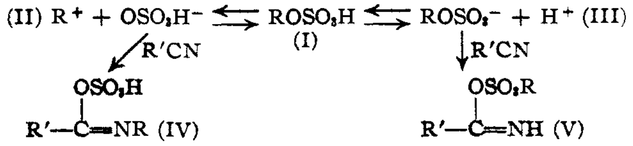
A Novel Method for the Preparation of Dimethylneopentylcarbinol

BY JOHN J. RITTER

In an attempt to effect the acetonitrile-diisobutene reaction[1] in cold concentrated sulfuric acid it has been observed that dimethylneopentylcarbinol is formed as the principal product. The expected N-*t*-octylacetamide, which is produced in good yield in acetic–sulfuric acid solution, appears in much diminished amount. In 92% sulfuric acid the yield of the carbinol reaches 70% of the calculated value without formation of hydrocarbon polymer. However, diisobutene alone is completely polymerized by cold 92% sulfuric acid, and the amide alone is simply dissolved under the same conditions and may be recovered on subsequent dilution.

In a typical experiment, a solution of 8.2 g., 0.2 mole, of acetonitrile in 100 g. of 92% sulfuric acid was prepared by dropwise addition of the nitrile to the acid at 0–5° with mechanical stirring. Diisobutene (22.4 g., 0.2 mole) was then added dropwise at 0–5° with continued stirring. The hydrocarbon dissolved promptly and substantially completely. Dilution of the reaction mixture by pouring on cracked ice separated an oil layer which was removed, neutralized, dried over anhydrous potassium carbonate and distilled at ordinary pressure. Eighteen grams of dimethylneopentylcarbinol, b. p. 145–147°, $d^{23.5}_4$ 0.8309, $n^{23}\text{D}$ 1.4301, was obtained. A residue (5 g.) in the distilling flask solidified on cooling and was identified as N-*t*-octylacetamide. A parallel experiment using 98% sulfuric acid yielded 60% of the calculated amount of carbinol with a somewhat larger residue of amide. No hydrocarbon polymer could be detected in either case.

The hydration of certain readily polymerizable olefins has been accomplished[2] by the use of a solution of concentrated sulfuric acid in *excess* of diethyl ether, in which the acid exists as the oxonium sulfate. In the case at hand, the assumption that acetonitrile serves a similar purpose through formation of the analogous nitrilium sulfate $RC{\equiv}NH^+ + SO_4H^-$[3] seems excluded as sulfuric acid was used in high excess over acetonitrile (4.7 mole:1 mole). It is suggested that the nitrile–olefin–sulfuric acid reaction may proceed along two competing routes determined by two modes of ionization (II and III) of the alkyl sulfuric acid (I) first formed



Conditions favoring II result in N-alkylation (IV), and lead ultimately to an amide R'CONHR, while ionization to yield III which would presumably be favored in somewhat diluted sulfuric acid (92%), leads to the ester of an imide sulfate V which on hydrolysis gives rise to the carbinol ROH.

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[1] John J. Ritter and P. Paul Minieri, THIS JOURNAL, **70**, 4045 (1948).

[2] O. Aschan, "Naphthenverbindungen, Terpene und Campherarten," W. de Gruyter, Berlin, 1929, p. 207.

[3] Hantzsch, *Ber.*, **64**, 674 (1931).

Formation of Secondary Alcohols in the Free Radical Decomposition of Aldehydes

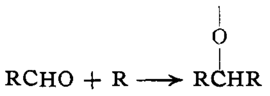
BY FREDERICK F. RUST, FRANK H. SEUBOLD AND WILLIAM E. VAUGHAN

Aliphatic aldehydes are known[1] to decompose by a chain mechanism to hydrocarbon and carbon monoxide in accord with the equations

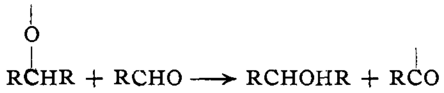
$$\text{RCHO} + \overset{|}{\text{R}} \longrightarrow \text{RH} + \text{R}\overset{|}{\text{C}}\text{O} \qquad (1)$$

$$\text{R}\overset{|}{\text{C}}\text{O} \longrightarrow \overset{|}{\text{R}} + \text{CO} \qquad (2)$$

This transformation is accompanied by side reactions which are incompletely understood. A brief study of the decompositions of *n*-butyraldehyde and *n*-heptaldehyde, sensitized by di-*t*-butyl peroxide, has shown the formation of di-*n*-propylcarbinol and di-*n*-hexylcarbinol, respectively, to be significant secondary reactions. The implication is that the chain-carrying alkyl radical will add to the carbon atom of the carbonyl group as well as effect the more frequent removal of a hydrogen atom (equation 1)

 (3)

$$\text{RCHO} + \text{R} \longrightarrow \text{R}\overset{\overset{|}{\text{O}}}{\overset{|}{\text{C}}}\text{HR} \qquad (3)$$

 (4)

$$\text{R}\overset{\overset{|}{\text{O}}}{\overset{|}{\text{C}}}\text{HR} + \text{RCHO} \longrightarrow \text{RCHOHR} + \text{R}\overset{|}{\text{C}}\text{O} \qquad (4)$$

Reaction (3) is, at least formally, the reverse of the well-demonstrated decomposition of the *t*-alkoxy radicals[2,3]

$$\text{RR'R''CO—} \longrightarrow \text{RCOR'} + \text{R''} \qquad (5)$$

and it is possible that both (3) and (5) are reversible to some degree. In the case of the *n*-butyraldehyde decomposition, di-*n*-propylcarbinol is formed both in the liquid phase at 115° and in the gas phase at 235°. In the latter case hexane—presumably from combination of propyl radicals—is formed in only slightly lesser amount than the alcohol; whereas, in liquid phase the same hydrocarbon, although present, is of lesser importance.

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[1] For summary, see Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946.

[2] Milas and Surgenor, THIS JOURNAL, **68**, 205, 643 (1946).

[3] Raley, Rust and Vaughan, *ibid.*, **70**, 88 (1948).

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^{20}_D 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°,[4] n^{20}_D 1.4199,[4] carbon 72.3% and hydrogen 13.8%. The 3,5-dinitrobenzoate was prepared; m. p., 64.5° (lit. m. p., 64°).[5] 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°[6] and contains 78.0% carbon and 14.0% hydrogen.

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(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).

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The Reaction between Morpholine and Chloral[1]

BY G. B. L. SMITH[2], MEYER SILVER[3] AND ERNEST I. BECKER

The products of the reaction of an aqueous solution of morpholine and chloral at 25° are chloroform and morpholine formate.[4] 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,[5] 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 preparation 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[6] and with N-methyl-α-homopiperonylamine and piperidine to give the monoformyl derivatives.[7]

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.). Isopropyl 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^{25}_D 1.4840, d^{26}_4 1.145.[8]

Anal. Calcd. for $C_5H_9NO_2$: 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°).[9] 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,[10] 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^{25}_D 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.

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(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).

(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).

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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-