified using 5.5 instead of 4 moles of phosphorus pentachloride. Otherwise little or no pentachloropyrrolenine was obtained.

Synthesis of Polyfluorinated Heterocycles by Indirect Fluorination with Silver Fluorides. IV. Fluorothiadiazoles[1,2]

HANSJUERGEN SCHROEDER, RUDI RÄTZ, WILLI SCHNABEL, HENRI ULRICH, EHRENFRIED KOBER, AND CHRISTOPH GRUNDMANN

The Ohio State University Research Foundation, Columbus, Ohio

Received November 21, 1961

The reaction of 2,5-dibromo-1,3,4-thiadiazole with silver fluoride gave 2-bromo-5-fluoro-1,3,4-thiadiazole and isocyanogen tetrafluoride which was also prepared from the respective tetrabromide. 3-Perfluoroalkyl-5-fluoro-1,2,4-thiadiazoles were obtained in a two-step synthesis by reaction of perhalogenated alkylamidines with trichloromethanesulfonyl chloride, and fluorination of the reaction products with silver fluoride, in one case with SbF_3Cl_2 (Swarts mixture).

In the previous publications of this series[2–4] the advantage of using silver fluorides as inorganic fluorinating agents for the preparation of perfluorinated aza-aromatic heterocycles from the appropriate chloro compounds has been demonstrated. It seemed desirable to extend these studies to the synthesis of perfluoro heterocycles containing sulfur in addition to nitrogen. This work concerns the fluorination of certain chlorinated and brominated thiadiazoles.

The reaction of 2,5-dibromo-1,3,4-thiadiazole[5] (I) with silver fluoride did not give the desired difluorinated compound but 2-bromo-5-fluoro-1,3,4-thiadiazole (II). The yield was only 16%, since compound I decomposed to a considerable extent upon treatment with silver fluoride. From the same reaction, besides II a low-boiling by-product was obtained, the analysis of which agreed with the formula of isocyanogen tetrafluoride (III), $F_2C{=}N{-}N{=}CF_2$. For proof of structure, III was prepared by an independent synthesis from isocyanogentetrabromide[6] (IV). Fluorination with SbF_3Cl_2 (Swarts mixture) failed but the conversion was achieved by means of silver fluoride in 23% yield. The samples, the degradation product from the reaction of I with silver fluoride and the product of the reaction of IV with silver fluoride, were identical.

Other attempts to prepare 2,5-difluoro-1,3,4-thiadiazole (V) were also unsuccessful. Compound II could not be converted to V by means of AgF or AgF_2. The reaction of I with SbF_3Cl_2 (Swarts

(1) This article is based on work performed during 1956 and 1957 under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corp., New York, N. Y.

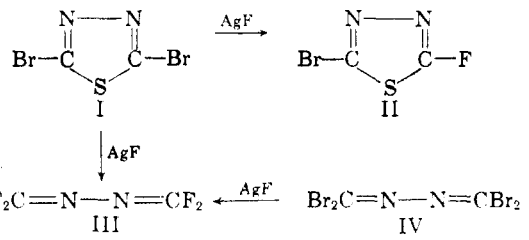
(2) Preceding communication: H. Ulrich, E. Kober, H. Schroeder, R. Rätz, and C. Grundmann, *J. Org. Chem.*, **27**, 2585 (1962).

(3) H. Schroeder, E. Kober, H. Ulrich, R. Rätz, H. Agahigian, and C. Grundmann, *J. Org. Chem.*, **27**, 2580 (1962).

(4) E. Kober, H. Schroeder, R. Rätz, H. Ulrich, and C. Grundmann, *J. Org. Chem.*, **27**, 2577 (1962).

(5) R. Stollé and K. Fehrenbach, *J. prakt. Chem.*, [2] **122**, 306 (1929).

(6) J. Thiele, *Ann.*, **303**, 57, 70 (1898).



I II III IV

mixture) failed to give any product except high-melting resins. No starting material could be recovered by steam distillation. Diazotization of 2,5-diamino-1,3,4-thiadiazole in anhydrous hydrogen fluoride and in 48% aqueous hydrogen fluoride, either in a monel-metal flask or in a polyethylene beaker, led to a brown polymer, insoluble in the common organic solvents.

