

### Experimental

**Isolation of Di-*n*-propyl Carbinol.**—*n*-Butyraldehyde (7.93 moles) and di-*t*-butyl peroxide (0.79 mole) were heated at 2 atmospheres pressure and 115° for sixteen and one-half hours in an all-glass system. The evolved propane and carbon monoxide were bled off at a rate which would maintain pressure. The product was washed with concentrated sodium bisulfite solution. The remaining organic phase was separated and steam distilled to remove hexane and unreacted di-*t*-butyl peroxide. The remaining product was dried and fractionated. The fraction distilling at 153–155.5° had an index  $n_D^{20}$  1.4193 and contained 71.6% carbon and 13.7% hydrogen. The corresponding literature values for 4-heptanol are b. p. 153.4–154.4°,  $n_D^{20}$  1.4199,<sup>4</sup> carbon 72.3% and hydrogen 13.8%. The 3,5-dinitrobenzoate was prepared; m. p., 64.5° (lit. m. p., 64°).<sup>5</sup> This alcohol was isolated in a yield of 8–10% based on the consumed aldehyde. Over 70% of the aldehyde was converted to propane and carbon monoxide.

**Isolation of Di-*n*-hexyl Carbinol.**—*n*-Heptaldehyde (1.75 moles) and di-*t*-butyl peroxide (0.34 mole) were heated at 130° for five and one-half hours in a glass system provided with a reflux condenser. Carbon monoxide (0.61 mole) was evolved and hexane (0.59 mole) was recovered by distillation. Finally nearly all of the material which could be steam distilled was separated and the remainder, after drying, was run through a falling film molecular still at 71°. The distillate amounting to 24 cc. was cooled in ice and the crystals filtered off. The solid waxy material was evaporated under 0.1 mm. pressure onto an ice-cooled thimble. This material melted at 40.5–41° and analyzed 77.7% carbon and 13.8% hydrogen. Di-*n*-hexylcarbinol has a reported melting point of 41–42°<sup>6</sup> and contains 78.0% carbon and 14.0% hydrogen.

(4) Dillon and Lucas, *THIS JOURNAL*, **50**, 1712 (1928).

(5) Adkins, Connor and Cramer, *ibid.*, **52**, 5192 (1930).

(6) Kipping, *J. Chem. Soc.*, **57**, 536 (1890).

SHELL DEVELOPMENT COMPANY  
EMERYVILLE, CALIFORNIA

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## The Reaction between Morpholine and Chloral<sup>1</sup>

BY G. B. L. SMITH<sup>2</sup>, MEYER SILVER<sup>3</sup> AND ERNEST I. BECKER

The products of the reaction of an aqueous solution of morpholine and chloral at 25° are chloroform and morpholine formate.<sup>4</sup> It was believed that in anhydrous solution N-containing analogs of DDT could be obtained. It was hoped that the alcohol-like product, similar to that for morpholine and formaldehyde,<sup>5</sup> would condense with a second molecule or morpholine to give an analog of DDT. However, in the present work it was found that when a slight excess of morpholine was added to a solution of chloral in isopropyl or *n*-butyl ether, N-formylmorpholine was formed in 90–92% yield. The product was identified by its physical constants, by analysis, and by prepara-

(1) This work was begun under the guidance of Professor G. B. L. Smith and completed under the supervision of Professor Ernest I. Becker.

(2) Present address: Naval Ordnance Testing Station, Inyokern, California.

(3) Present address: Nopco Chemical Company, Harrison, New Jersey. This paper was taken from the Master's Thesis of Meyer Silver, June, 1947, Department of Chemistry, Polytechnic Institute of Brooklyn.

(4) Ling Yang and Pin-Fong Hu, *J. Chinese Chem. Soc.*, **10**, 190 (1943).

(5) M. Zief and J. P. Mason, *J. Org. Chem.*, **8**, 1 (1943).

tion of derivatives of the morpholine and formic acid obtained from its hydrolysis. Chloroform was recovered in 84% yield as the only other product of the reaction.

