149. *Studies on Indene Derivatives. Part V.*

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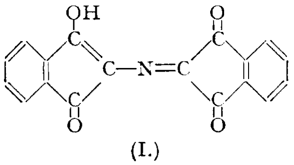
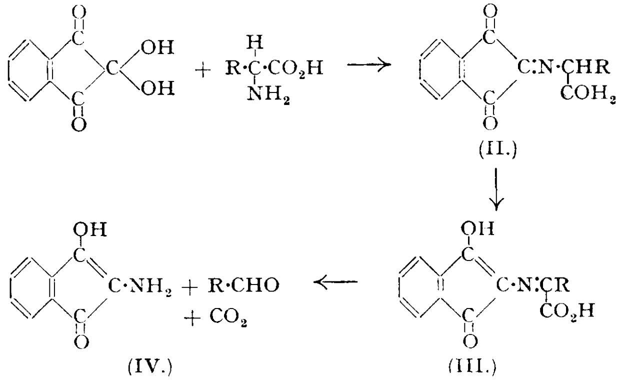
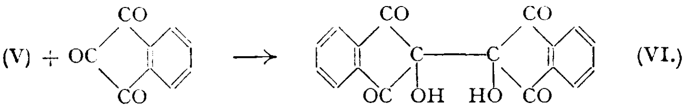
The reaction between " ninhydrin " (triketoindane hydrate) and α-amino-acids leads to the formation of hydrindantin and bis-1 : 3-diketoindanyl. It is suggested that the latter compound arises from the former. Hydrindantin is possibly formed by the condensation of ninhydrin with 2-hydroxy-1 : 3-diketoindane.

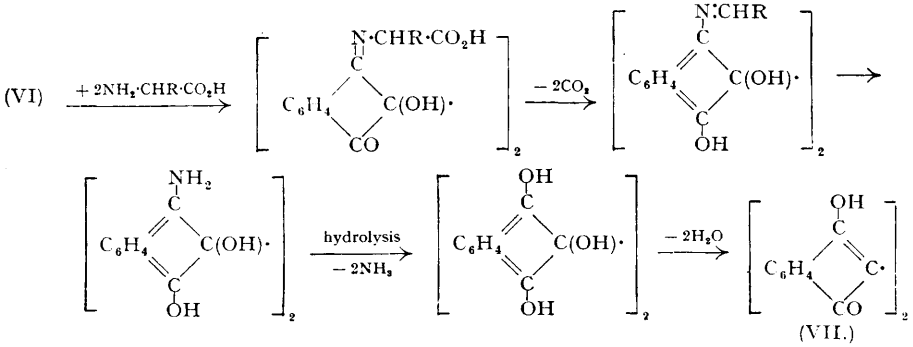
Ruhemann (*J.*, 1911, **99**, 1492) observed that when α-amino-acids containing an unsubstituted amino-group are treated with ninhydrin a violet colour is produced. Grassmann and Arnim (*Annalen*, 1934, **509**, 289) suggested that the coloured substance is diketoindanylidenediketoindanylamine (I). Schönberg *et al.* (*J.*, 1948, 176) suggested a mechanism for the action of unsubstituted α-amino-acids on various diketones, and a similar mechanism may be applicable to the ninhydrin reaction mentioned above. Each of the compounds (II—V) could be colour contributors.



(I.)







2-Hydroxy-1 : 3-diketoindane (V) could react with ninhydrin to yield hydrindantin (VI) which by further reaction with α-amino-acid could yield bis-1 : 3-diketoindanyl (VII). In accordance with this, both (VI) and (VII) have been isolated from the ninhydrin reaction.

Experimental.

Action of Ninhydrin on α-Amino-acids.—(a) *Alanine.* Ninhydrin (0·7 g.), dissolved in water (50 c.c.), was mixed at room temperature with alanine (0·3 g.) dissolved in water (20 c.c.), and the mixture heated on a water-bath for 10 minutes; an intense blue coloration was developed, accompanied by evolution of carbon dioxide and acetaldehyde. The mixture was cooled, and the resulting reddish-violet solid was collected, washed with hot water, dried, and crystallised from benzene, giving violet needles, m. p. 297°

(decomp.), proved to be bis-1 : 3-diketoindanyl by m. p. and mixed m. p. and properties; yield *ca.* 20%. The filtrate was acidified with dilute hydrochloric acid, and the reddish precipitate formed was crystallised from acetone–water (3 : 1 by vol.), affording colourless crystalline needles, m. p. 230° (decomp.), proved to be hydrindantin by m. p., mixed m. p., and the characteristic intense blue coloration with sodium hydroxide solution; yield *ca.* 50%.

(b) *Valine.* The same procedure being used for valine, the same two compounds were isolated.

Action of Hydrindantin (VI) *on α-Amino-acids.*—(a) *Alanine.* A suspension of 0·5 g. of hydrindantin in 100 c.c. of water was placed in a Claisen flask fitted with an upright condenser, to which was attached a Liebig condenser and a receiver. A continuous current of carbon dioxide was passed through, and a solution of 0·2 g. of alanine in 25 c.c. of water was added. In the receiver was placed a solution of 2 : 4-dinitrophenylhydrazine (0·2 g. in 25 c.c. of alcohol). The mixture in the flask was distilled until its volume was reduced to about 25 c.c. (20 minutes). The contents of the receiver were treated with concentrated hydrochloric acid (5 c.c.) and cooled in ice; acetaldehyde 2 : 4-dinitrophenylhydrazone was obtained, m. p. 167° (cf. Bryant, *J. Amer. Chem. Soc.*, 1932, **54**, 3760).

In the reaction vessel a violet substance separated out which was filtered off, dried, and recrystallised from benzene, giving violet needles, m. p. 297° (decomp.), of bis-1 : 3-diketoindanyl (m. p., mixed m. p., and properties); yield 0·35 g.

(b) On heating a mixture of alanine (0·2 g.) with hydrindantin (0·5 g.) in 50 c.c. of water, carbon dioxide was evolved, and ammonia was detected in the reaction mixture.

(c) *Phenylaminoacetic acid.* By the same procedure as in (a), hydrindantin and phenylaminoacetic acid (0·33 g. in 20 c.c. of water) afforded a violet colour; after 15 minutes' heating, the distillate (filtered if necessary) was treated with an alcoholic solution of phenylhydrazine and cooled in ice; benzaldehyde phenylhydrazone was obtained. Recrystallised from alcohol, this had m. p. and mixed m. p. 158° (decomp.). The mixture in the distilling flask afforded the same substance as in (a) (m. p. 297°, mixed m. p., and properties).

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