The difficulties encountered, especially the facile desulfurization of 1,3,4-thiadiazoles upon treatment with silver fluoride, prompted us to shift our investigation to the isomeric 1,2,4-thiadiazole series. For the preparation of suitably chlorinated starting compounds, we utilized a new method for synthesis of 3-alkyl(or aryl)-5-chloro-1,2,4-thiadiazoles from amidines and trichloromethanesulfonyl chloride (VI) recently described by Goerdeler.[7] While his studies were confined to the reaction of alkyl(and aryl)amidines with VI, our objective required the employment of halogen-substituted alkylamidines in this synthesis. In order to find out whether this reaction could be carried out with haloalkylamidines, monochloroacetamidine hydrochloride (VII) was allowed to react with VI in a model experiment, and as desired, 3-monochloromethyl-5-chloro-1,2,4-thiadiazole (VIII) was obtained. Its conversion to 3-trichloromethyl-5-chloro-1,2,4-thiadiazole (IX), an appropriate starting material for a perfluorinated thiadiazole derivative, was achieved in 90% yield by passing gaseous chlorine into a refluxing carbon tetrachloride solution of VIII irradiated with ultraviolet light.

Compound IX was also obtained in a one-step reaction from trichloroacetamidine hydrochloride (X) through the Goerdeler synthesis. The starting compound X was prepared in high yield by the reaction of hydrogen chloride with trichloroacetamidine in ligroin; only impure products were obtained in ether or benzene.

The fluorination of IX was attempted with silver fluoride and with SbF_3Cl_2 (Swarts mixture). Reaction of IX with silver fluoride produced a product that contained two chlorine atoms and two fluorine atoms. Since silver fluoride preferably replaces nuclear bound chlorine, the structure of 3-dichloromonofluoromethyl-5-fluoro-1,2,4-thiadiazole (XI) was assigned to the reaction product. However, the reaction of IX with SbF_3Cl_2 (Swarts mixture) gave another product containing three fluorine atoms and only one chlorine atom. Since SbF_3Cl_2 in general reacts more readily with chlorinated alkyl groups than nuclear chlorine, the product obtained was 3-trifluoromethyl-5-chloro-1,2,3-thiadiazole (XII). Proof of structure was established by replacement of the halogen atom in 5- position with an alkoxy group. As expected XI reacted with sodium ethylate to form 3-dichloromonofluoromethyl-5-ethoxy-1,2,4-thiadiazole (XIII) and XII was converted in the same manner into 3-trifluoromethyl-5-ethoxy-1,2,4-thiadiazole (XIV).

Both compounds XI and XII could be converted into the desired 3-trifluoromethyl-5-fluoro-1,2,4-thiadiazole (XV) by the same method. Refluxing XI with silver fluoride for twenty-four hours replaced the residual chlorine atoms in the methyl group by fluorine to produce XV in 31% yield. The best yield of XV (84%) was obtained by refluxing XII with silver fluoride for four hours. These experiments again demonstrate the advantage of using silver fluoride for replacement of nuclear chlorine as compared to replacement of aliphatic chlorine.

Our results suggested the employment of perfluorinated alkylamidines in the Goerdeler synthesis in order to obtain 5-chloro-1,2,4-thiadiazoles with perfluorinated side chains in 3-position; then only the substitution of one chlorine atom was needed. Heptafluorobutyroamidine hydrochloride (XVI) reacted with VI as expected to give 3-heptafluoropropyl-5-chloro-1,2,4-thiadiazole (XVII). Fluorination of XVII was achieved by means of silver fluoride to produce 3-heptafluoropropyl-5-fluoro-1,2,4-thiadiazole (XVIII). Traces of chlorine in the reaction product were removed by refluxing it with silver fluoride. Thus a combination of the Goerdeler method and our fluorination procedures give good yields of perfluorinated 1,2,4-thiadiazole derivatives in a simple two-step synthesis.

