hydrolyzed. All products were identified by their melting points and mixed melting points with known pure samples.

Benzil (I) yielded 0.4 g. of benzoic acid from the alkaline solution and 0.4 g. of benzoic acid from the ester hydrolysis.

4,4'-Dimethoxybenzil (II) yielded 0.5 g. of anisic acid from the alkaline solution and 0.3 g. of anisic acid from the ester hydrolysis.

4-Methoxybenzil (III) yielded 0.8 g. of a mixture of benzoic and anisic acids from the alkaline solution and 0.1 g. of the mixed acids from the hydrolysis of the esters.

Phenylbenzylglyoxal (IV) yielded 0.7 g. of a mixture of phenylacetic and benzoic acids from the alkaline solution and 0.2 g. of unchanged material from the ethereal solution.

Mesitylbenzylglyoxal (V) yielded 0.8 g. of a mixture of phenylacetic and trimethylbenzoic acids from the alkaline solution and 0.2 g. of unchanged material from the ethereal solution.

Summary

A simple mechanism for the alkaline peroxide cleavage of alpha diketones is herein presented.

WASHINGTON, D. C.

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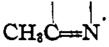
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Polyazines. I. The Structure of the Dimethyl Aziethane of Curtius and Thun[1]

BY B. G. ZIMMERMAN AND H. L. LOCHTE

Curtius and Thun[2] in the course of their study of the reactions of ketones with hydrazine hydrate obtained a compound to which they assigned the formula,  $\begin{array}{l}CH_3C{=}N\\ \quad\ |\quad\ \ |\\ CH_3C{=}N\end{array}$. This insoluble microcrystalline compound which gradually decomposes on heating to 270° without melting is obtained in the reaction between equimolecular amounts of hydrazine hydrate and diacetyl. Although Diels[3] and Diels and Pflaumer[4] encountered the same substance in their work, they apparently were not interested in its structure and dismissed it with the statement that their substance was identical with that of Curtius and Thun.

The low solubility and high melting point of the compound makes the Curtius and Thun formula very unlikely and indicates that the compound should be classed as a polyazine formed by polycondensation or "C polymerization"[5] of the two bifunctional compounds involved. A closer study shows that it is an unsymmetrical polyazine of the type $H_2N{-}N{=}C(CH_3)[C(CH_3){=}N{-}N{=}C(CH_3)]_nC(CH_3)O$ with a moderately high value of *n*.

Ebullioscopic molecular weight determinations, using benzene as solvent, with freshly prepared and recrystallized substance yield an apparent molecular weight of only 300 to 400; but these values probably have little significance since the apparent molecular weight increases rapidly with concentration. Staudinger[6] recently reported similar difficulties in his work with polymers. Since the solubility of our polyazine decreases rapidly with age or with repeated recrystallization ebullioscopic molecular weight determinations on such aged samples are impossible.

Analyses of freshly prepared and recrystallized material show definitely the unsymmetrical structure of the polyazine and indicate a value of 6–10 for *n*.

Material which becomes insoluble upon repeated recrystallization or other treatment decomposes without melting on heating to 300°.

Analyses of such samples indicate a much higher value of *n* and can no longer be employed to differentiate between the unsymmetrical and one of the symmetrical structures possible.

Experimental Part

Diacetyl Monohydrazone.—Prepared according to the method of Diels and Pflaumer,[4] the melting point of this compound was found as reported at 67.5° (corr.). After standing in a desiccator for nine months the white crystalline compound had changed to a yellow microcrystalline powder decomposing slowly without melting on heating to 250°.

Monoacetyl Derivative of Diacetyl Hydrazone.—This compound, also prepared according to Diels and Pflaumer,[4] is colorless and melts at 163.4° (corr.). It hydrolyzes readily in hot alkaline solution yielding the yellow polyazine.

Diacetyl Dihydrazone and Polyazine.—Three grams of diacetyl, 12 g. of hydrazine hydrate, and 12 g. of sodium carbonate in 50 cc. of water were refluxed for five hours. Two products were isolated, a white crystalline material

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[1] Presented at a Sectional Meeting of the American Chemical Society at Waco, Texas, April 25, 1936.

[2] Curtius and Thun, *J. prakt. Chem.*, [2] **44**, 175 (1891).

[3] Diels, *Ber.*, **35**, 350 (1902).

