distance and regularity in distribution of the micelles, rather than their size (which remains unchanged in most of the above experiments), determines the scattering it follows that, to a high degree, phase relationship between the micelles is involved in the scattering by these densely packed cellulose systems. Such a phase relationship will not exist in the scattering by particles in more dispersed systems. In the latter case formulas given by Guiniér and others[3] are appropriate and enable the determination of the *size* of the particles; whereas the application of Bragg's law appears to be applicable in this densely packed system enabling calculation of the average *distance* between the particles.

(3) A. Guiniér, "Radiocrystallographie," Chapter XII, Dunod, Paris; *C. R. Acad. Sci.* Paris, **204**, 1115 (1937); Thesis, Paris, 1939; R. Hosemann, *Z. Physik*, **113**, 751 (1939); **114**, 133 (1939); O. Kratky, *J. Polymer Sci.*, **3**, 195 (1948).

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Synthesis of N^1-*p*-Fluorophenyl-N^5-isopropyldiguanide[1]

BY CHARLOTTE A. HART AND CALVIN A. VANDERWERF

In connection with an investigation of the pharmaceutical properties of aromatic fluorine-containing compounds, N^1-*p*-fluorophenyl-N^5-isopropyldiguanide, the fluoro-analog of paludrine, has been synthesized by a modification of the method described by Curd and Rose[2] for the preparation of disubstituted diguanides. Pharmaceutical testing of the product is in progress.

Experimental[3]

***p*-Fluorophenyldicyandiamide.**—Exactly 33.0 g. (0.3 mole) of *p*-fluoroaniline[4] was added to 150 ml. of 5 *N* hydrochloric acid and diazotized by the addition of 21 g. (0.30 mole) of sodium nitrite in a saturated water solution while the temperature was maintained at 0–5°. The diazotized solution was added quickly with stirring to a solution of 28 g. (0.33 mole) of dicyandiamide[5] in 850 ml. of water at 20°. A total of 32 g. (0.25 mole) of sodium carbonate monohydrate was added in portions over the course of one and one-half hours, in order to maintain the alkalinity of the solution. The orange-red triazene which precipitated was separated by filtration and partially dried by means of a rubber dam.[6] It was then added in portions during the course of one hour to a stirred solution of 45 ml. of concentrated hydrochloric acid in 200 ml. of acetone at 10–15°. The mixture was stirred for two additional hours, 600 ml. of water was added, and the resulting green precipitate of crude *p*-fluorophenyldicyandiamide (28.0 g., 52%), m. p. 178–190°, was isolated by filtration.

The product was purified by repeated treatment with charcoal in boiling 1 *N* sodium hydroxide solution, followed in each case by re-precipitation with hydrochloric acid, and finally by a single recrystallization from methanol. In this manner, 9.5 g. (18%) of almost colorless material melting at 204.0–205.4° was obtained.

Anal. Calcd. for $C_8H_7N_4F$: C, 53.9; H, 4.0; N, 31.5. Found: C, 54.0; H, 3.6; N, 31.3.

N^1-*p*-Fluorophenyl-N^5-isopropyldiguanide Monoacetate.—A mixture of 5.5 g. (0.03 mole) of *p*-fluorophenyldicyandiamide dissolved in 50 ml. of ethanol, 6 g. (0.10 mole) of isopropylamine and 3.9 g. of copper sulfate pentahydrate dissolved in 20 ml. of water was refluxed on a steam-bath for four days, during which time a red-brown precipitate was formed. The solvent and excess isopropylamine were then removed by distillation and a solution of 15 ml. of concentrated hydrochloric acid in 150 ml. of water was added. Hydrogen sulfide was bubbled into the mixture until no further precipitation occurred, the solid material was removed by filtration, and the filtrate was poured in a thin stream into a 20% solution of sodium hydroxide. The N^1-*p*-fluorophenyl-N^5-isopropyldiguanide separated as a gummy precipitate.

Inasmuch as the free base is difficult to recrystallize, the product was isolated as the acetate, as follows: the crude base was extracted from the mixture with ether, the ether extract dried over anhydrous sodium sulfate, and the ether removed. The residue was dissolved in dry toluene and the filtered solution treated with glacial acetic acid until a strong odor of acetic acid persisted. The precipitate was filtered, washed with toluene, and dried to yield 7.4 g. (82%) of colorless, non-hygroscopic, water-soluble crystals of N^1-*p*-fluorophenyl-N^5-isopropyldiguanide monoacetate, melting at 169–171°. Recrystallized from 2-butanone, the pure material melted at 171.2–172.1°.

Anal. Calcd. for $C_{13}H_{20}O_2N_5F$: C, 52.5; H, 6.8; N, 23.6. Found: C, 52.6; H, 6.6; N, 23.4.

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[1] The authors are indebted to the Office of Naval Research for a grant which made this and continuing investigations possible.

[2] Curd and Rose, *J. Chem. Soc.*, 729 (1946).

[3] All melting points are corrected; boiling points are uncorrected.

[4] Prepared by the method of Bradlow and VanderWerf, THIS JOURNAL, **70**, 654 (1948).

[5] Obtained through the courtesy of American Cyanamid Company.

[6] A sample of the triazene which had been dried and then purified by re-precipitation from sodium hydroxide solution decomposed at 124–126° with gas evolution.

3,4-Dichlorotetramethylene Sulfone

BY T. EARL JORDAN AND FRANK KIPNIS[1]

It has been found that following the method of Van Zuydewijn[2] which involved passing chlorine into a boiling solution of butadiene sulfone in benzene, 3,4-dichlorotetramethylene sulfone is obtained in approximately 50% yield. By using, instead, sulfuryl chloride in 25% excess with a little iodine, the yield is 67% and with 100% excess, the yield is 92–93%. Attempts to chlorinate further resulted in no definite compounds.

The preferred procedure is as follows: Butadiene sulfone is first prepared by the reaction of butadiene and sulfur dioxide in a bomb for several hours at about 100° and is recrystallized from alcohol. To a solution of 118 g. (1 mole) of this substance in 800 ml. of benzene containing a small crystal of iodine and maintained at 55–60° in a two-liter flask provided with a reflux condenser, stirrer and calcium chloride guard tube, 160 ml. (240 g.) of sulfuryl chloride is added with stirring during two and a half hours, after which stirring is continued for three hours at the same temperature. Excess sulfuryl chloride and the benzene are recovered by distillation at atmospheric pressure, after which the product distils at 145–150° under 5 mm. pressure; m. p. 99–100°. Recrystallization from *n*-butanol gives colorless crystals, m. p. 124°; yield 176 g. (93%). The product is soluble in acetone, cyclohexanone, hot

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[1] Present address: Oxford Products, Inc., Cleveland, Ohio.

[2] Van Zuydewijn and E. de Roy, *Rec. trav. chim.*, **57**, 445 (1938).