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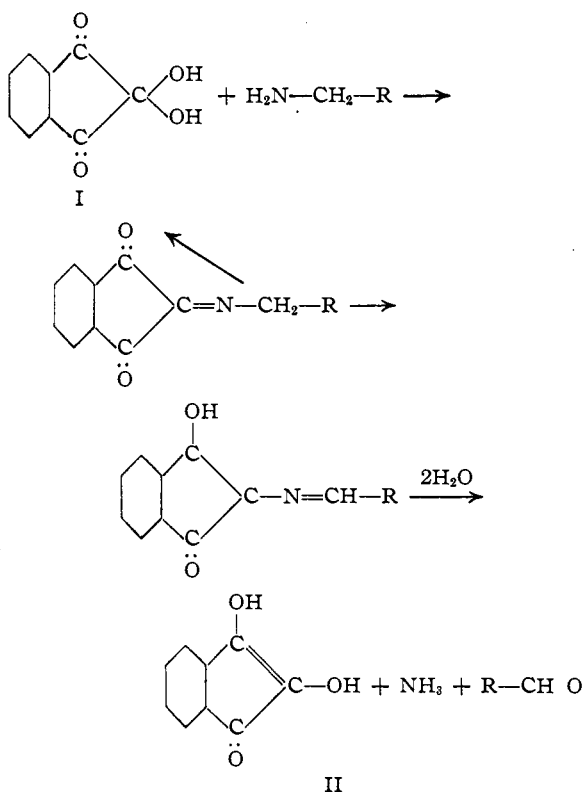
Reactions between Cyclic Triketones and Amines. Color Reactions of Ninhydrin and *peri*-Naphthindane Triones

BY RADWAN MOUBASHER AND ABDEL MAGID OTHMAN

Riffart¹ has reported that when triketohydrindene hydrate (ninhydrin) (I) is treated with primary amines, an intense blue coloration is developed but nothing is mentioned about the nature and mechanism of this reaction.

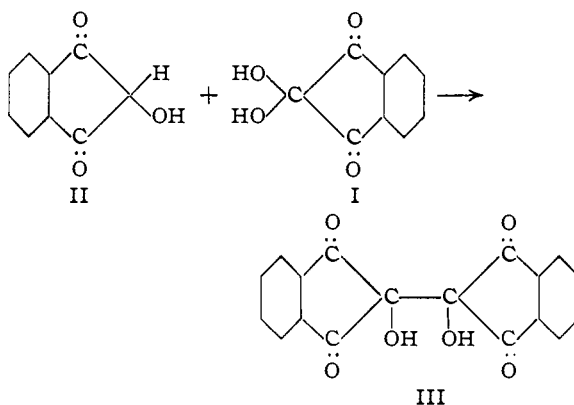
This color reaction takes place similarly (*inter alia*) with other cyclic triketones, namely, *peri*-naphthindane trione hydrate and *m*-nitro-*peri*-naphthindane trione hydrate. An interpretation of the nature of this reaction can be based on the observation recently made by Schönberg, Moubasher and Mostafa,² who noted the formation of ammonia and the aldehyde corresponding to the amine, together with the reduction products of the triketones, namely, hydrindantine (III), dihydroxy-keto-*peri*-naphthindene and *m*-nitro-dihydroxy-keto-*peri*-naphthindene, respectively.

The following mechanism is advanced



Hydrindantine (III) is formed after acidification of the reaction mixture, since 2-hydroxydiketohydrindene (II) reacts in acidic medium with nin-

hydrin (found in excess) yielding hydrindantine (Moubasher).³



The intense blue coloration is due to the double salt formed by the action of the amine present in excess, and the reduction product of the triketones (*e. g.*, 2-hydroxydiketohydrindene (II) in case of ninhydrin). When this reaction mixture is acidified, the color is immediately discharged and the reduction product is regenerated.

