

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 $\alpha^{25}_D +0.532$, $l = 1$, $[\alpha]^{25}_D +48^\circ$.

Anal. Calcd. for $C_{12}H_{18}ON_2$: C, 71.52; H, 8.31. Found: C, 71.44; H, 8.15.

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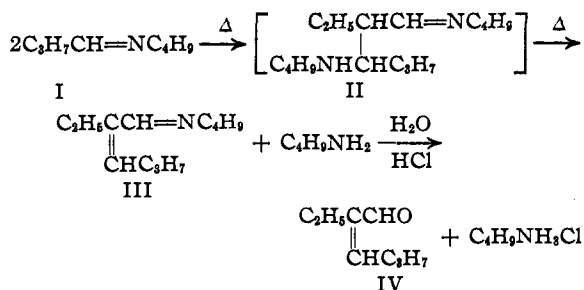
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Aldol Condensations with Aliphatic Schiff Bases

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.*, **13**, 933 (1894); Henry, *Compt. rend.*, **120**, 839 (1895); Mailhe, *Bull. soc. chim.*, **4**, 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^{20}_D 0.764; n^{20}_D 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^{20}_D 0.847; n^{20}_D 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

BY WALTER H. HARTUNG¹ AND HARRY F. KOEHLER

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)

(1) Present address: School of Pharmacy, University of Maryland, Baltimore, Maryland.

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

was slowly added during a period of about fifty minutes, being careful not to let the temperature rise above $+5^{\circ}$. Stirring was continued for an additional two hours, during which the temperature was allowed to rise to 15° . The mixture was then washed with three 100-ml. portions of water and the benzene distilled off on a steam-bath. The residue was then distilled at lowest possible pressures. The product distilled at $165\text{--}185^{\circ}$ at 2 mm.; yield, 70.6 g., 79%. Found: N (Kjeldahl), 6.26; calcd. N for $C_{12}H_{17}O_3N$, 6.28.

***t*-Octylnitrophenol.**—This was prepared from *t*-octylphenol in a similar manner. The product distilled at $157\text{--}168^{\circ}$ at 1 mm.; 97% yield. Found: N, 5.58; calcd. N for $C_{14}H_{21}O_3N$, 5.61.

The nitration of *s*-hexyl-*m*-cresol was carried out similarly and every evidence indicated that the reaction proceeded normally. However, at the distillation temperature, the product began to decompose, and the decomposition progressed spontaneously and could not be stopped by cooling the distillation flask.

Neither compound showed any decided fungicidal activity when tested against a mold culture by the Agar Cup Plate Method.³

(3) These tests were made by S. R. Pence and W. A. Feirer, to whom the authors acknowledge their thanks.

MEDICAL-RESEARCH DIVISION
SHARPE AND DOHME, INC.

GLENOLDEN, PENNSYLVANIA RECEIVED OCTOBER 23, 1940

The Qualitative Determination of Cadmium in the Presence of Copper

BY ALBERT C. HOLLER

This paper describes a qualitative determination of cadmium in the presence of copper. The principle is that described by Sachs,¹ who states that a number of insoluble hydroxides are colored by a 1% alcoholic solution of phenolphthalein. He ascribes this to the activated adsorption of phenolphthalein on the hydroxide.

The procedure was worked out to fit into the method used to analyze group II as described by Engelder,² but may be applicable to other schemes.

The copper and cadmium were present in approximately equal amounts (about 30 mg. of each). It has been determined that cadmium can be detected in the presence of copper when the copper-cadmium ratio is as large as 10 to 1.

Procedure.—The filtrate from the lead separation is neutralized with ammonium hydroxide and the bismuth hydroxide is filtered off in the usual way.² If copper is present the filtrate will be colored deep blue. The solution is neutralized with nitric acid and 5 cc. of concd. nitric acid added. The solution is evaporated to dryness

(1) Sachs, *THIS JOURNAL*, **62**, 3514 (1940).

(2) Engelder, "Elementary Qualitative Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1933, pp. 119 and 124.

and the residue ignited below a dull red heat until the volatilization of ammonium salts is complete. The baked residue is then dissolved in 1.5 cc. of dilute nitric acid and the volume adjusted with water to 25 cc. Twelve cc. of 0.5 *N* sodium hydroxide is added to the solution. The hydroxides of cadmium and copper are filtered off and washed once with water. The hydroxides are then spotted with a 1% alcoholic solution of phenolphthalein and moistened with a few drops of water.

A crimson color indicates the presence of cadmium.

Copper hydroxide does not adsorb phenolphthalein when the hydroxide is prepared using a 10% excess of the salt (cupric nitrate) and thus does not form a colored compound.

I wish to express my appreciation to Mr. H. R. Heiple who helped me prepare this paper.

DEPARTMENT OF CHEMISTRY

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The Exchange of Sulfate Ion with Water

BY JAMES L. HYDE

The oxygen exchange of sulfate ion has been studied in acid, neutral and alkaline solutions. Heavy oxygen water, prepared by fractional distillation,¹ was obtained through the courtesy of Professor Merle Randall, and was distilled from alkaline permanganate before use. Analysis of the water² was performed with a mass spectrometer. After placing each sample, whose composition is shown in the table below, in a sealed tube in a thermostated bath for the indicated time, two cubic centimeters of water was distilled off *in vacuo*, and this water analyzed in the same way. The precision of analysis was $\pm 1\%$.

The alkaline exchange experiment was performed in a sealed platinum bulb similar to the silver one used by Winter, Carlton and Briscoe³ in order to avoid any possible interference by glass. The results are tabulated below.

In a recent publication Hall and Alexander,⁴ who used solutions containing lower concentrations of hydrogen ion and hydroxyl ion, respectively, reported results which were similar except for the fact that their exchange in acid solution was incomplete.

Our results are also in agreement with those of all other observers^{3,5,6} for the neutral solution.

(1) Randall and Webb, *Ind. Eng. Chem.*, **31**, 227 (1939).

(2) Cohn and Urey, *THIS JOURNAL*, **60**, 879 (1938).

(3) Winter, Carlton and Briscoe, *J. Chem. Soc.*, 131 (1940).

(4) Hall and Alexander, *THIS JOURNAL*, **62**, 3455 (1940).

(5) Datta, Day and Ingold, *J. Chem. Soc.*, 1968 (1937).

(6) Titani and Goto, *Bull. Chem. Soc. Japan*, **13**, 667 (1938); **14**, 77 (1939).