

methyl iodide in ether-benzene and displacing the ether with benzene to a volume of 50 cc. After six hours, the solution was chilled and poured into an ice-cold mixture of 60 cc. of acetic acid and 12 cc. of hydriodic acid (sp. gr. 1.7) with stirring and ice cooling. Evaporation of the benzene in vacuum in a bath kept below 40° resulted in separation of yellow crystals of the iodo compound III, which were collected, after the mixture had stood overnight in the refrigerator, and washed with cold 90% acetic acid. A solution of the product (m.p. about 110° with liberation of iodine) in 25 cc. of pure dioxane was added to a warm mixture of 20 cc. of dioxane, 12 cc. of 36% hydrochloric acid and 2 g. of stannous chloride. The brown solution soon became light yellow; after being refluxed for 15 minutes it was poured into 250 cc. of hot water and the dioxane was removed by distillation. A crystalline precipitate (700 mg., m.p. 145°) resulted and on crystallization from benzene-methanol afforded 460 mg. (46%) of IV, m.p. 164.5–165.5°. After four more crystallizations the substance was obtained as greenish-yellow plates, m.p. 165.2–166°.

Anal. Calcd. for $C_{20}H_{15}Br$: C, 71.65; H, 4.51. Found: C, 71.79; H, 4.88.

5-Cyano-9,10-dimethyl-1,2-benzanthracene was obtained by heating IV (150 mg.) under reflux for six hours with a solution prepared by adding pyridine dropwise to a suspension of 150 mg. of cuprous cyanide in 4 cc. of nitrobenzene until the solid dissolved. The solution was poured into hot hydrochloric acid and the mixture was extracted exhaustively with benzene and the extract steam distilled. The residue was extracted with benzene and the very red solution passed through a column of alumina; the eluate was light yellow and on dilution with methanol gave 50 mg. (40%) of yellow, hair-like filaments, m.p. 158–158.5° (fluorescent in ultraviolet light).

Anal. Calcd. for $C_{21}H_{15}N$: C, 89.65; H, 5.37. Found: C, 89.68; H, 5.50.

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NEW COMPOUNDS

3-Isothiocyanocyclohexene and Derivative

3-Bromocyclohexene was prepared in 60% yield from cyclohexene and N-bromosuccinimide in purified carbon tetrachloride. The product was collected at 54–63° (10 mm.); n_D^{25} 1.5300.

In a 200-ml. flask fitted with a stirrer and dropping funnel was placed a solution of 25.1 g. (0.309 mole) of dry, C.P. sodium thiocyanate in 85 ml. of absolute methanol. To this stirred solution 49.8 g. (0.309 mole) of 3-bromocyclohexene was added dropwise over a period of two hours. Little heat was evolved during the course of the reaction. The reaction mixture was stirred at room temperature for an additional two hours. The sodium bromide which separated was filtered from the reaction mixture, and the methanol removed from the filtrate by vacuum distillation. At this point more sodium bromide had separated. This was removed by filtration, and the solid washed with petroleum ether. The combined filtrate and washings were vacuum distilled. 3-Isothiocyanocyclohexene (32.8 g., 76%) was collected at 70–76° (3 mm.); n_D^{25} 1.5565; d_4^{25} 1.068. When first distilled the material was colorless, but on standing it became a faint yellow color. Analysis of the product for isothiocyanate¹ showed it to be 98% isothiocyanate.

(1) S. Siggia and J. G. Hanna. *Anal. Chem.*, **20**, 1084 (1948).

Anal. Calcd. for C_7H_9NS : C, 60.4; H, 6.5; N, 10.1; S, 23.0. Found: C, 60.2; H, 6.6; N, 10.0; S, 23.0.

Upon reaction of the isothiocyanate with concentrated aqueous ammonia a thiourea, m.p. 133–134°, was readily obtained.

Anal. Calcd. for $C_7H_{12}N_2S$: C, 53.8; H, 7.7; N, 17.9. Found: C, 53.8; H, 7.7; N, 17.8.

(2) Analysis by Dr. Carol K. Fitz, Melrose, Mass.

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Some Fluorinated Propanes

1,2-Dibromo-1,1,2-trichloro-3,3,3-trifluoropropane.—A solution of 759 g. (4.75 moles) of bromine and 946.5 g. (4.75 moles) of 1,1,2-trichloro-3,3,3-trifluoropropane¹ was placed in a three-necked flask equipped with an internal water cooled coil, sealed stirrer and thermometer. The flask was illuminated for 96 hours with a G.E. AH-4 lamp, with the reactants maintained below 25°. Most of the unreacted starting material was pumped off at 60 mm. The pressure was then slowly reduced to 5 mm., yielding 855.4 (2.38 moles, 50% yield) of the saturated dibromide. It was recrystallized from ethanol-water, m.p. 151–152° (sealed tube). A carbon tetrachloride solution of the dibromide liberated bromine on exposure to ultraviolet light, indicating that the bromination is reversible at room temperature.

Anal. Calcd. for $C_3Br_2Cl_3F_3$: C, 10.03; Ag equiv.² (Br and Cl), 71.85. Found: C, 10.3; Ag equiv., 72.1.

2-Bromo-1,2-dichloro-1,1,3,3,3-pentafluoropropane and 2-Bromo-1,1,2-trichloro-1,3,3,3-tetrafluoropropane.—A mixture of 71.0 g. (0.198 mole) of 1,2-dibromo-1,1,2-trichloro-3,3,3-trifluoropropane, 0.198 mole of antimony trifluorodichloride³ and 10 ml. of 1,1,2-trichloro-1,2,2-trifluoroethane (as solvent) was shaken in a steel bomb at room temperature for six hours, and at 120–130° for six hours. The reaction product was washed with dilute hydrochloric acid, water and dried over calcium chloride. On fractional distillation there was obtained 35.9 g. (64% yield) of 2-bromo-1,2-dichloro-1,1,3,3,3-pentafluoropropane, b.p. 90.1–91.8°, m.p. 23.5–24.5° (cooling curve), n_D^{25} 1.3795 and 1.9 g. (3% yield) of 2-bromo-1,1,2-trichloro-1,3,3,3-tetrafluoropropane, b.p. 131–133°. The tetrafluoride was recrystallized from ethanol-water, 68–69° (sealed tube). The position of the entering fluorine atoms was deduced from the presence of bromine in each of the above compounds, coupled with the previous observations of perhalogenated propanes^{4,5} that the chlorine atoms of the trichloromethyl group are replaced more readily by fluorine than the halogen atoms of the dichloromethylene group.

Anal. Calcd. for $C_3BrCl_2F_5$: C, 12.78; Ag equiv. (Cl and Br), 93.95. Found: C, 12.7; Ag equiv., 93.9. Calcd. for C_3BrClF_4 : C, 12.08; Ag equiv. (Cl and Br), 74.57. Found: C, 12.5; Ag equiv., 74.9.

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(1) Obtained from Halogen Chemicals, Inc., 616 King St., Columbia, S. C.

(2) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **13**, 882 (1948).

(3) "Organic Reactions," Vol. II, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 61.

(4) A. L. Henne and Mary W. Renoll, *THIS JOURNAL*, **61**, 2489 (1939).

(5) A. L. Henne, A. M. Whaley and J. K. Stevenson, *ibid.*, **63**, 3478 (1941).