

in 20 cc. of dry benzene was added slowly to 5.0 g. of 2,2-dimethylethyleneimine in 50 cc. of dry benzene. Some heat was evolved; the temperature of the solution was 50° after the addition of all the isocyanate. The solution was allowed to stand for two to three days and then poured into 400 cc. of petroleum ether (60–70°). A slight cloudiness developed and after the walls of the flask were scratched, crystallization began and continued for ten to fifteen minutes. The white microcrystalline powder was removed by filtration; yield 9.8 g., m. p. 100–102.5°. Recrystallization from benzene–petroleum ether mixture (2.5:10 parts by volume) gave long needles; m. p. 104–105°.

Rotation. 0.1104 g. made up to 10 cc. in dry benzene gave $\alpha_D^{25} + 0.532$, $l = 1$, $[\alpha]_D^{25} + 48^\circ$.

Anal. Calcd. for $C_{11}H_{15}ON_2$: C, 71.52; H, 8.31. Found: C, 71.44; H, 8.15.

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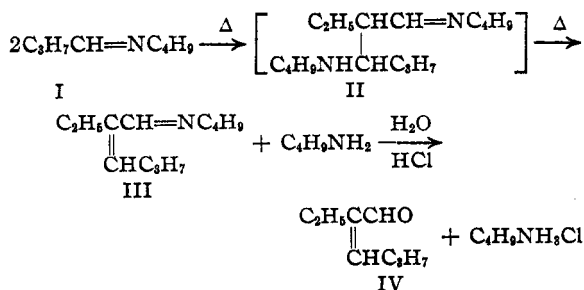
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Aldol Condensations with Aliphatic Schiff Bases

BY WILLIAM S. EMERSON, S. M. HESS AND F. C. UHLE

Several investigators¹ have mentioned the readiness with which aliphatic Schiff bases polymerize without examining the products of the reaction. Picon² showed that when ethylidene ethylamine was treated with sodium in liquid ammonia, a condensation of the aldol type took place. Hydrogenation of this product gave a 60% yield of 1,3-di-(ethylamino)-butane. Likewise Strain³ postulated an aldol condensation as the first step in the thermal polymerization of aliphatic imines to pyridine derivatives, and Kharasch, Richlin and Mayo⁴ have isolated the aldol condensation product of butylidene aniline.

We have found that the purely aliphatic Schiff base, *n*-butylidene-*n*-butylamine (I) is converted to 2-ethyl-2-hexenal-butylamine (III) by merely heating at 140–150° for three hours.



(1) Schiff, *Ann.*, **140**, 92 (1866); Chancel, *Bull. soc. chim.*, [3] **11**, 933 (1894); Henry, *Compt. rend.*, **120**, 839 (1895); Mailhe, *Bull. soc. chim.*, [4] **25**, 321 (1919).

(2) Picon, *Compt. rend.*, **175**, 695 (1922).

(3) Strain, *THIS JOURNAL*, **54**, 1221 (1932).

(4) Kharasch, Richlin and Mayo, *ibid.*, **62**, 494 (1940).

When 48.8 g. (0.67 mole) of *n*-butylamine and 48.2 g. (0.67 mole) of *n*-butyraldehyde were heated at 20 mm. in a Claisen flask, *n*-butylidene-*n*-butylamine (I) distilled at 45–50° in the course of thirty-five minutes. It was then separated from the water and redistilled, b. p. 140–150°; yield 72.5 g. (85%). A sample which was again distilled boiled at 140–145°; d_4^{20} 0.764; n_D^{20} 1.4211; M^{20}_D calcd. 42.4; M^{20}_D found 42.2.

Anal. Calcd. for $C_8H_{17}N$: N, 11.02. Found: N, 10.93.

2-Ethyl-2-hexenalbutylamine (III) was prepared by refluxing 72.5 g. of *n*-butylidene-*n*-butylamine for three hours. This product was dried over sodium sulfate and then distilled, b. p. 213–235°; yield 33.9 g. (65%). A sample was redistilled at 217–220°; d_4^{20} 0.847; n_D^{20} 1.4745; M^{20}_D calcd. 60.5; M^{20}_D found 60.4.

Anal. Calcd. for $C_{12}H_{23}N$: N, 7.74. Found: N, 7.70.

The structure of III was established by refluxing 10 g. with 25 cc. of 6 *N* hydrochloric acid for thirty-five minutes. The upper layer was then separated and distilled giving 3 g. of the known unsaturated aldehyde, 2-ethyl-2-hexenal (IV), b. p. 170–171° (173–174°),⁵ whose 2,4-dinitrophenylhydrazone melted at 122° (122°).⁶

The production of III easily can be accounted for by an initial condensation of the aldol type leading to II which then loses butylamine to produce III.

(5) Gorhan, *Monatsh.*, **26**, 73 (1905).

(6) Backes, *Compt. rend.*, **196**, 277 (1933).

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Some Alkyl Nitrophenols

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p-Nitrophenol has been reported to be beneficial in the treatment of fungus disease of the skin.² In view of the well-known fact that the germicidal activity of a phenol is increased by the introduction of an alkyl group, it was believed worth while to synthesize analogous alkyl nitrophenols, hoping that the alkyl group might have a corresponding effect also on the fungicidal activity of nitrophenol. Two such compounds were therefore synthesized by direct nitration of alkyl phenols prepared by the condensation of the alcohol with phenol in the presence of zinc chloride. The position of the nitro group in the alkylphenol was not determined.

***s*-Hexylnitrophenol.**—To a stirred solution of 71.2 g. of *s*-hexylphenol (0.4 mole) in 175 ml. of benzene in a three-necked, round-bottom flask, equipped with a stirrer, reflux condenser and dropping funnel, cooled by means of an ice-salt-bath to below +5°, 125 g. of dilute nitric acid (1:1)

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(2) Robertson, *Brit. Med. J.*, 1339 (1935); Marriatt and Robertson, *ibid.*, 136 (1935).