

3. The new analytic method has been applied to some preliminary studies of isomerization transformation of cyclopropane to propylene.

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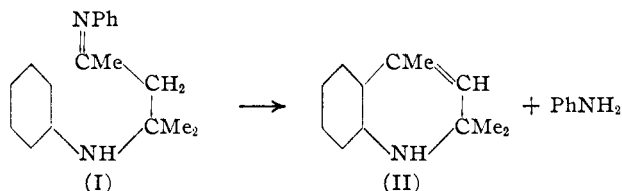
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## The Alleged Formation of Aliphatic Keto-Anils<sup>1</sup>

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The constitution of the keto-anils,  $\text{ArN} = \text{CAlk}_2$ , described by Knoevenagel<sup>2</sup> was discussed by Short and Watt,<sup>3</sup> who demonstrated the presence of an NH group. Knoevenagel prepared and analyzed eight anils and twenty-five derivatives and the authors adopted his formulas, which were apparently confirmed by the analysis of a benzyl derivative which, however, could not be recrystallized owing to its excessive solubility.<sup>4</sup> Reddelien and Thurm<sup>2</sup> have recently shown that acetoneanil possesses the formula  $\text{C}_{12}\text{H}_{15}\text{N}$  instead of  $\text{C}_9\text{H}_{11}\text{N}$  and that its properties are entirely different from those of typical anils. Its properties are in fact consistent with its formulation as a dihydroquinoline derivative (II) derived from a dimeric form (I) of the true acetoneanil by loss of aniline.<sup>5</sup>



In agreement with the conclusions of Reddelien and Thurm we find that (1) the formula of "acetoneanil" is  $\text{C}_{12}\text{H}_{15}\text{N}$  and this is confirmed by the analysis of its acetyl and benzoyl derivatives, (2) the acetyl derivative readily loses the acetyl group on hydrolysis but the "anil" itself does not suffer hydrolysis, (3) reduction of acetoneanil with sodium and alcohol yields the base  $\text{C}_{12}\text{H}_{17}\text{N}$  described by Knoevenagel but this cannot be a tetramethylindoline since no trace of aniline is formed as by-product, (4) a considerably higher yield of "acetoneanil" is obtained by increasing the

(1) This communication takes the place of a more extended manuscript which was submitted for publication before the appearance of the paper by Reddelien and Thurm which covers the same experimental ground.

(2) For a complete list of references see a memoir by Reddelien and Thurm, *Ber.*, **65**, 1521 (1932).

(3) Short and Watt, *J. Chem. Soc.*, 2293 (1930).

(4) Reëxamination of the original specimen conducted in collaboration with Mr. J. S. Watt has shown the compound is in reality an impure specimen of "acetoneanil." The picrolonate separated from alcohol in rectangular yellow prisms m. p. 173° dec. *Anal.* Calcd. for  $\text{C}_{22}\text{H}_{23}\text{O}_6\text{N}_3$ : C, 60.40; H, 5.26; N, 16.02. Found: C, 60.43, 60.22; H, 5.20, 5.34; N, 16.09.

(5) See also von Auwers, *Ber.*, **66**, 59 (1933).

ratio of acetone to aniline employed in the preparation. The new formula is also indirectly supported by the failure to effect condensation between acetone and *s*-trichloroaniline.

### Experimental Part

**"Acetoneanil"** (2,2,4-Trimethyldihydroquinoline).—The fraction of b. p. 135–137.5° (13 mm.) solidifies on cooling and after repeatedly pressing on porous tile is obtained in the form of white crystals melting at 25°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>15</sub>N: C, 83.2; H, 8.7; N, 8.1. Found: C, 83.3, 83.1; H, 8.5, 8.6; N, 7.9, 8.0.

**N-Acetyl-2,2,4-trimethyldihydroquinoline** may be obtained by acetylation as described by Reddelien and Thurm or by the addition of acetyl chloride to an ice-cold Grignard complex prepared from "acetoneanil" (20 g.) and ethylmagnesium bromide (1.1 mole) in absolute ether. The yield of product boiling at 163–164° (15 mm.) is 20 g. It is extremely soluble in the usual organic solvents but separates from petroleum ether solution on cooling in a carbon dioxide–acetone bath. The white crystals so obtained melt sharply at 54° but turn green on prolonged exposure to air.

*Anal.* Calcd. for C<sub>14</sub>H<sub>17</sub>ON: C, 78.1; H, 7.9; N, 6.5; mol. wt., 215. Found: C, 78.3,<sup>a</sup> 78.2; H, 8.2,<sup>a</sup> 8.0; N, 6.56,<sup>a</sup> 6.5; mol. wt. (in freezing benzene), 212, 218.

<sup>a</sup> Specimen m. p. 49–51°.

When the acetyl compound is heated to 180° in a slow stream of dry hydrogen chloride, slight resinification occurs, but 2,4-dimethylquinoline (picrate: yellow plates melting at 193–194° either alone or after admixture with an authentic specimen) may be obtained by steam distillation of the product after addition of alkali.

**N-Benzoyl-2,2,4-trimethyldihydroquinoline**, prepared by the action of benzoic anhydride upon "acetoneanil" in the presence of xylene (compare Reddelien and Thurm) or by the addition of benzoyl chloride to an ice-cold Grignard complex prepared from "acetoneanil" and methylmagnesium iodide in absolute ether, separates from alcohol (charcoal) in almost white crystals, m. p. 83–84°.

*Anal.* Calcd. for C<sub>19</sub>H<sub>19</sub>ON: C, 82.3; H, 6.9; N, 5.1. Found: C, 82.4; H, 7.0; N, 5.2.

Hydrolysis of the product gives "acetoneanil" and benzoic acid.

**2,2,4-Trimethyltetrahydroquinoline**.—Reduction of "acetoneanil" as described by Knoevenagel and Krauch<sup>6</sup> gave the product melting at 39.5° but no trace of aniline could be detected.

*Anal.* Calcd. for C<sub>12</sub>H<sub>17</sub>N: C, 82.3; H, 9.7; N, 8.0. Found: C, 82.2; H, 9.8; N, 8.0.

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(6) Knoevenagel and Krauch, *Ber.*, **55**, 2309 (1922).