NOTES

Some Additional Derivatives of Piperazine

By David E. Adelson[1] and C. B. Pollard

During the course of experimental work in the past it was found expedient to prepare certain compounds for the sake of comparison with others then in the process of synthesis. The composition and properties of these compounds are given in the following table.

Name	Empirical formula	M. p., °C., corr.	Analyses, %, N Calcd.	Found
Piperazinium-1,4-bis-(dichloroacetate)[a]	$C_8H_{14}O_4N_2Cl_4$	181	8.15	8.22
Piperazinium-1,4-bis-(*o*-acetoxybenzoate)	$C_{22}H_{26}O_8N_2$	112–113	6.28	6.27
N,N′-Piperazino-bis-(3-propanediol-1,2)	$C_{10}H_{22}O_4N_2$	176–177	11.96	12.01
Tetrabenzoate	$C_{38}H_{38}O_4N_2$	150–150.5	4.31	4.18
Piperazino-1,4-bis-(ethyl β-propionate)-2HBr[b]	$C_{14}H_{28}O_4N_2Br_2$		6.25	6.29

[a] Calcd.: Cl, 41.20. Found: Cl, 41.00. [b] Free base decomposes below 100°.

Organic Chemical Laboratory
University of Florida
Gainesville, Florida

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[1] Present address: Department of Chemistry, Columbia University, New York, N. Y.

The Replacement of Chlorine by Fluorine in Organic Compounds

By Hans Billroth Gottlieb

Double decomposition with alkali fluorides to replace by fluorine a carbon-linked chlorine atom is a method which is only rarely reported in the literature to have been used satisfactorily. The preparation of phthalyl fluoride[1] and formyl fluoride[2] are such rare instances. The above-mentioned decomposition method is used here for the preparation of 1-fluoro-2,4-dinitrobenzene, a compound previously obtained by nitration of *p*-fluoronitrobenzene.[3]

1-Chloro-2,4-dinitrobenzene (202 g., purified by distillation at 158–160° at 1 mm.) was dissolved in 202 g. of nitrobenzene. To this mixture was added 40 g. of finely powdered (120 mesh) anhydrous potassium fluoride; the entire mass was agitated vigorously and heated to 200–205° for one-half hour. The reaction product was then cooled to 120°, another 40 g. of anhydrous potassium fluoride was added, and the suspension again heated for one-half hour to 205° with good stirring. After the reaction mixture had cooled, suction was applied and the filtrate was treated twice more in the above manner with 80-g. portions of finely powdered potassium fluoride. (Repeated heating with fresh amounts of the fluoride is essential, since part of the fluoride is coated by potassium chloride and thus becomes unreactive.) The mixture of potassium fluoride and chloride collected on a suction funnel was washed with hot dry toluene and the extracts united with the oil obtained from the melt. This oil was subjected to fractional distillation and the fraction which distilled between 127–140° at 1 mm. was separated. Refractionation through a 30-cm. column yielded 123 g. of a product which boiled at 149–154° at 3 mm. This was a mixture of 96.8% 1-fluoro-2,4-dinitrobenzene with 3.2% of unchanged chloro compound. It still contained 0.57% of chlorine and crystallized at 10–11°. The product was allowed to solidify and was then warmed gradually and stirred until it was about half melted. The crystalline residue collected on a suction funnel was pure 1-fluoro-2,4-dinitrobenzene (yield 30%, calculated on the basis of the 1-chloro-2,4-dinitrobenzene employed). The substance melted at 24–25° like Holleman and Beekman's product, was free from chlorine, and gave the correct analysis for nitrogen.

Anal. Calcd. for $C_6H_3FN_2O_4$: N, 15.05. Found: N, 15.20, 15.18.

The product reacted slowly with warm water at 60° splitting off hydrofluoric acid.

The replacement of chlorine attached to phosphorus by double decomposition with alkali fluoride has been described by Lange and Krueger,[4] who studied the reaction of phosphorus pentachloride with potassium fluoride. The method has been applied here also to the formation of diphenoxyphosphine oxyfluoride, $(C_6H_5O)_2FOP$, from the corresponding chlorine compound. The procedure was the same as in the above example, but care had to be taken to keep the temperature at 90–100° during the reaction. The diphenoxyphosphine oxyfluoride was obtained as a water-clear liquid, which distilled at 150–155° at 6 mm.

Anal. Calcd. for $C_{12}H_{10}FO_3P$: C, 57.12; H, 3.99. Found: C, 57.15, 57.28; H, 4.23, 4.00.

It not only decomposed rapidly with water, but was also unstable when standing in daylight. Only 7% of pure diphenoxyphosphine oxyfluoride could be obtained by refractionation, as the substance decomposed partially at its boiling point *in vacuo*, yielding triphenyl phosphate and the volatile phosphorus oxyfluoride. The latter dis-

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[1] Damm, Hambly, Paul and Semmons, *J. Chem. Soc.*, 15–21 (1933).

[2] Nesmejanov and Kahn, *Ber.*, **67**, 370 (1934).

[3] Holleman and Beekman, *Rec. trav. chim.*, **23**, 240 (1904.)

[4] Lange and Krueger, *Ber.*, **65**, 1253 (1932).