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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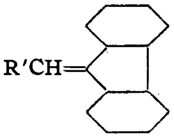
Reactions of Pyrene-3-aldehyde

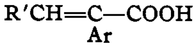
BY M. WEIZMANN AND E. BOGRACHOV

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



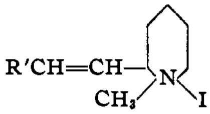
II



$$R'CH{=}\underset{Ar}{C}—COOH$$

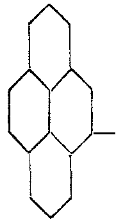
III

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).

none (I, R = C_6H_5). It was recrystallized from glacial acetic acid, xylene or butanol and melted at 158°.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.4; H, 4.8. Found: C, 90.2; H, 4.8.

The yellow **phenylhydrazone**, recrystallized from xylene, melted at 236°.

Anal. Calcd. for $C_{31}H_{22}N_2$: N, 6.6. Found: N, 7.0.

(d) **β-Acetylnaphthalene.**—Analogously, 3.4 g. of β-acetylnaphthalene gave an almost quantitative yield of the yellow α-(2-naphthoyl)-β-(3′-pyrenyl)-ethylene (I, R = β-naphthyl). Recrystallization from xylene or glacial acetic acid gave crystals, melting at 184°.

Anal. Calcd. for $C_{29}H_{18}O$: C, 91.1; H, 4.7. Found: C, 90.9; H, 4.6.

The orange-colored **phenylhydrazone** crystallized from xylene, and melted at 246°.

Anal. Calcd. for $C_{35}H_{24}N_2$: N, 5.9. Found: N, 6.2.

9-(3′-Pyrenylidene)-fluorene.—The condensation of 4.6 g. of the aldehyde with 3.3 g. of fluorene was carried out, using sodium ethoxide as catalyst.[3] The yellow-orange fulvene (II) separated spontaneously from the solution, and melted after recrystallization from xylene, butanol or glacial acetic acid at 210°.

Anal. Calcd. for $C_{30}H_{18}$: C, 95.2; H, 4.8. Found: C, 94.9; H, 5.0.

α-Phenyl-β-(3-pyrenyl)-acrylic Acid (III, R = C_6H_5).—One mole each of pyrene-3-aldehyde and sodium phenylacetate was heated in boiling acetic anhydride (1.5 to 2 moles) for two hours. After cooling, the reaction mixture was diluted with water, and the solid residue filtered and washed with alcohol. From glacial acetic acid, the acid was obtained in yellow needles of m. p. 259°; yield, 30%.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.2; H, 4.6. Found: C, 86.5; H, 4.9.

α-(1-Naphthyl)-β-(3′-pyrenyl)-acrylic acid (III, R = 1-naphthyl) was obtained analogously from pyrene-3-aldehyde and sodium 1-naphthylacetate; yellow needles of m. p. 290° (from nitrobenzene).

Anal. Calcd. for $C_{29}H_{18}O_2$: C, 87.4; H, 4.5. Found: C, 87.1; H, 4.7.

α-(3-Pyrenyl)-β-(2′-pyridyl)-ethylene Methiodide (IV).—To a solution of pyrene-3-aldehyde (4 g.) and α-picoline methiodide (4 g.) in a small quantity of absolute alcohol, 10 to 15 drops of piperidine was added at 180°. Heating was continued for thirty minutes; then the red precipitate was filtered, washed with alcohol, dried, and recrystallized from nitrobenzene: m. p. 295°; yield, 65%.

Anal. Calcd. for $C_{24}H_{18}IN$: C, 64.4; H, 4.0; N, 3.1. Found: C, 64.1; H, 4.0; N, 3.3.

α-(3-Pyrenyl)-β-(6′-methyl-pyridyl-2′)-ethylene methiodide was prepared in 70% yield from 2.3 g. of pyrene-3-aldehyde and 4 g. of 2,6-lutidine methiodide, as described above. It was recrystallized from nitrobenzene, and formed red shiny crystals of m. p. 275°.

Anal. Calcd. for $C_{25}H_{20}IN$: N, 3.0. Found: N, 3.1.