[4] Diels and Pflaumer, *ibid.*, **48**, 223 (1915).

[5] Carothers, THIS JOURNAL, **51**, 2550 (1929); *Chem. Rev.*, **8**, 358 (1931); *Trans. Faraday Soc.*, **32**, 39 (1936).

[6] Staudinger and co-workers, *Ber.*, **68**, 2313–2357 (1935).

suspended throughout the liquid, and a yellow solid floating as a top layer. The colorless compound was found to be the diacetyl dihydrazone of Curtius and Thun.[2]

Anal. Calcd. for $C_4H_{10}N_4$: C, 42.16; H, 8.79; N, 49.05; mol. wt., 114. Found: C, 42.26; H, 8.85; N, 48.85; mol. wt., 117 (ebullioscopic in benzene); m. p. 157.8°.

The yellow material was recrystallized repeatedly from benzene. At each recrystallization a portion remained insoluble in hot benzene. For analysis, the recrystallized soluble portion was dried in a vacuum desiccator over paraffin for a period of four hours.

Anal. (recrystallized soluble portion). Calcd. ($n = 6$): C, 56.72; H, 7.49; N, 33.09. Found: C, 56.60; H, 7.80; N, 33.21. Mol. wt. (ebullioscopic in benzene), 300 to 400, increasing with concentration.

On heating, decomposition was first observed at 110° and continued with progressive darkening to above 300° without melting.

The yellow, easily electrified, insoluble powder was washed repeatedly with water, benzene, alcohol and ether and then dried in a vacuum desiccator over concentrated sulfuric acid.

Anal. Calcd. ($n = 100$): C, 58.37; H, 7.38; N, 34.06. Found: C, 58.26; H, 7.54; N, 33.95.

On heating, decomposition was not observed below 200° and no melting occurred up to 300°.

Continued Condensation of Monohydrazone.—Eight and one-tenths grams of monohydrazone in 40 cc. of water was treated with 75 cc. of 1:5 hydrochloric acid. A yellow precipitate, insoluble in all common solvents, formed immediately.

Anal. Found: C, 58.45; H, 7.44; N, 34.26; m. p., gradual decomposition up to 300° without melting.

The same reaction took place on treating 1 g. of monohydrazone in alcohol with 10 cc. of a saturated alcoholic solution of picric acid.

Anal. Found: C, 58.50; H, 7.34; N, 33.96. Melting point observations were identical with the above polyazine.

Condensation of Diacetyl Dihydrazone with Diacetyl.—Three and three-tenths grams of dihydrazone was dissolved in 150 cc. of alcohol by heating, and 4.1 cc. of diacetyl was added with shaking. After standing overnight a voluminous yellow gel had formed. This did not dissolve on heating. Repeated recrystallization from benzene again showed a gradual transformation into the insoluble polyazine.

Anal. (recrystallized soluble portion). Found: C, 56.44; H, 7.50; N, 32.94, thus indicating again a value of about 6 for n.

The behavior on heating again showed decomposition starting at about 120° but no melting at 300°. Mol. wt. (boiling benzene): 300 to 400 depending on concentration. While apparently clear at first such solutions will soon show a distinct Tyndall effect on continued boiling.

Anal. (insoluble portion). Found: C, 58.25; H, 7.46; N, 34.13; m. p., gradual decomposition to 300° without melting.

Hydrolysis of the Polyazine.—The reversibility of the condensation, yielding the polyazine, is clearly shown by the fact that 1 g. of polyazine refluxed with 20 cc. of hydrazine hydrate and 75 cc. of alcohol yields, after seven days, diacetyldihydrazone (m. p. 158.1°) in 20% yield.

Anal. Calcd. for $C_4H_{10}N_4$: N, 49.05. Found: N, 49.15.

Results obtained in the study of polyazine formation with various other di- and triketones will be reported later.

Conclusion

The compound known as aziethane is a polyazine of moderately high molecular weight and not the compound containing a four-membered ring.

Polyazines with identical properties and closely agreeing analyses were obtained by the following four methods:

1. Reaction between diacetyl and hydrazine hydrate.
2. Polymerization of the monohydrazone on treatment with various acids, or prolonged standing.
3. Decomposition of the acetyl derivative of the monohydrazone according to the method of Diels.
4. Reaction between the dihydrazone and diacetyl.

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