

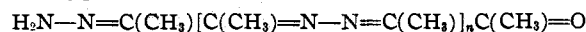
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Polyazines. II. The Reaction of Hydrazine Hydrate with Acetylacetone, Acetylacetone, and Benzil^{1,2}BY BERNHARD G. ZIMMERMAN³ AND H. L. LOCHTE

The reaction between the two bifunctional types of compounds, diketones and hydrazine hydrate, should generally yield polyazines which are formed by continued condensation of ketone and hydrazine. Cyclic compounds are formed directly only in those special cases which lead to the formation of 5- or 6-membered rings.^{4,5} Four- and seven-membered rings apparently are formed in such cases only rarely and then in small yield.

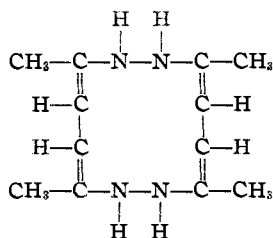
Kinetic theory and probability considerations lead us to predict that in cases in which there is simultaneous formation of both cyclic and open chain compounds, the yield of cyclic products can be increased by working in very dilute solutions.⁶

A previous communication⁵ on the reaction between diacetyl and hydrazine hydrate showed that the main product obtained is a polyazine of the type



The present paper presents results obtained with several other diketones.

The reaction between acetylacetone and hydrazine hydrate was first studied by Gray,⁷ who isolated two crystalline products. Equimolecular amounts of the reactants yielded a 12-membered ring compound to which he assigned the formula



while the reaction between two moles of ketone and three of hydrazine hydrate yielded the azine-hydrazone

(1) Based on part of a dissertation submitted by B. G. Zimmerman in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Texas, June, 1937.

(2) Presented at the 95th meeting of the American Chemical Society at Dallas, Texas, April 18-22, 1938.

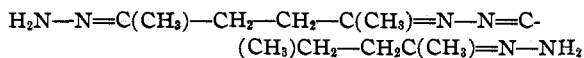
(3) Present address: General Aniline Works, Inc., Grasselli, N. J.

(4) Carothers, *Chem. Rev.*, **8**, 358 (1931).

(5) Zimmerman and Lochte, *THIS JOURNAL*, **58**, 948 (1936).

(6) Ruggli, *Anh.*, **392**, 92 (1912).

(7) Gray, *J. Chem. Soc.*, **79**, 682-688 (1901).

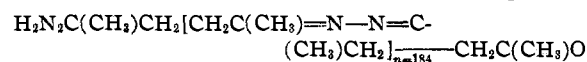


The direct formation of a 12-membered ring in a concentrated solution, as reported by Gray, is unexpected; but Gray gave not only complete analyses which are of no value as a means of differentiating between the cyclic and open chain polymeric structure, but also reported derivatives, solubility in various solvents, and made molecular weight determinations. Gray, however, did not report a melting point for this crystalline 12-membered ring. Molecular weights found agreed closely with those required for the 12-membered ring. Smith and McCoy⁸ also obtained the same substances, but gave no additional information.

In view of Gray's results a number of attempts were made to repeat his work, but experiments under conditions reported by Gray, as well as in very dilute solution in which the yield of such a compound should have been better, failed to reveal any crystalline substance that could be identified as Gray's compound.

Gray's directions yielded a viscous oil which remained liquid for months. Analysis of a fraction boiling at 114-115° at 2 mm. agreed with results obtained by Gray, as did cryoscopic molecular weight determinations in benzene. Even after careful fractionation of the liquid, no crystalline 12-membered ring could be isolated.

Dilute solutions yielded in all cases mainly 3,6-dimethylpyridazine which has been prepared in a number of different ways, but Gray,⁷ Smith and McCoy,⁸ and Paal and Ueber⁹ all agreed that it could not be prepared by direct reaction between acetylacetone and hydrazine hydrate. Apparently, the only essential difference between their experiments and ours lay in the fact that our work was done in very dilute solution. About 3% yield of a crystalline polymer of the type



also could be isolated from the same dilute solution. In benzene solution, the azine-hydrazone

(8) Smith and McCoy, *Ber.*, **35**, 2169 (1902).

(9) Paal and Ueber, *ibid.*, **36**, 497 (1903).

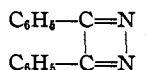
of Gray was obtained in excellent yield. In concentrated solutions, using no solvents and heating on a steam-bath for two weeks, only a black tar, from which no crystalline products could be isolated, was obtained.

The reaction of benzil, diacetyl, and acetylacetone with benzil dihydrazone yielded only mixed polyazine resins. No definite structure could be assigned to these resins.

Two crystalline azines, the mono- and diazine, were isolated from the reaction between benzil monohydrazone and diacetyl.

