resulting from breakdown of the dimer. It was further purified by redistilling, and through the sodium bisulfite compound, made in a minimum of aqueous methyl alcohol solution. The washed bisulfite compound in water was treated with sodium bicarbonate and gently warmed to regenerate the ketone. Thus purified the unsaturated ketone distilled at 157.5–159°, sp. gr. (20°C.) 0.9813, analysis C, 77.62; H, 7.51; calcd. C, 77.74; H, 7.46. The semicarbazone recrystallized from alcohol melted at 222° and showed N, 24.76; calcd., N, 25.45.

Bicyclo-(0,2,3)-heptanone-7.—The unsaturated ketone was reduced, in dilute alcohol solution, by colloidal palladium and hydrogen at substantially atmospheric pressure. The saturated ketone distills at 164–165°, sp. gr. 0.9958 (20°C.), $n^{20}D$ 1.5030. It forms a semicarbazone melting at 216° (semicarbazone of norcamphor melts at 196.5–197.5°).

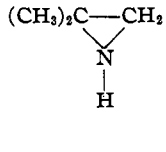
Oxidation of Bicyclo-(0,2,3)-heptanone-7.—The ketone was oxidized by refluxing for three hours with dilute nitric acid, equal parts of concentrated nitric and water. On gently evaporating the resulting solution nearly to dryness, the product crystallized on cooling and on purification proved to be glutaric acid, melting point 98°.

NEW YORK, N. Y. RECEIVED DECEMBER 5, 1940

The Preparation and Attempted Resolution of 2,2-Dimethylethyleneimine

BY THEODORE L. CAIRNS

Previous investigations[1] of the possible asymmetry of the nitrogen atom in substituted ethyleneimines have all failed because it was not possible to synthesize the desired compounds. A method for the preparation of 2,2-dimethylethyleneimine (I) has now been developed. This compound gave a sulfonamide, insoluble in alkali, identical with one previously prepared[1a] by a different method. Compound I did not reduce permanganate and when treated with dilute sulfuric acid the ring opened to give 1-amino-2-methyl-2-propanol.



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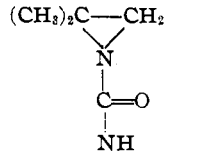


II

The substituted urea derivative (II) derived from compound I and *l*-α-phenylethylisocyanate was subjected to fractional crystallization, but no evidence of separation into diastereoisomers was obtained. Compound II exhibited mutarotation in boiling benzene, but the change in rotation could always be accounted for by decomposition.

There are certain objections to a compound having a carbonyl group directly attached to the nitrogen atom.[2] However, the whole problem is provided with a theoretical basis by the calculations of Kincaid and Henriques[3] and the synthesis of more suitable derivatives is now being investigated.

Experimental[4]

2,2-Dimethylethyleneimine.—To a solution of 100 g. of 2-methyl-2-amino-1-propanol (Commercial Solvents Corporation) in 200 cc. of water was added with shaking 110 g. of sulfuric acid in 200 cc. of water. The solution was distilled at atmospheric pressure until the temperature of the reaction mixture reached 115°, and then at 25–30 mm. and a temperature of 150–170° for one hour. The flask was cooled and broken and the brown crystalline mass crushed. This was treated with an excess of 40% aqueous sodium hydroxide and the mixture distilled until about 120 g. of distillate was obtained. The distillate was saturated with potassium hydroxide and the organic layer separated and dried with potassium hydroxide and finally with sodium. Distillation gave 30–40 g. of a mobile, colorless liquid of ammoniacal odor; b. p. 69–70°, $n^{25}D$ 1.4052.

Anal. Calcd. for C_4H_9N: C, 67.55; H, 12.76. Found: C, 67.59; H, 12.70.

***l*-α-Phenylethyl Isocyanate.**—A solution of 20 g. *d*-α-phenylethylamine[5] in 200 cc. of toluene was saturated with dry hydrogen chloride. A heavy white precipitate was formed. An additional 100 cc. of toluene was added and phosgene passed into the mixture for a few minutes. The mixture was then heated to boiling and phosgene bubbled through for four hours. The solution was cooled to room temperature, decanted from a very small amount of a white crystalline solid, and fractionated under reduced pressure; yield 16.5 g.; b. p. 82–83° at 12–14 mm.

Rotation. 0.3541 g. made up to 10 cc. with benzene gave $\alpha^{24}D$ −0.09°, l = 1, $[\alpha]^{24}D$ −2°.

***d*-N-(α-Phenylethyl)-urea.**—Treatment of a few drops of *l*-α-phenylethyl isocyanate in benzene solution with anhydrous ammonia gave white crystals, which, after crystallization from water, had m. p. 121–122°.

Rotation. 0.2225 g. made up to 10 cc. in absolute alcohol gave $\alpha^{25}D$ 1.086, l = 1, $[\alpha]^{25}D$ +48.8°.

Anal. Calcd. for $C_9H_{12}ON_2$: C, 65.83; H, 7.31. Found: C, 65.75; H, 7.16.

The literature[6] gives m. p. 122–123° and $[\alpha]D$ 46.2.

***d*-(1-α-Phenylethylcarbamyl)-2,2-dimethylethyleneimine.**—A solution of 10.35 g. *l*-α-phenylethyl isocyanate

(1) (a) Adams and Cairns, THIS JOURNAL, **61**, 2464 (1939). (b) Meisenheimer and Chou, *Ann.*, **539**, 70 (1939). (c) Mole and Turner, *Chem. and Ind.*, 582 (1939). (d) Maitland, *Ann. Repts. Chem. Soc.*, **36**, 243 (1939).

(2) Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938, Vol. I, p. 334.

(3) Kincaid and Henriques, THIS JOURNAL, **62**, 1474 (1940).

(4) Analyses by Dr. L. Weisler.

(5) "Organic Syntheses," Vol. XVII, 1937, p. 80.

(6) Marckwald and Methe, *Ber.*, **38**, 801 (1905).

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°.

Anal. Calcd. for $C_{13}H_{18}ON_2$: C, 71.52; H, 8.31. Found: C, 71.44; H, 8.15.

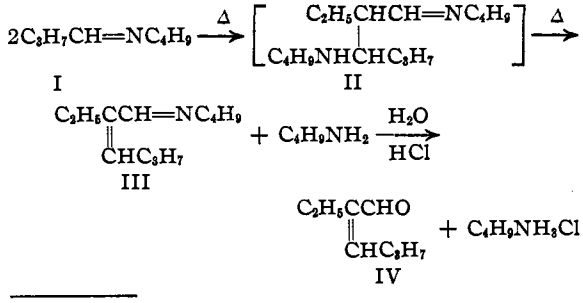
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK RECEIVED JULY 30, 1940

Aldol Condensations with Aliphatic Schiff Bases

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

Several investigators[1] have mentioned the readiness with which aliphatic Schiff bases polymerize without examining the products of the reaction. Picon[2] 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 Strain[3] postulated an aldol condensation as the first step in the thermal polymerization of aliphatic imines to pyridine derivatives, and Kharasch, Richlin and Mayo[4] 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.



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}_{20} 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}_{20} 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.

(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).

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

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

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS RECEIVED DECEMBER 2, 1940

Some Alkyl Nitrophenols

BY WALTER H. HARTUNG[1] 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).