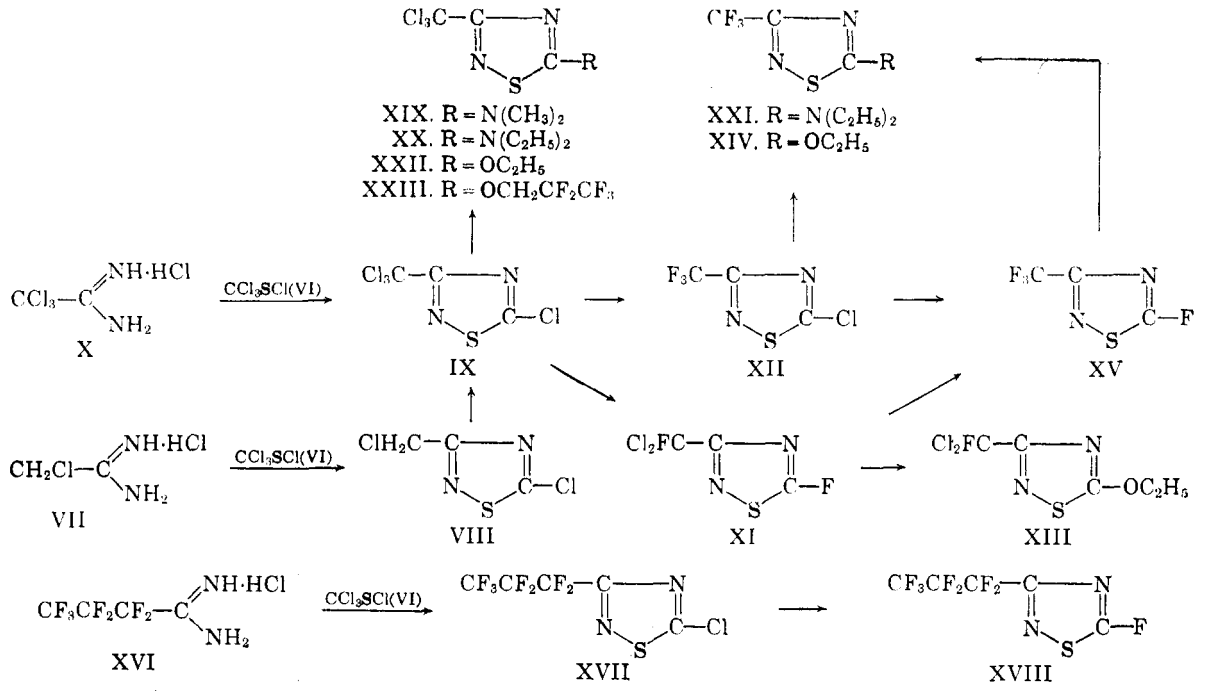
All 5-halo-1,2,4-thadiazoles prepared reacted easily with amines and sodium alcoholates to the corresponding 5-substituted derivatives. Thus the perchlorinated IX was converted into 3-trichloromethyl-5-dimethylamino-1,2,4-thiadiazole (XIX) and 3-trichloromethyl-5-diethylamino-1,2,4-thiadiazole (XX), compound XII gave with diethylamine 3-trifluoromethyl-5-diethylamino-1,2,4-thiadiazole (XXI). In addition to the alkoxy compounds XIII and XIV, 3-trichloromethyl-5-ethoxy-1,2,4-thiadiazole (XXII) and 3-trichloromethyl-5-pentafluoropropoxy-1,2,4-thiadiazole (XXIII) were prepared.

Experimental[8]

Isocyanogen Tetrafluoride (III).—A mixture of isocyanogen tetrabromide (IV, 7.45 g., 0.02 mole) and silver fluoride (30.3 g., 0.24 mole) was warmed slowly in a flask equipped

(7) J. Goerdeler, *et al.*, *Ber.*, **90**, 182 (1957).

(8) All melting points were determined with the Fisher-Johns apparatus. Microanalyses were by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.



with an efficient condenser until a vigorous reaction started. When the reaction moderated, the mixture was kept at a bath temperature of 60° for 1 hr. and the liquid components were stripped. This procedure was carried out eight times to give 14.4 g. of a slightly brown liquid. To remove the last traces of bromine the product was heated with and distilled from fresh silver fluoride (20 g.) four times and then subjected to fractional distillation to give 4.7 g. (23%) of pure III, b.p. 68–73° (760 mm.); $n^{25}D$ 1.2950.

Anal. Calcd. for $C_2F_4N_2$: C, 18.76; F, 59.36; N, 21.88. Found: C, 17.29; F, 59.61; N, 22.60.