As expected, acetylacetone and hydrazine hydrate yielded only the 5-membered ring, 3,5-dimethylpyrazole; no polymeric substance could be isolated as a by-product.

According to Curtius,¹⁰ benzil monohydrazone decomposes in an aqueous solution to yield the four-membered ring



All attempts to isolate such a 4-membered ring were unsuccessful.

Experimental

Condensation of Acetylacetone with Hydrazine Hydrate in Dilute Solution.—Ninety-seven grams of acetylacetone and 42.5 g. of hydrazine hydrate were dissolved in 5 liters of water, and heated on a steam-bath for six weeks.

The crystals that separated on evaporating most of the water and cooling were filtered off and recrystallized four times from a large volume of 50% alcohol. Except for slight solubility in ethanol, the white crystals were insoluble in all common solvents; m. p., softens at 260° and melts at 276° with decomposition.

Anal. Calcd. for $\text{O}=\text{C}(\text{CH}_3)-\text{CH}_2[\text{CH}_2-\text{C}(\text{CH}_3)=\text{N}-\text{N}=\text{C}(\text{CH}_3)-\text{CH}_2]_{134}-\text{CH}_2\text{C}(\text{CH}_3)=\text{N}-\text{NH}_2$: C, 65.41; H, 9.10; N, 25.39; mol. wt., 20,366. Found: C, 65.28; H, 9.08; N, 25.42; mol. wt., micro Rast camphor, 9.314 mg. of product dissolved in 84.40 mg. of camphor showed a depression in the freezing point of 0.200°, mol. wt., 21,836. Check determinations indicated molecular weights from 18,000 to 22,000.

Picrate.—This separated as shiny yellow crystals when a dilute alcoholic solution of picric acid was added to a hot alcoholic solution of the polymer. Recrystallized from much ethanol, it melted at 170–176° with decomposition.

Anal. Calcd. for $n = 184$: N, 20.63. Found: N, 20.62.

Platinic Chloride Salt.—An orange-yellow crystalline salt formed when a 10% solution of platinum chloride was added to a hot alcoholic solution of the polymer. The salt was washed with water, alcohol, ether, and dried; m. p. 260–266° dec.

(10) Curtius, *J. prakt. Chem.*, [2] **39**, 131 (1899).

Anal. Calcd. for $n = 184$: Pt, 31.00. Found: (micro) Pt, 30.89, 30.93.

Hydrochloride.—Five-tenths gram of the polymer was dissolved in hot alcohol and dry hydrogen chloride passed in. The resulting white salt melts at 200–201° with decomposition to a red mass.

Anal. Calcd. for $n = 184$: Cl, 24.10. Found: Cl, 24.07.

The hydrochloride is very soluble in water. Neutralization equivalent (calcd. 146.5, found 146.7) corresponds to the structural unit of the polymer.

Each of these salts has thus resulted from reaction with each structural unit.

3,6-Dimethylpyridazine.—The filtrate from the polymer was fractionated at 40 mm. in a stream of hydrogen. The 40–200° fraction was then fractionated at 37 and 31 mm. The fraction boiling at 119–122° at 31 mm. was then re-fractionated at 2 mm. The main fraction boiling at 64° at 2 mm. solidified on cooling. After further purification, it melted at 34–35°. Complete analysis of the base as well as the analysis and properties of the picrate, platinic chloride, and hydrochloride agreed with those reported by Paal and Koch.¹¹ The platinum chloride was found to contain either one or four molecules of water of crystallization.

Gray's Azine-Hydrazone ($\text{C}_{12}\text{H}_{14}\text{N}_6$).—This compound reported by Gray was obtained when 10 cc. of acetylacetone was dissolved in 300 cc. of benzene and 15 cc. of hydrazine hydrate added with shaking for one hour. After numerous recrystallizations from ethanol it melted at 136–137° (Gray reported 132°).

Benzil Monohydrazone and Diacetyl.—Six and five-tenths grams of benzil and 2.5 g. of diacetyl dissolved in 125 cc. of alcohol were refluxed for eighteen hours. On cooling, the yellow crystals which formed were filtered off and recrystallized from alcohol; m. p., 85.8°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$: C, 73.94; H, 5.25; N, 9.59; mol. wt., 292. Found: C, 74.01; H, 5.69; N, 9.67; mol. wt. (ebullioscopic in benzene), 285.

On continued refluxing of the filtrate, a second yellow product was isolated. After recrystallization from benzene, the melting point was found to be 238.3° with decomposition.

Anal. Calcd. for $\text{C}_{32}\text{H}_{26}\text{N}_4\text{O}_2$: C, 77.07; H, 5.26; N, 11.24; mol. wt., 498. Found: C, 77.29; H, 5.49; N, 11.17; mol. wt. (micro Rast camphor), 505.

