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°.

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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).

proportionation caused the phosphorus analysis to be 0.5–0.6% too low.

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The Behavior of Diphenylmagnesium Bromide with Benzoquinone

BY DAVID E. WORRALL AND SUMNER COHEN

Bamberger and Blangey[1] got tars only by the action of methylmagnesium iodide on benzoquinone, although small amounts of several crystalline products were obtained from xyloquinone. Using duroquinone, Smith and Crawford[2] found that a non-tractable oil was the principal product with phenylmagnesium bromide. It occurred to us that the substitution of a heavier radical (diphenyl) not only would raise the melting point but might act as a brake on the reactivity, thereby facilitating the isolation of the primary addition product or products. Actually it increased the Wurtz-like effect inherent in the Grignard reagent and the principal products, aside from unchanged reactants, are dibiphenyl and hydroquinone.

Experimental

The reagent was prepared from 0.1 g. mole of *p*-bromodiphenyl, using activated magnesium with a small volume of ether. An average of about 2 g. of dibiphenyl separated out, an amount that varied somewhat in different preparations. Benzoquinone (0.4 m. equiv.) dissolved in ether was added to the mixture. A dark blue precipitate formed, doubtless a molecular compound, that reacted with excess of reagent on shaking, losing its color and depositing a yellow oil that partially solidified. A permanent blue color was reached before all of the material was introduced. After decomposition with dilute acid the portion insoluble in ether and in water yielded 6.8 g. or 44% of crude dibiphenyl, which was recrystallized from nitrobenzene and identified by analysis. Hydroquinone was identified in the aqueous portion although most of the original quinone turned up as a tar after steam distillation of the ether layer. A mixture of 6–7 g. of diphenyl with bromodiphenyl was recovered by steam distillation. Slightly more than a gram of non-volatile material soluble in hot water and in alkali was isolated and identified as *p*-hydroxydiphenyl. About the same amount of hydrocarbon was obtained by treating the Grignard reagent with azobenzene. If the reactants in the original experiment were mixed rapidly or in the reverse order, little decolorization of the blue precipitate was observed and even after standing overnight no increase was noted in the quantity of hydrocarbon normally present in the reagent. No attempt was made to isolate addition products from the oil. Similar experiments with phenyl and *n*-butylmagnesium bromides failed to reveal any hydrocarbon formation from the action of benzoquinone. Small amounts of phenol and butyl alcohol from the action of atmospheric oxygen were formed.

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(1) Bamberger and Blangey, *Ann.*, **384**, 272 (1911).

(2) Smith and Crawford, THIS JOURNAL, **50**, 869 (1928).

COMMUNICATIONS TO THE EDITOR

l-EPHEDRINE, A DEGRADATION PRODUCT OF ALKALOIDS IN ACONITUM NAPELLUS

Sir:

We have been engaged in a study of degradation reactions of aconitine and its accompanying alkaloids in *aconitum napellus*. The latter, according to H. Schulze and G. Berger [*Arch. d. Pharm.*, **262**, 553 (1924)], is a mixture of the following bases: aconitine, benzoylaconine, homoisaconitine, aconine and neopollin. This material was available in the form of aconitin hydrochloricum, amorph. (Merck).

The destructive distillation of aconitine hydrochloride, amorph., over four to five its amount of crystalline barium hydroxide yields besides a large fraction of hydrocarbons and methylamine, a strongly basic oil which ultimately can be separated by steam distillation.

For purification it is distilled in a vacuum of 0.5 mm. and the fraction obtained at the bath temperature of 50–70° is collected. The analysis showed the presence of one methylimide group, no methoxy, a content of carbon, hydrogen and nitrogen corresponding to the formula $C_{11}H_{17}ON$. The mixture boils at 260–262° (uncorr.) it is slightly levorotatory and has a refractive index of n^{20} 1.528. The total yield is 2%. *Anal.* Calcd. for $C_{11}H_{17}ON$: C, 73.74; H, 9.50; N, 7.82; (N)-CH_3, 8.37. Found: C, 74.52; H, 8.98; N, 7.70; (N)-CH_3, 7.82.

From this, besides other salts, a hydrochloride was obtained in crystalline form which, after