Similar reactions with chloral or chloral hydrate have been reported in which ethylenediamine gives the diformyl derivative<sup>6</sup> and with N-methyl- $\alpha$ -homopiperonylamine and piperidine to give the monoformyl derivatives.<sup>7</sup>

### Experimental

**Materials.**—Anhydrous chloral was prepared by shaking crude chloral with concentrated sulfuric acid and distilling the chloral from the mixture, b. p. 96–97° (767 mm.). Morpholine was dried over fused potassium hydroxide, filtered and distilled, b. p. 125–128° (767 mm.). Iso-propyl ether was washed with ferrous sulfate to remove peroxides, dried, and distilled, b. p. 67–69° (759 mm.). *n*-Butyl ether was distilled, b. p. 140–142° (760 mm.).

**Procedure.**—In a 500-ml., 3-neck, round-bottom flask, equipped with a reflux condenser, dropping funnel and mechanical stirrer, was placed a solution of 74 g. (49.2 ml., 0.50 mole) of chloral in 150 ml. of *n*-butyl ether. To the stirred solution was added rapidly 48 g. (48 ml., 0.55 mole) of morpholine. A white precipitate formed, and the solution rapidly reached the boiling point of the *n*-butyl ether.

The condenser was set for downward distillation and distilled at atmospheric pressure to remove the chloroform. The remainder was distilled at reduced pressure to remove the *n*-butyl ether and finally to give 53 g. (0.46 mole, 92%) of formylmorpholine, b. p. 239.5–240.5° (760 mm.) (cor.), b. p. 120–122° (19–20 mm.), m. p. 20–21°,  $n_D^{20}$  1.4840,  $d_4^{20}$  1.145.<sup>8</sup>

**Anal.** Calcd. for C<sub>6</sub>H<sub>9</sub>NO<sub>2</sub>: C, 52.17; H, 7.83; N, 12.17; morpholine, 75.5. Found: C, 52.27; H, 7.30; N, 12.12; morpholine 75.3.

A portion of the morpholide was hydrolyzed with 10% sulfuric acid and distilled. Neutralization and concentration of the filtrate gave sodium formate, m. p. 254.5° (cor.) (reported m. p. 253°).<sup>9</sup> The sulfuric acid solution was made alkaline and distilled to give morpholine which was identified by its picrate, m. p. 149–150°, m. m. p. with authentic morpholine picrate 149–150°, and by its thiuram disulfide prepared according to Shupe,<sup>10</sup> m. p. 150–151° (reported m. p. 150–151°).

The forerun obtained in the original reaction was distilled through a 12-in. Hempel column packed with glass beads to give 50 g. (0.418 mole, 83.8%) chloroform b. p. 59–61°,  $n_D^{20}$  1.4483.

When isopropyl ether was substituted for *n*-butyl ether the same yield of N-formylmorpholine was obtained, but the chloroform could not be separated readily from this ether.

(6) A. W. Hofmann, *Ber.*, **5**, 247 (1872).

(7) E. Merck, German Patent 334,555 (M. 66126), Kl. 120.

(8) P. Médard, who prepared the compound from morpholine and formic acid, reported the following constants: b. p. 234° (760 mm.), m. p. 17.5° (*Bull. soc. chim.*, [5] **3**, 1343 (1936)).

(9) Lange's "Handbook," 6th Ed., 1946.

(10) I. S. Shupe, *J. Assoc. Offic. Agr. Chemists*, **23**, 824 (1940).

CHEMISTRY DEPARTMENT

POLYTECHNIC INSTITUTE OF BROOKLYN

BROOKLYN 2, NEW YORK

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## Hydrocarbon By-products from the Methyl Chloride-Silicon Reaction

BY ROBERT O. SAUER, W. J. SCHEIBER AND E. M. HADSELL

During a fairly large-scale study of the synthesis of methylchlorosilanes by the direct reac-