This reaction is given only by primary amines of the type $R-CH_2-NH_2$ and $\begin{matrix} R \\ | \\ R_1-CH-NH_2 \end{matrix}$ where R and R₁ may be either alkyl or aryl groups. Tertiary butylamine gave negative results.

Experimental

The interaction between the triketones and the primary amines was principally carried out by allowing the amine to react with the triketone in boiling water for thirty minutes in an atmosphere of carbon dioxide using the apparatus previously described by Schönberg, Moubasher and Mostafa.³ On distillation of the reaction mixture, the aldehyde or the ketone formed passed over with steam and was identified as the 2,4-dinitrophenylhydrazone by m. p. and by the m. p. of a mixture with known compounds.

Action of Ninhydrin on Ethylamine, Butylamine and Benzylamine.—Ninhydrin (1 g.) and ethylamine (3.5 g.), butylamine (3 g.) or benzylamine (2.5 g.) and water (100 cc.) were boiled for thirty minutes in a stream of carbon dioxide in a distilling flask provided with an efficient reflux condenser in series with a Liebig condenser that was dipped into a solution of 2,4-dinitrophenylhydrazine (0.5 g.) in alcohol (25 cc.). At the end of the reaction, the contents of the receiver were warmed for some time, treated with 15 cc. of hydrochloric acid and left to cool. Acetaldehyde, butyraldehyde or benzaldehyde was obtained as the 2,4-dinitrophenylhydrazone and identified by the m. ps. (162, 123 and 235°, respectively); yield was about 25%.

The intense blue reaction mixture in the distilling flask was acidified with dilute hydrochloric acid, whereupon a colorless solution was obtained. When the solution was

(1) Riffart, *Biochem. Z.*, **131**, 78 (1923); *Chem. Zentr.*, **94**, II, 827 (1923).

(2) Schönberg, Moubasher and Mostafa (Mrs. Said), *J. Chem. Soc.*, **2**, 176 (1948).

(3) Moubasher, *ibid.*, **2**, 1038 (1949).

left to cool for some hours after filtration, if necessary, a colorless solid was formed. Recrystallized from acetone-water mixture as colorless needles, this solid melted with decomposition at 225°, and did not depress the m. p. of an authentic sample of hydrindantine. It gave the blue coloration with sodium hydroxide solution that is characteristic of hydrindantine; yield 0.5 g.

Action of *peri*-Naphthindanetrione Hydrate on Ethylamine, Butylamine and Benzylamine.—*peri*-Naphthindanetrione hydrate (1 g.) and ethylamine (3.5 g.) or butylamine (3 g.) or benzylamine (2.5 g.) were mixed in the distilling flask in presence of water (100 cc.) and the same procedure was carried out as in the case of ninhydrin. Acetaldehyde 2,4-dinitrophenylhydrazone, butyraldehyde 2,4-dinitrophenylhydrazone and benzaldehyde 2,4-dinitrophenylhydrazone were isolated and identified as above. The yield in all these cases is about 30%. At the end of the reaction the contents of the distilling flask were acidified and cooled. Dihydroxyketo-*peri*-naphthindene separated as silky red crystals which melted at 255°, did not depress the melting point of an authentic specimen and gave the characteristic blue color with sodium hydroxide solution; yield 0.4 g.

Action of *m*-Nitro-*peri*-naphthindanetrione Hydrate on Ethylamine, Butylamine or Benzylamine.—*m*-Nitro-*peri*-naphthindanetrione hydrate (1 g.) and ethylamine (3.5 g.), butylamine (3 g.) or benzylamine (2.5 g.) were treated in the same way as above and the corresponding aldehydes were isolated and identified as above. When the reaction mixture was acidified with hydrochloric acid and left to cool for several minutes, *m*-nitrodihydroxyketo-*peri*-naphthindene recrystallized from alcohol as silky red needles, melted at 265° and did not depress the melting point of an authentic sample; yield 0.6 g.

