required for each gram of material. The solution was treated with charcoal, filtered and 0.5 g. of sodium nitrate added to the colorless filtrate; yield 69%.

Ten grams of the arsonium nitrate was dissolved in 1300 cc. of boiling water and sodium chloride added until the solution became cloudy. When the mixture was cooled and the sides of the container rubbed, the colorless crystalline chloride separated. The product was dissolved in absolute alcohol and precipitated by ether. The chloride, which seemed to contain alcohol of crystallization, was dried at 160°.

When 3.0 g. of the nitrate, dissolved in 400 cc. of hot water, was treated with 20 g. of solid sodium bromide, the arsonium bromide precipitated in practically quantitative yield. The compound was dissolved in hot water, treated with charcoal, filtered and 0.5 g. of sodium bromide added to the filtrate. The compound precipitated when the sides of the container were scratched.

The arsonium iodide was obtained by the process described except that sodium iodide was added to the aqueous solution. The crude iodide was suspended in hot acetone and just enough hot water added to bring it into solution. After addition of charcoal the mixture was filtered; the iodide precipitated, in practically quantitative yield, in the form of sparkling brown crystals.

Tetra-(3-aminophenyl)-arsonium Chloride (XII) and Bromide.—A right angle tube, about one-half inch in diameter, was fused onto the side of a wide mouth Erlenmeyer flask very near the bottom; this served as an inlet tube. A short outlet tube was fused onto the flask just below the neck. The flask was fitted with a stirrer which passed through a mercury seal.

A solution of 10 g. of tetra-(3-nitrophenyl)-arsonium chloride in 95 cc. of acetic acid was poured into the flask and 70 g. of powdered stannous chloride dihydrate added. The mixture was stirred and a rapid stream of hydrogen chloride passed into it. A clear solution was obtained and the crystalline tin double salt of the amino compound separated rapidly. When hydrogen chloride began to escape through the side arm, the mixture was cooled and filtered on a Jena funnel. The product was dissolved in water and treated with 20% sodium hydroxide solution until strongly alkaline, the precipitated arsonium chloride (6 g.) filtered, washed with sodium hydroxide solution, then with water.

The acetylamino compound was obtained when 1.5 g. of the amine and 5 cc. of acetic anhydride were boiled for several minutes. After twenty-four hours the precipitated product was filtered; yield 1.5 g.

To obtain the arsonium bromide in practically quantitative yield, the arsonium chloride was dissolved in the smallest possible amount of hot water and three times the calcd. amount of solid sodium bromide added.

Summary

Amino derivatives of methyltriphenyl- and tetraphenylarsonium salts have been described.

Based on preliminary pharmacological tests of a representative compound it seems that these products are ineffective as germicides.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Diaryl- and Dicycloalkylethanolamines

BY JOSEPH B. NIEDERL AND ROBERT LAY[1]

In the course of the investigation of physiological properties of certain types of aromatic, particularly phenolic amino compounds,[2] it became desirable to prepare a series of diaryl- and dicyloalkylethanolamines. Structurally related diaryl- and dialkylethanolamines had been prepared previously by other workers, for instance, Paal and Weidenkaff[3] and Krabbe and co-workers.[4]

The substances listed in the table were prepared by the action of the appropriate Grignard reagents upon glycine ethyl ester hydrochloride.

Experimental

The general method of procedure was to add small amounts of dry glycine ethyl ester hydrochloride (1 mole) to the ether solution of a Grignard reagent prepared as usual from the corresponding halide (10 moles) and magnesium (10 moles), the solution being kept cold during the addition. After all the hydrochloride had been added the cooling was stopped and the reaction proceeded of its own accord with gentle boiling of the ether. After about fifteen minutes the reaction had moderated and the flask was then placed on the water-bath and boiled for several hours. The ether solution was cooled, two layers usually being formed, and poured on ice and hydrochloric acid mixture to decompose the Grignard complex. After the decomposition, the mixture was allowed to stand for a day or two. The hydrochloride of the aminoalcohol, which formed a layer between the ether and water layers, was filtered and dried on porous tile. The ether and water layers were separated, the aqueous solution cooled and made alkaline with concentrated ammonium hydroxide, added slowly

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(1) Abstracted from Part I of the thesis presented by Robert Lay to the Faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) J. B. Niederl and M. I. Dexter, THIS JOURNAL, **63**, 1475 (1941).

(3) Paal and Weidenkaff, *Ber.*, **38**, 1686 (1905).

(4) Krabbe and co-workers, *ibid.*, **69**, 1569 (1936); **71**, 64 (1938); **72**, 381 (1939).