3,5-Dimethylpyrazole.—This compound was prepared according to the directions of Rosengarten¹² and Dedichen¹³ and the filtrate examined for polymeric by-products, but none could be isolated. This compound was found to be satisfactory as a selective inhibitor for some microorganisms.¹⁴

Molecular Weight Determinations.—In the course of attempts to determine the molecular weight of these moderately high molecular weight polyazines, it was observed that the molecular weight appeared to increase with concentration of the polymer in benzene in spite of the fact that the solutions appeared to be perfectly clear up to the

(11) Paal and Koch, *Ber.*, **37**, 4385 (1904).

(12) Rosengarten, *Ann.*, **279**, 238 (1894).

(13) Dedichen, *Ber.*, **39**, 1848 (1906).

(14) Zimmerman and Lewis, U. of Texas, unpublished results.

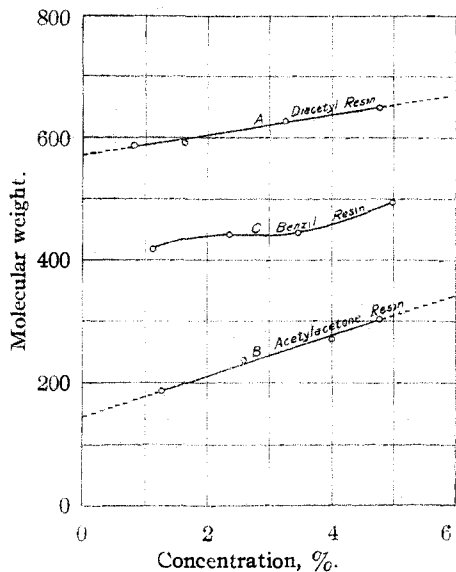


Fig. 1.—Molecular weight-concentration curves.

point at which the benzene started to freeze. Figure 1 shows results obtained with three different resins. Meanwhile Staudinger and co-workers¹⁵ reported similar dif-

(15) Staudinger and co-workers, *Ber.*, **68** 2313 (1935).

ficulties with polymers, and offer an explanation for this observed increase in molecular weight with an increase in concentration.

Summary

Acetylacetone and hydrazine hydrate react to yield 3,6-dimethylpyridazine, the azine-hydrazone of Gray, and an insoluble crystalline polyazine.

The 12-membered ring of Gray could not be isolated under any conditions.

Benzil dihydrazone reacts with benzil, diacetyl, and acetylacetone to yield resins.

The 4-membered ring, formed by the decomposition of benzil monohydrazone, of Curtius could not be isolated.

Acetylacetone and hydrazine hydrate yield 3,5-dimethylpyrazole without polymeric by-product.

Cryoscopic molecular weight determinations of polyazines with benzene as solvent yield values that appear to increase with concentration of polymer.

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Reducing Action of Primary Grignard Reagents

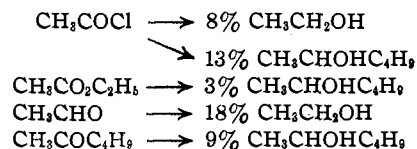
BY FRANK C. WHITMORE, A. H. POPKIN, J. S. WHITAKER, K. F. MATTIL AND J. D. ZECH

The reducing action of *t*-butylmagnesium chloride on trimethylacetyl, isobutyryl, *n*-butyryl¹ and *t*-butylacetyl² chlorides has been reported already. Similar studies have now been made to find the effect of branching, in both the Grignard reagent and the carbonyl compound, on the yields of the reduction products.

n-Butylmagnesium bromide and trimethylacetyl chloride produced neopentyl alcohol in 27% yield together with a 69% yield of *n*-butyl-*t*-butylcarbinol representing a total yield of 96% of the reduction products. In the case of *t*-butylmagnesium chloride, the yield of neopentyl alcohol was 95% with a 1% yield of di-*t*-butylcarbinol.

Several other reactions of the Grignard reagent were studied next with emphasis on the by-product obtained. Excess *n*-butylmagnesium

bromide gave the usual products with acetyl chloride, ethyl acetate, acetaldehyde and 2-hexanone and, in addition, the by-products indicated



The preparation of a series of tertiary carbinols for subsequent dehydration studies involved the addition of methylneopentyl ketone to some primary Grignard compounds. With ethylmagnesium bromide, evidence of a trace of methylneopentylcarbinol was obtained but its identity was not established positively. This reduction product was identified when higher Grignard reagents were used. The yields of methylneopentylcarbinol were 5.5% using *n*-propylmagnesium bromide, 5.7% using *n*-butylmagnesium bromide

(1) Greenwood, Whitmore and Crooks, *THIS JOURNAL*, **60**, 2028 (1938).

(2) Whitmore and Heyd, *ibid.*, **60**, 2030 (1938).