2-Bromo-5-fluoro-1,3,4-thiadiazole (II).—A mixture of 2,5-dibromo-1,3,4-thiadiazole (I, 12.2 g., 0.05 mole) and silver fluoride (32 g., 0.25 mole) was heated slowly. At a bath temperature of 110° an exothermic reaction started and the oil bath was removed for 3 min. to avoid loss of product through the condenser. To complete the reaction, the mixture was then heated at 135° for 5 min. By distillation at normal pressure 1.2 g. of isocyanogentetrafluoride (III) was isolated. Using then a moderate vacuum (40 mm; 100° bath temperature) a quickly solidifying oil distilled. Purification by vacuum sublimation (14 mm; 50° bath temperature) and recrystallization from ethanol gave 1.5 g. (16%) of II; m.p. 76–77°.

Anal. Calcd. for C_2BrFN_2S: C, 13.12; Br, 43.76; F, 10.38; S, 17.52. Found: C, 12.92; Br, 45.88; F, 10.47; S, 17.38.

Trichloroacetamidine Hydrochloride (X).—Hydrogen chloride was passed for 10 min. at room temperature into a solution of 60 g. of trichloroacetamidine[9,10] in 1000 ml. of ligroin. The excess hydrogen chloride was evaporated *in vacuo* and the separated X was filtered; yield 67 g. (90%); m.p. 223° dec.

Anal. Calcd. for $C_2H_4Cl_4N_2$: C, 12.14; H, 2.04; Cl, 71.66; N, 14.16. Found: C, 13.07; H, 2.19; Cl, 70.80; N, 14.28.

Heptafluorobutyroamidine Hydrochloride (XVI).—Hydrogen chloride was passed for 10 min. into a solution of heptafluorobutyroamidine[11] in 250 ml. of methylene chloride. After evaporation of the excess hydrogen chloride, the separated XVI was filtered (43 g., 91.5%), m.p. 158°. After 6 hr. the only slightly hygroscopic product melted at 154°, despite keeping it in the refrigerator over phosphorus pentoxide; therefore, an exact analysis could not be obtained.

Anal. Calcd. for $C_4H_4ClF_7N$: Cl, 14.27. Found: Cl, 15.88.

Compound XVI was described previously by preparation in ether solution[11] and was identified only by its melting point (128°). When this procedure was repeated, we found that pure XVI cannot be obtained in ethereal solution as also was found for compound X.

3-Monochloromethyl-5-chloro-1,2,4-thiadiazole (VIII).—A solution of sodium hydroxide (100 g., 2.5 moles) in water (200 ml.) was added dropwise with stirring during 2 hr. to a mixture of monochloroacetamidine hydrochloride[12] (VII, 64.5 g., 0.5 mole), trichloromethanesulfenyl chloride (VI, 93 g., 0.5 mole), and methylene chloride (500 ml.). The temperature was kept between −4° and +1° by ice-salt cooling. Then the methylene chloride layer was separated, washed twice with 50 ml. of water, and dried with sodium sulfate. After evaporation of the solvent, the residue was distilled *in vacuo* to give 43.1 g. of VIII (51%); b.p. 58° (1 mm.), $n^{20}D$ 1.5619.

Anal. Calcd. for $C_3H_2Cl_2N_2S$: N, 16.57. Found: N, 16.19.

3-Trichloromethyl-5-chloro-1,2,4-thiadiazole (IX) was prepared as follows: (1) in the same manner from trichloroacetamidine hydrochloride (X, 75 g.), trichloromethanesulfenyl chloride (VI, 70 g.), sodium hydroxide (65 g.) in water (130 ml.), in the presence of 500 ml. of methylene chloride, yield 50 g. (56%); (2) by chlorination of 3-monochloromethyl-5-chloro-1,2,4-thiadiazole (VIII): gaseous chlorine was passed slowly for 3 days into a solution of VIII (11.5 g.) in carbon tetrachloride (35 ml.) at a bath temperature of 88° with exposure to ultraviolet light. The solvent was then evaporated and the remaining product distilled *in vacuo*, yield of IX 14.6 g. (90%); b.p. 73° (0.3 mm.); $n^{21}D$ 1.5720.

Anal. Calcd. for $C_3Cl_4N_2S$: C, 15.14; Cl, 59.61; N, 11.77; S, 13.47. Found: C, 15.25; Cl, 59.65; N, 11.91; S, 13.21.

(9) K. Dachlauer, German Patent 671,785 (1939).

(10) H. Schroeder and Ch. Grundmann, *J. Am. Chem. Soc.*, **78**, 2450 (1956).

(11) D. R. Husted, U. S. Patent 2,676,985.

(12) W. Klarer and F. Urech, *Helv. Chim. Acta*, **27**, 1762 (1944).

