CLII.—*Substituted Cinnamic Amides and Acids.*

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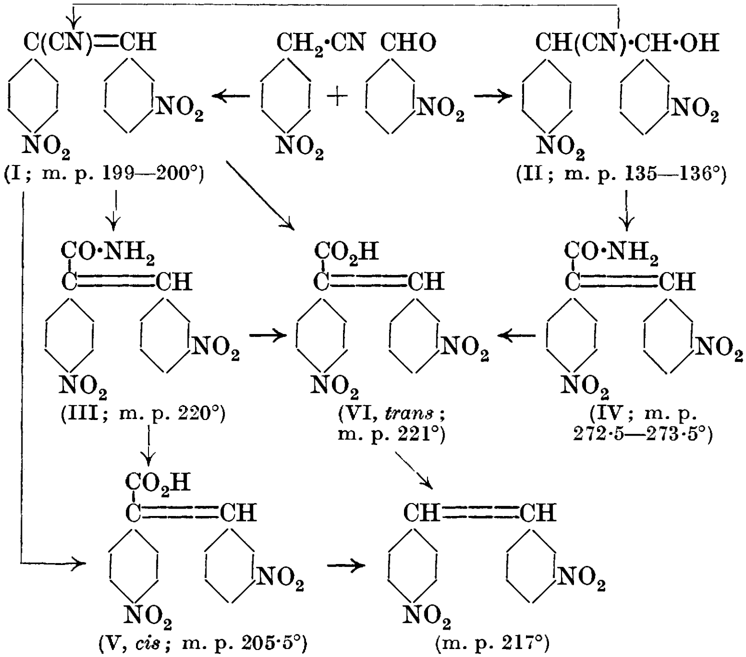
In a previous paper (this vol., p. 577) the configuration of a 3 : 4′-dinitrochlorostilbene resulting from the elimination of one molecule of hydrogen chloride from the stilbene dichloride was determined by the fact that sulphuric acid converted it into 4-nitrophenyl 3-nitrobenzyl ketone. The constitution of this ketone was deduced from its non-identity with the isomeric 3-nitrophenyl 4-nitrobenzyl ketone obtained by oxidation of the intermediate aldol compound isolated during the condensation of *p*-nitrophenylacetic acid with *m*-nitrobenzaldehyde and therefore having the structure

$$(p)NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(OH){\cdot}C_6H_4{\cdot}NO_2(m).$$

Another synthesis of 4-nitrophenyl 3-nitrobenzyl ketone [from

3 : 4′-dinitro-α-phenylcinnamamide, utilising Weerman's modification of the Hofmann reaction (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, **10**, 308; *Annalen*, 1913, **401**, 1; *Rec. trav. chim.*, 1917, **37**, 1)], which confirmed the foregoing conclusions, is now described.

When *p*-nitrophenylacetonitrile and *m*-nitrobenzaldehyde are combined, with sodium ethoxide or piperidine as condensing agent, according to the method of Remse (*Ber.*, 1890, **23**, 3135), 3 : 4′-dinitro-α-phenylcinnamonitrile (I) and 3 : 4′-*dinitro*-β-*hydroxy*-α-*phenyldihydrocinnamonitrile* (II) are formed in about equal quantities. Neither Remse (*loc. cit.*) nor Freund (*Ber.*, 1901, **34**, 3107), both of whom carried out this same experiment, mentions the formation of (II), their sole product being (I).* The aldol compound (II) may be converted into (I) by the action of sulphuric acid, pyridine or piperidine.



Two quite different stereoisomeric *amides* (III and IV) are produced when (I) and (II) are hydrolysed with sulphuric acid. Amide (IV) on further hydrolysis with sulphuric acid yields only one acid (VI), but amide (III) under the same conditions gives a mixture of

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* From *o*-nitrobenzaldehyde and *p*-nitrophenylacetonitrile, however, Freund (*loc. cit.*) did isolate two compounds analogous to (I) and (II) above.

(V) and (VI); the same mixture is also formed when the nitrile (I) is directly hydrolysed to the acid stage. When amide (III) is hydrolysed with nitrous acid, however, acid (V) is almost the sole product.

The two *acids* (V) and (VI) can be separated, by Stoërmer and Prigge's method (*Annalen*, 1915, **409**, 20), by taking advantage of their widely differing strengths. Acid (VI) is the weaker, and from analogy with Stoërmer's results (see also Stoërmer and Voht, *ibid.*, 1915, **409**, 36) it is provisionally called the "*trans*" modification; the term applies to the relative positions of the phenyl and carboxyl groups, and not to the two phenyl groups.

Acids (V) and (VI) can both be decarboxylated by heating with piperidine, and yield the same form of 3 : 4′-dinitrostilbene.

EXPERIMENTAL.

3 : 4′-*Dinitro-β-hydroxy-α-phenyldihydrocinnamonitrile* (II).—When the condensation of *p*-nitrophenylacetonitrile and *m*-nitrobenzaldehyde in presence of piperidine or sodium ethoxide was allowed to proceed for only a few hours the product contained not only 3 : 4′-dinitro-α-phenylcinnamonitrile (I), m. p. 199—200° after recrystallisation from acetic acid (Remse and Freund give m. p. 195°), but also an equal amount of the intermediate *aldol* (II), which was isolated from the alcoholic mother-liquors, the total yield of the two nitriles being 85—90%. After many recrystallisations from acetic acid the aldol was obtained in yellow, crystalline aggregates, m. p. 135—136° (Found: C, 57·2; H, 3·6. $C_{15}H_{11}O_5N_3$ requires C, 57·5; H, 3·5%). It is easily soluble in pyridine, nitrobenzene, acetone, or ethyl acetate, less soluble in alcohol or benzene, and somewhat sparingly soluble in chloroform, carbon tetrachloride, or light petroleum. (II) can be converted into (I) by dissolution in cold concentrated sulphuric acid, by dissolving it in hot pyridine and keeping the solution for several days, or by keeping the crude reaction mixture (in presence of alcoholic piperidine) for a week.