TABLE I

PHYSICAL CONSTANTS AND ANALYSES OF ETHANOLAMINES

No.	2-Aminoethanol	M. p., °C. (uncor.)	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
I	1,1-Di-*o*-anisyl-	115	$C_{16}H_{19}O_3N$	5.13	4.74
	(a) Hydrochloride	199	$C_{16}H_{20}O_3NCl$	4.52	4.41
	(b) Picrate	197[a]	$C_{22}H_{22}O_{10}N_4$	11.13	11.13
II	1,1-Di-*p*-anisyl-	112	$C_{16}H_{19}O_3N$	5.13	4.80
	(a) Hydrochloride	148	$C_{16}H_{20}O_3NCl$	4.52	4.35
	(b) Picrate	159[a]	$C_{22}H_{22}O_{10}N_4$	11.13	11.39
	(c) Phenylthiourea	158	$C_{23}H_{24}O_3N_2S$	6.86	6.92
	(d) N-Benzoyl	118	$C_{23}H_{23}O_4N$	3.71	3.31
III	1,1-Di-*p*-phenetyl-	80	$C_{18}H_{23}O_3N$	4.65	4.81
	(a) Hydrochloride	127	$C_{18}H_{24}O_3NCl$	4.20	4.22
	(b) Picrate	135[a]	$C_{24}H_{26}O_{10}N_4$	10.57	10.07
IV	1,1-Di-*o*-tolyl-	152	$C_{16}H_{19}ON$	5.81	5.68
	(a) Hydrochloride	247[a]	$C_{16}H_{20}ONCl$	5.04	5.22
	(b) Picrate	219[a]	$C_{22}H_{22}O_8N_4$	11.91	11.70
V	1,1-Di-*m*-tolyl-	79	$C_{16}H_{19}ON$	5.81	5.40
	(a) Hydrochloride	175	$C_{16}H_{20}ONCl$	5.04	5.21
	(b) Picrate	185[a]	$C_{22}H_{22}O_8N_4$	11.91	11.72
VI	1,1-Di-*p*-tolyl-	125	$C_{16}H_{19}ON$	5.81	5.68
	(a) Hydrochloride	195[a]	$C_{16}H_{20}ONCl$	5.04	4.65
	(b) Picrate	186[a]	$C_{22}H_{22}O_8N_4$	11.91	11.64
VII	1,1-Dicyclohexyl-	101	$C_{14}H_{27}ON$	6.22	6.00
	(a) Hydrochloride	202	$C_{14}H_{28}ONCl$	5.34	5.14
	(b) Picrate	154[a]	$C_{20}H_{30}O_8N_4$	12.33	11.97
VIII	1,1-Di-*p*-diphenyl ether	135	$C_{26}H_{23}O_3N$	3.53	3.64
	(a) Hydrochloride	149[a]	$C_{26}H_{24}O_3NCl$	3.23	3.05
	(b) Picrate	163[a]	$C_{32}H_{26}O_{10}N_4$	8.95	8.82

[a] With decomposition.

with constant stirring. This alkaline solution was allowed to stand overnight and the free aminoalcohol filtered off and dried. The alkaline solution was extracted with ether, the ether dried with sodium sulfate and dry hydrogen chloride passed into it to recover the aminoalcohol as its hydrochloride.

The hydrochlorides were purified by dissolving them in a little alcohol and precipitating them by the addition of ether. The free aminoalcohols were recrystallized from water. In some cases no hydrochloride separates after the original decomposition due to its solubility in water. Also in several cases the free aminoalcohol formed a gum upon the addition of ammonium hydroxide and was best obtained by extracting the alkaline solution with ether, drying the ethereal solution with sodium sulfate, forming the hydrochloride by passing dry hydrogen chloride gas into it, dissolving this in water, and reprecipitating with ammonia.

The picrates were obtained by adding a saturated aqueous solution of picric acid to the filtrate from which the alcohols had been recrystallized. They were recrystallized from hot water.

To obtain the benzoyl derivatives 0.3 g. of the aminoalcohol was dissolved in 5 cc. of ether and shaken with 5 cc. of 15% sodium hydroxide with the portionwise addition of 0.6 g. of benzoyl chloride. The ether was evaporated by drawing air through it. The precipitate was filtered off and recrystallized from alcohol.

The phenylthiourea derivatives were prepared by adding to 0.1 g. of the aminoalcohol 0.2 cc. of phenyl isothiocyanate and shaking the mixture for several minutes. The semi-solid that formed was washed with dilute alcohol and dissolved in 95% alcohol, filtered and placed in the icebox. The crystals were separated and dried.

Summary

A series of 1,1-diaryl- and 1,1-dicycloalkylethanolamines has been made by the action of the Grignard reagent on glycine ethyl ester hydrochloride.

WASHINGTON SQUARE COLLEGE
NEW YORK, N. Y.
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