Action of Ninhydrin, *peri*-Naphthindanetrione Hydrate and *m*-Nitro-*peri*-naphthindanetrione Hydrate on *s*-Butylamine.—When ninhydrin (0.5 g.), *peri*-naphthindane tri-

one hydrate (0.7 g.) or *m*-nitro-*peri*-naphthindanetrione hydrate (0.8 g.) and *s*-butylamine (3 g.) in water (50 cc.) were treated as above, methyl ethyl ketone was obtained in the form of 2,4-dinitrophenylhydrazone which melted at 115° and did not depress the melting point of an authentic sample. The yield was about 30% with all these triketones. The reaction mixture in the distilling flask was acidified and left to cool, whereupon hydrindantine (after some hours), dihydroxyketo-*peri*-naphthindene and *m*-nitro-dihydroxyketo-*peri*-naphthindene were formed, respectively, and identified as above.

Action of Ninhydrin, *peri*-Naphthindanetrione Hydrate and *m*-Nitro-*peri*-naphthindanetrione Hydrate on 1,3-Diaminopropane, Putrescine, Histamine, Cadaverine, Glucosamine, Spermine or Insulin.—When any of the triketones (1 g.), water (100 cc.) and any of the amines (1 g.) were mixed together, intensive blue coloration developed immediately. The mixture, heated on a boiling water-bath for thirty minutes, then cooled, acidified with hydrochloric acid and left to cool gave rise to hydrindantine, dihydroxyketo-*peri*-naphthindene or *m*-nitrodihydroxyketo-*peri*-naphthindene which could be isolated and identified by their m. ps. and their effects on the melting points of authentic samples.

Summary

1. The interaction between cyclic triketones and amines is discussed. The amine gives the corresponding aldehyde and ammonia and the triketone is converted to the corresponding reduction product.

2. A mechanism concerning the nature of the color reaction of the cyclic triketones and primary amines is advanced.

CAIRO, EGYPT

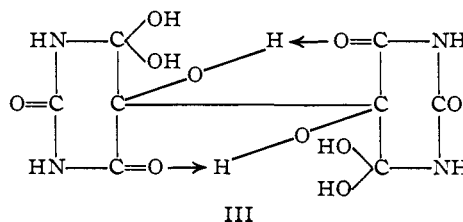
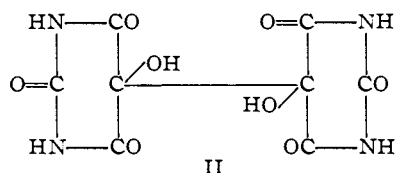
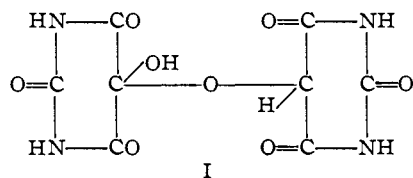
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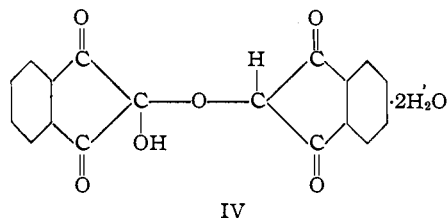
Reactions of Alloxan and Alloxantine. Structure of Alloxantine and Hydrindantine

BY RADWAN MOUBASHER AND ABDEL MAGID OTHMAN

Of the various structural formulas proposed for alloxantine, the hemiacetal formula (I) and the pinacol formula (II) have received the most support. Davidson and Epstein¹ comparatively recently have presented evidence favoring the latter and Nightingale² and Winslow³ independently presented evidence favoring the former.



Similarity between hydrindantine and alloxantine (I) has been frequently pointed out⁴ and owing to this similarity hydrindantine has been formulated as (IV).



(1) Davidson and Epstein, *J. Org. Chem.*, **1**, 306 (1936).

(2) Nightingale, *THIS JOURNAL*, **59**, 802 (1937).

(3) Winslow, *ibid.*, **61**, 2089 (1939).

(4) Ruhemann, *J. Chem. Soc.*, **99**, 797 (1911).