3-Heptafluoropropyl-5-chloro-1,2,4-thiadiazole (XVII) was prepared by the same procedure as used for the synthesis of VIII and IX except for employing heptafluorobutyroamidine hydrochloride (XVI, 40 g.), trichloromethanesulfonyl chloride (VI, 30 g.), sodium hydroxide (26 g.) in 80 ml. of water, and 230 ml. of methylene chloride in the reaction, yield of XVII 23.8 g. (51.5%), b.p. 90° (100 mm); $n^{29}D$ 1.3918.

Anal. Calcd. for $C_5ClF_7N_2S$: N, 9.71; S, 11.11. Found: N, 9.58; S, 10.84.

3-Trifluoromethyl-5-chloro-1,2,4-thiadiazole (XII).—3-Trichloromethyl-5-chloro-1,2,4-thiadiazole (IX, 60 g.) was added dropwise, with stirring, during one hour to a fluorination mixture consisting of antimony trifluoride (100 g.), antimony trichloride (15 g.), and 10 g. of chlorine, which was kept at 150°. After refluxing for 4 hr., the reaction mixture was distilled to give 39 g. of product. Fractionated distillation gave 31 g. of XII (65%); b.p. 67° (95 mm.); $n^{28}D$ 1.4348.

Anal. Calcd. for $C_3ClF_3N_2S$: C, 19.11; Cl, 18.80; F, 30.23; N, 14.86. Found: C, 19.10; Cl, 18.85; F, 30.98; N, 14.92.

3-Dichloromonofluoromethyl-5-fluoro-1,2,4-thiadiazole (XI).—A mixture of 3-trichloromethyl-5-chloro-1,2,4-thiadiazole (IX, 20 g.) and silver fluoride (100 g.) was heated slowly in a flask equipped with an efficient condenser. At a bath temperature of 140° an exothermic reaction started which proceeded for 5 min. without further heating; then the reaction mixture was refluxed for 5 min. more. The liquid components (14 g.) were stripped and fractional distillation gave 8.1 g. of XI (47%) and 5 g. of more and less fluorinated by-products, b.p. of XI 103° (100 mm.), $n^{24}D$ 1.4840.

Anal. Calcd. for $C_3Cl_2F_2N_2S$: C, 17.57; Cl, 34.59; F, 18.53; N, 13.66; S, 15.64. Found: C, 17.63; Cl, 34.51; F, 18.28; N, 13.83; S, 15.64.

3-Trifluoromethyl-5-fluoro-1,2,4-thiadiazole (XV).—(1) Fluorination of 3-trifluoromethyl-5-chloro-1,2,4-thiadiazole (XII): A mixture of XII (15 g.) and silver fluoride (30 g.) was refluxed for 4 hr.; then the reaction product was stripped. Fractional distillation *in vacuo* gave 11.5 g. of XV (84%); b.p. 56° (175 mm.); b.p. 90° (760 mm.); $n^{31}D$ 1.3860. (2) Fluorination of 3-dichloromonofluoromethyl-5-fluoro-1,2,4-thiadiazole (XI): A mixture of XI (12.6 g.) and silver fluoride (30 g.) was refluxed for 24 hr.; then the reaction product was stripped. Fractional distillation gave 3.3 g. of XV (31%).

Anal. Calcd. for $C_3F_4N_2S$: C, 20.23; F, 44.16; N, 16.28; S, 18.63. Found: C, 20.69; F, 43.50; N, 16.36; S, 18.46.

3-Heptafluoropropyl-5-fluoro-1,2,4-thiadiazole (XVIII).—A mixture of 3-heptafluoropropyl-5-chloro-1,2,4-thiadiazole (XVII, 14 g.) and silver fluoride (20 g.) was heated at 105° to start the reaction, and was then refluxed for 30 min. The reaction product (11.7 g., $n^{29}D$ 1.3848) was stripped and refluxed with 20 g. of fresh silver fluoride for 6 hr. to give 10.6 g. of liquid products ($n^{24}D$ 1.3635). Final refluxing with 10 g. of AgF_2 for 2 hr. gave 9.7 g. (73.5%) of pure XVIII, b.p. 82° (175 mm.); $n^{30}D$ 1.3530.

Anal. Calcd. for $C_5F_8N_2S$: F, 55.85; N, 10.30; S, 11.78. Found: F, 55.70; N, 9.87; S, 11.27.

