A New Synthesis of O-Substituted Hydroxylamines

BY PRICE TRUITT, LOREN M. LONG AND MARJORIE MATTISON

It has been reported[1] that monochloramine condenses with substances containing the =N—CS—S—Na group.

$$(CH_3)N—CS—S—Na + ClNH_2 \longrightarrow (CH_3)_2N—CS—S—NH_2 + NaCl$$

This suggested the possibility of the analogous reaction of chloroamine with sodium alcoholates to give O-substituted hydroxylamines.

$$RONa + ClNH_2 \longrightarrow RONH_2 + NaCl$$

This method has been applied with the sodium salts of β-phenoxyethanol and benzyl alcohol, giving very poor yields (1 to 5%) of the hydroxylamines. However, similar attempts with isoamyl, cyclohexyl, β-phenylethyl and 4-methoxybenzyl alcohols failed to give the desired products, ammonia (as ammonium chloride) being isolated in each case. This reaction is being studied further, using monochloroamine and various substituted chloroamines.

Experimental

An ether solution of monochloroamine was added to a stirred solution of the alcoholate in benzene, cooled in an ice–salt-bath. A white precipitate appeared at once. The reaction mixture was stirred in the ice–salt-bath for several hours (at room temperature overnight), and refluxed for one hour, cooled and poured into water. The ethereal extract was extracted with 10% hydrochloric acid and the acid layer was concentrated at reduced pressure. When white crystals appeared, the cooled mixture was filtered, the solid product washed with absolute ether and recrystallized from a mixture of absolute ethanol and ether.

One mole of β-phenoxyethanol, 0.25 mole of sodium and 0.081 mole of monochloroamine gave 0.8 g. of O-β-phenoxyethylhydroxylamine hydrochloride melting at 172–174° with decomposition.

Anal. Calcd. for $C_8H_{12}O_2NCl$: N, 7.39; Cl, 18.70. Found: N, 7.57; Cl, 18.56.

One-half mole of benzyl alcohol, 0.25 mole of sodium and 0.155 mole of monochloroamine gave 0.25 g. of O-benzylhydroxylamine hydrochloride melting at 229–235° with decomposition. Behrend[2] reported the melting point of this compound as 229–235°.

Anal. Calcd. for $C_7H_{10}ONCl$: N, 8.78. Found: N, 8.83.

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[1] R. Hanslik, U. S. Patent 2,261,024, October 28, 1942.

[2] L. Behrend, *Ann.*, **257**, 207 (1890).

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Reactions of Pyrene-3-aldehyde

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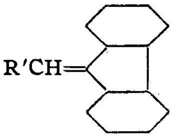
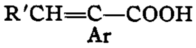
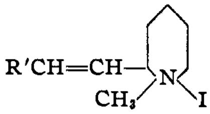
Pyrene-3-aldehyde reacts readily with the reactive methylene groups in malonic acid[1] and nitromethane.[2] A number of other condensation reactions have been studied, all leading to colored substances characterized by extended conjugated systems. With various methyl ketones (3-pyrenylidene)-compounds of type (I) have been obtained; fluorene gave 9-(3′-pyrenylidene)-fluorene (II) and phenylacetic and α-naphthylacetic acids condensed to form the corresponding α-aryl-β-(3-pyrenyl)-acrylic acids (III). From the methiodides of picoline, lutidine and quinaldine, stilbazole homologs were formed, *e. g.*, α-(3-pyrenyl)-β-(2′-pyridyl)-ethylene methiodide (IV). Another substance which belongs in this group is *sym*-di-(3-pyrenyl)-ethylene (V) available from (polymeric) pyrene-3-thioaldehyde by heating it in boiling ethyl benzoate or naphthalene, with or without Raney nickel.

R′CH=CHCOR I

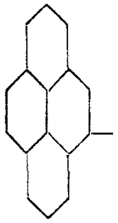

II


$$\underset{\text{Ar}}{R'CH=C}—COOH$$
III

R′CH=CHR′ V


IV

NR′ =



Experimental

Condensation of Pyrene-3-aldehyde with Methyl Ketones

(a) **Acetone.**—To a solution of 4.6 g. of pyrene-3-aldehyde in 40 cc. of acetone, 1 cc. of a concentrated aqueous solution of sodium hydroxide was added with stirring. The stirring was continued for two hours, and the voluminous precipitate filtered off, washed with alcohol and acetone, and dried. The yellow 3-pyrenylideneacetone (I, R = CH_3) crystallized from acetic acid (or butanol); m. p. 152°. The yield was almost quantitative.

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.9; H, 5.2. Found: C, 88.7; H, 5.1.

The phenylhydrazone, prepared in acetic acid solution, separated after twenty-four hours; the orange-yellow plates were recrystallized from butanol; m. p. 238°.

Anal. Calcd. for $C_{26}H_{20}N_2$: N, 8.0. Found: N, 7.8.

(b) **Pinacolone.**—To a concentrated solution of 4.6 g. of pyrene-3-aldehyde in absolute alcohol, gradually 1 g. of sodium metal, and then 2 g. of pinacolone were added. After a while, the yellow crystals of 3-pyrenylidenepinacolone (I, R = —$C(CH_3)_3$) began to precipitate; after recrystallization from glacial acetic acid, it melted at 155°; yield, 80%.

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.5; H, 6.4. Found: C, 88.6; H, 6.4.

The picrate, prepared in glacial acetic acid solution, formed red leaflets, m. p. 150°.

Anal. Calcd. for $C_{29}H_{23}O_8N_3$; N, 7.8. Found: N, 7.8.

(c) **Acetophenone.**—In the manner described for pinacolone, 2.2 g. of acetophenone gave, in almost quantitative yield, the deep yellow 3-pyrenylideneacetophe-

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[1] E. Bergmann and E. Bograchov, THIS JOURNAL, **62**, 3016 (1940).

[2] E. Bograchov, *ibid.*, **66**, 1612 (1944).