The Two Stereoisomeric Forms of 3 : 4′-*Dinitro-α-phenylcinnamamide* (III and IV).—Each of the nitriles (I) and (II) (20 g.) was carefully dissolved in warm concentrated sulphuric acid (340 c.c.), water (46 c.c.) added, and the mixture heated on the steam-bath for 6 hours. When cold, the solution was poured into 2 litres of water, and the precipitated amide washed with hot dilute ammonia and with water (yield 96—99%). The *amide* (III), obtained from (I), separated from acetic acid in almost colourless needles, m. p. 220° (Found: C, 57·4; H, 3·6. $C_{15}H_{11}O_5N_3$ requires C, 57·5; H, 3·5%). It is sparingly soluble in the usual organic solvents, and is not hydrolysed to the acid by boiling with hydrochloric acid for 2 days. The higher-melting form of the *amide* (IV), obtained from

(II), is even less soluble than (III) in organic solvents. It separates from acetic acid in microscopic prisms and from nitrobenzene in thin plates, m. p. 272·5—273·5° (Found : C, 57·2; H, 3·9%).

Conversion of the Amide (*III*) *into* 4-*Nitrophenyl* 3-*Nitrobenzyl Ketone.*—A paste of the finely powdered amide (20 g.) and boiling methyl alcohol was cooled and added, with shaking, to a solution of sodium hypochlorite during 1 hour. The mixture was then heated at 80° for ½ hour, much unchanged amide filtered off, the warm liquor acidified with dilute sulphuric acid, and the dark brown precipitate repeatedly crystallised from alcohol (charcoal). The slightly brown needles thus obtained melted at 132°, alone or mixed with 4-nitrophenyl 3-nitrobenzyl ketone. The yield was exceedingly poor, but the constitution of the ketone was proved.

cis *and* trans *Forms of* 3 : 4′-*Dinitro-α-phenylcinnamic Acid* (V and VI).*—Amide (III) (17 g.) was boiled with a mixture of strong sulphuric acid, acetic acid, and water (125 c.c. of each) for 2 days, the product poured into water, and the filtered solid digested with hot sodium carbonate solution; the addition at 95° of a slight excess of acetic acid precipitated, in 48% yield, the weaker "*trans*" acid (VI), which crystallised from ethyl acetate in large, pale yellow prisms, m. p. 221° (Found: C, 57·2; H, 3·2; equiv., 316. $C_{15}H_{10}O_6N_2$ requires C, 57·3; H, 3·2%; equiv., 314). This isomeride is much less soluble than (V) in methyl alcohol or ethyl acetate.

From the hot filtrate after removal of acid (VI), most of the stronger "*cis*" acid (V) separated out, mixed with a little (VI), and addition of hydrochloric acid to the cold filtrate increased the yield to 36%. After two crystallisations from acetic acid (V) was obtained in rosettes of slightly brown needles, m. p. 205·5° (Found : C, 56·9; H, 3·3%; equiv., 312). It is readily soluble in hot methyl or ethyl alcohol, or acetic acid, and is moderately soluble in cold ethyl acetate.

From the nitrile (I), by hydrolysis under the above conditions, 32% of acid (VI) and 38% of acid (V) were obtained.

Hydrolysis of amide (IV) during 3 days led to the formation of acid (VI) in 77% yield. No acid (V) was discovered, the cold filtrate after removal of (VI) by acetic acid remaining quite clear on addition of hydrochloric acid.

Hydrolysis of Amide (*III*) *with Nitrous Acid.*—To a solution of amide (III) in cold concentrated sulphuric acid an excess of sodium nitrite was added, with water-cooling. After 2 days, the solution was diluted with water and kept for a week, a little more nitrite being added occasionally. The solid was removed, washed, and

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* For a description of the piperidine salts of these two acids, see this vol., p. 580.

thoroughly digested on the filter with hot sodium carbonate solution. Acetic acid was added to the boiling filtrate in slight excess, and the solution again filtered hot to remove a very small amount of precipitate (VI). On cooling, the filtrate deposited acid (V) in 80% yield.

Decarboxylation of Acids (V) and (VI).—The acid (3 g.) was dissolved in boiling acetone, piperidine (½ c.c.) added, and the acetone distilled off. The intimate mixture thus obtained was heated at 225° for ½ hour, and, after cooling, the resinous product was washed several times with boiling acetone and finally recrystallised from acetic acid, when it melted at 216°, either alone or mixed with an authentic specimen of 3 : 4′-dinitrostilbene (for which see this vol., p. 580). The yields from acids (V) and (VI) were respectively 27% and 32%.

In conclusion, one of us (H. W.) desires to express his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant, and the other (H. A. H.) to the Chemical Society Research Fund Committee for a grant for materials. We also thank Professor Lapworth for his continued interest and advice.

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