3-Trichloromethyl-5-diethylamino-1,2,4-thiadiazole (XX).—A solution of diethylamine (14.6 g., 0.2 mole) in benzene (70 ml.) was added to a solution of 3-trichloromethyl-5-chloro-1,2,4-thiadiazole (IX, 23.8 g., 0.1 mole) in benzene (50 ml.). After keeping the reaction mixture for 0.5 hr. at 40°, the separated diethylamine hydrochloride was filtered and the filtrate was evaporated *in vacuo*. The residual XX was recrystallized from petroleum ether; yield: 25.3 g. (92%); m.p. 55°.

Anal. Calcd. for $C_7H_{10}Cl_3N_3S$: C, 30.61; H, 3.67; Cl, 38.74; N, 15.30; S, 11.67. Found: C, 30.43; H, 3.75; Cl, 38.78; N, 15.11; S, 11.69.

3-Trichloromethyl-5-dimethylamino-1,2,4-thiadiazole (XIX) was prepared in the same manner in 91% yield; m.p. 54°.

Anal. Calcd. for $C_5H_6Cl_3N_3S$: C, 24.36; H, 2.45; Cl, 43.14; N, 17.05; S, 13.00. Found: C, 24.37; H, 2.42; Cl, 43.24; N, 17.02; S, 12.80.

3-Trifluoromethyl-5-dimethylamino-1,2,4-thiadiazole (XXI) was prepared in the same manner from 3-trifluoromethyl-5-fluoro-1,2,4-thiadiazole (XV) but purified by vacuum distillation, yield 90%; b.p. 112° (5 mm.); m.p. 28°.

Anal. Calcd. for $C_5H_6F_3N_3S$: C, 30.45; H, 3.07; F, 28.90; N, 21.31; S, 16.26. Found: C, 30.49; H, 3.07; F, 28.90; N, 21.06; S, 16.24.

The following procedure is representative of the syntheses performed.

3-Trichloromethyl-5-ethoxy-1,2,4-thiadiazole (XXII).—A solution of sodium (805 mg., 0.035 mole) in anhydrous ethanol (20 ml.) was added within 5 min., with stirring, to a solution of 3-trichloromethyl-5-chloro-1,2,4-thiadiazole (IX, 8.3 g., 0.035 mole) in ethanol (20 ml.). Sodium chloride separated during the reaction and was filtered after 10 min., when the reaction mixture was neutral. The excess ethanol was evaporated *in vacuo*, the residue was distilled *in vacuo* to give 7.2 g. (83%) of XXII; b.p. 94.5° (1 mm.); $n^{30}D$ 1.5355.

Anal. Calcd. for $C_5H_5Cl_3N_2OS$: C, 24.26; H, 2.05; Cl, 42.97; N, 11.32; S, 12.95. Found: C, 24.03; H, 2.05; Cl, 43.28; N, 11.29; S, 13.03.

3-Trichloromethyl-5-pentafluoropropoxy-1,2,4-thiadiazole (XXIII).—Yield 78%; b.p. 82° (1 mm.); b.p. 216° (760 mm.).

Anal. Calcd. for $C_6H_2Cl_3F_5N_2OS$: C, 20.05; H, 0.57; Cl, 30.26; S, 9.12. Found: C, 19.96; H, 0.50; Cl, 31.52; S, 9.22.

3-Trifluoromethyl-5-ethoxy-1,2,4-thiadiazole (XIV).—Yield 55%; b.p. 103° (100 mm.); $n^{35}D$ 1.4177.

Anal. Calcd. for $C_5H_5F_3N_2OS$: C, 30.30; H, 2.54; F, 28.76; N, 14.14; S, 16.18. Found: C, 30.06; H, 2.76; F, 29.98; N, 14.35; S, 16.08.

3-Dichloromonofluoromethyl-5-ethoxy-1,2,4-thiadiazole (XIII).—Yield 58%; b.p. 161° (100 mm.); $n^{27}D$ 1.4973.

Anal. Calcd. for $C_5H_5Cl_2FNOS$: C, 25.99; H, 2.18; Cl, 30.69; F, 8.22; N, 12.12; S, 13.87. Found: C, 26.00; H, 2.32; Cl, 30.35; F, 8.55; N, 12.12; S, 13.86.

Acknowledgment.—We are very much indebted to the Olin Mathieson Chemical Corp. for their generous support of this work.