α-(3-Pyrenyl)-β-(2′-quinolyl)-ethylene methiodide was formed in 75% yield as a red-violet, insoluble substance from 2.3 g. of pyrene-3-aldehyde and 2.8 g. of quinaldine methiodide; m. p. 285°.

Anal. Calcd. for $C_{28}H_{20}IN$: N, 2.8. Found: N, 2.8.

sym-**Di-(3-pyrenyl)-ethylene** (V).—(a) 10 g. of pyrene-3-aldehyde was dissolved in 100 ml. of dry benzene. Dry hydrogen chloride and hydrogen sulfide were passed simultaneously through the cold solution. The yellow precipitate was filtered and washed with water, alcohol and ether. It could not be recrystallized, as it decomposed on heating in high-boiling solvents. In its crude state the polymeric pyrene-3-thioaldehyde melted at 260–270°.

Anal. Calcd. for $(C_{17}H_{10}S)_x$: C, 82.9; H, 4.1. Found: C, 82.5; H, 4.4.

(b) A mixture of 2 g. of the thioaldehyde, 1 g. of Raney nickel and 20 g. of boiling naphthalene was heated for one hour. After removal of the naphthalene *in vacuo*, a brown-red residue was obtained, which was washed with alcohol and recrystallized from ethyl benzoate: m. p. 315°; yield, 75% (calculated on pyrene-3-aldehyde).

Anal. Calcd. for $C_{34}H_{20}$: C, 95.3; H, 4.7. Found: C, 95.1; H, 4.8.

DEPARTMENT OF ORGANIC CHEMISTRY
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[3] Schlenk and Bergmann, *Ann.*, **479**, 56 (1930).

NEW COMPOUNDS

Hexahydrojulolidine

To a solution of julolidine,[1] 1,2,3,5,6,7-hexahydrobenzo-(i,j)-quinolizine (20 g., 0.115 mole), in alcohol (20 ml.) there was added Raney nickel (2 g.) and the mixture was shaken at 200° under a pressure of 2000 lb. of hydrogen. After removal of solvent and catalyst, the residue was distilled yielding 5 g. (low yield due to accidental loss) of a colorless oil: b. p. 76–80° at 3 mm.

Anal. Calcd. for $C_{12}H_{21}N$: C, 80.44; H, 11.73. Found: C, 80.55; H, 11.45.

The **picrate** of hexahydrojulolidine was readily prepared using an ethereal solution of picric acid. After recrystallization from hot water the picrate was obtained as an amorphous yellow solid, m. p. 165–167°.

Anal. Calcd. for $C_{18}H_{24}N_4O_7$: C, 52.94; H, 5.88. Found: C, 52.82; H, 5.69.

The **methiodide** of hexahydrojulolidine formed readily and could be recrystallized from a solution of alcohol and ether. It was obtained as an amorphous white solid, m. p. 294–298° with decomposition.

Anal. Calcd. for $C_{13}H_{24}IN$: C, 48.50; H, 7.47. Found: C, 48.51; H, 7.45.

Hexahydrojulolidine hydrochloride and also the quaternary methiodide derivative were found to be convulsants when tested intravenously in rabbits.

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[1] Glass and Weissberger, "Organic Syntheses," **26**, 40 (1946).

[2] Aided by a grant from the National Foundation for Infantile Paralysis, Inc.

Some Derivatives of Levulinic Acid

Levulinic acid diethylamide was prepared (a) by heating 50 g. of levulinic acid with 50 g. of diethylamine at 250° for ten hours (autoclave), yield 60%; and (b) by adding 13.4 g. of γ-chlorovaleroactone[1] to a cold solution of 15 g. of diethylamine in 50 cc. of ether; the reaction was completed on the water-bath and the solution filtered from diethylamine hydrochloride and distilled, yield 70%. The amide is soluble in water and boils at 108° (0.9 mm.); $n^{22}\text{D}$ 1.457.

Anal. Calcd. for $C_9H_{17}O_2N$: C, 63.2; H, 10.0; N, 8.2. Found: C, 63.3; H, 10.2; N, 8.2.

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[1] Clemo and Ramage, *J. Chem. Soc.*, 54 (1931).