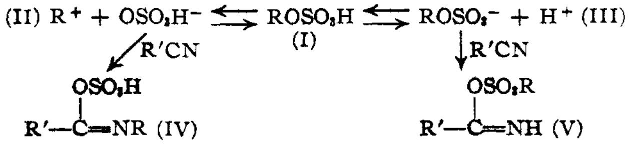
A Novel Method for the Preparation of Dimethylneopentylcarbinol

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}_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



$$\begin{tikzcd}
\text{(II) } R^+ + OSO_3H^- \arrow[r, shift left, leftarrow] \arrow[r, shift right] \arrow[d, "R'CN"] & \underset{\text{(I)}}{ROSO_3H} \arrow[r, shift left, leftarrow] \arrow[r, shift right] & ROSO_3^- + H^+ \text{ (III)} \arrow[d, "R'CN"] \\
R'{-}\overset{\overset{OSO_3H}{|}}{C}{=}NR \text{ (IV)} & & R'{-}\overset{\overset{OSO_3R}{|}}{C}{=}NH \text{ (V)}
\end{tikzcd}$$

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

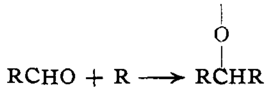
By Frederick F. Rust, Frank H. Seubold and William E. Vaughan

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

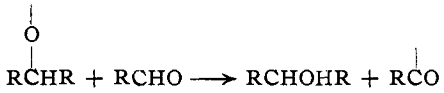
$$RCHO + R{-} \longrightarrow RH + R\overset{|}{C}O \qquad (1)$$

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

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)



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



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

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

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

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).