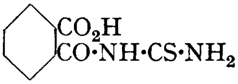
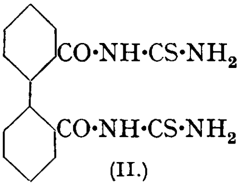
50. *Some Further Reactions of Diphenic Anhydride.*

By Frank Bell and Fred Briggs.

In a previous paper (J., **1938**, **1561**) the mode of interaction of diphenic anhydride with the simpler hydrocarbons and phenols was described; the work has been extended to include various nitrogen-containing compounds. In addition, the condensation of 4 : 4′-dinitrodiphenic anhydride with certain compounds has been examined.

Piutti (*Annalen*, 1882, **214**, 19) has described the interaction of phthalic anhydride with urea and thiourea to yield compounds of type (I). It is now found that the only isolable product from the interaction of diphenic anhydride with urea is diphenimide, but with thiourea *diphenoylthiourea* (II) is obtained.


(I.)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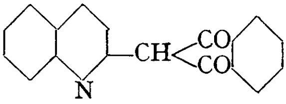
(III.)

Eibner and Hofmann (*Ber.*, 1904, **37**, 3011) established that the formula of the condensation product, quinophthalone, of quinaldine with phthalic anhydride is (III). It is found that diphenic anhydride readily yields an analogous *quinodiphenone.*

With aniline and methylaniline, diphenic anhydride yielded the expected N-*phenyl*- and N-*phenyl*-N-*methyl-diphenamic acids.* Conditions could not be found under which 2-*p*-aminobenzoyldiphenyl-2′-carboxylic acids could be produced by direct condensation. Dimethylaniline with diphenic anhydride gave a substance with the properties of a malachite-green.

4 : 4′-Dinitrodiphenic anhydride behaved analogously to diphenic anhydride in the following reactions. With ammonia it gave 4 : 4′-*dinitrodiphenamic acid*, with *m*-xylene or mesitylene in presence of aluminium chloride the corresponding derivatives of 4 : 4′-dinitro-2-benzoyldiphenyl-2′-carboxylic acid. Condensation with quinaldine occurred smoothly to give *quino*-4 : 4′-*dinitrodiphenone* and with thiourea there was obtained a small yield of 4 : 4′-*dinitrodiphenoylthiourea.*

When an intimate mixture of equal parts of diphenic anhydride and aluminium chloride is heated to 220° for a few minutes, the diphenic anhydride is quantitatively transformed into fluorenone-4-carboxylic acid. A similar experiment with 4 : 4′-dinitrodiphenic anhydride gave 4 : 4′-dinitrodiphenic acid as the only isolable product after decomposition of the reaction mass with hydrochloric acid. Much decomposition had occurred.

EXPERIMENTAL.

An asterisk indicates microanalysis by Dr. G. Weiler of Oxford.

Reactions of Diphenic Anhydride.—(a) *With aniline.* N-*Phenyldiphenamic acid* was obtained by solution of diphenic anhydride in hot aniline; stannic chloride had no influence on the course of the reaction. The acid crystallised from aqueous acetic acid in needles, m. p. 181—183° (Found: equiv., 317. $C_{20}H_{15}O_3N$ requires equiv., 317). It was recovered unchanged from boiling acetic anhydride, and underwent hydrolysis with 50% sulphuric acid to yield diphenic acid and aniline. Attempts to prepare a pure nitro-derivative were unsuccessful.

(b) *With methylaniline.* N-*Phenyl*-N-*methyldiphenamic acid* was obtained by solution of diphenic anhydride in hot methylaniline; aluminium chloride had no influence on the course of the reaction, but stannic chloride occasioned the additional formation of a dark purple colouring matter. The acid crystallised from acetic acid in needles, m. p. 181° (Found: equiv., 331. $C_{21}H_{17}O_3N$ requires equiv., 331); it was hydrolysed by 50% sulphuric acid to yield diphenic acid.

(c) *With dimethylaniline.* (i) A mixture of dimethylaniline (10 c.c.), diphenic anhydride (5 g.), and stannic chloride (5 c.c.) was heated at 110—120° for 2 hours. Excess of sodium hydroxide was then added, and unchanged dimethylaniline removed in steam. The residual solution was filtered and approximately neutralised with hydrochloric acid. The green precipitate obtained was redissolved in sodium bicarbonate solution, reprecipitated with hydrochloric acid, dried, and extracted with benzene, and the extract precipitated with light petroleum. The green product could not be crystallised from any of the common solvents. It was insoluble in 4N-sodium hydroxide but readily soluble in N/10-sodium hydroxide or sodium bicarbonate to yield a bright green solution. It dissolved in hydrochloric acid to a reddish-brown solution which dyed wool green.

(ii) A similar condensation using aluminium chloride as condensing agent resulted in a green compound similar to that previously described and also a deep blue compund. Neither of these could be obtained in a crystalline form in spite of repeated attempts. It was thought that the use of diphenic acid chloride might yield a more uniform product. Accordingly, aluminium chloride (5 g.) was added to a solution of diphenic acid chloride (5 g.) and dimethylaniline (10 c.c.) in carbon disulphide. The mixture was boiled under reflux for ½ hour, and then worked up as under (i). A small amount of a colourless material was isolated which melted at about 250° to a deep green liquid (Found *: C, 80·8; H, 6·3%). It instantly gave a deep green liquid in contact with acids and had all the properties of a dye base.

(d) *With α-picoline.* This underwent no condensation with diphenic anhydride either alone or in presence of zinc chloride.

(e) *With quinaldine.* A mixture of quinaldine (10 g.) and diphenic anhydride (10 g.) was heated at 150° for 2 hours. The product was alternately extracted with dilute hydrochloric acid and dilute aqueous ammonia until quite solid. The residual *quinodiphenone* crystallised readily from benzene or pyridine in bright yellow needles, m. p. 226—228° (Found*: C, 81·6;

H, 4·5. $C_{24}H_{15}O_2N$ requires C, 82·5; H, 4·3%), difficultly soluble in alcohol and acetone. The condensation follows essentially the same course even in the presence of zinc chloride and at higher temperature. Quinodiphenone dissolved readily in boiling alcoholic potash and on cooling a pale yellow potassium salt separated in hexagonal crystals; this regenerated the original material with hydrochloric acid.

(f) *With urea.* Diphenic anhydride (10 g.) and urea (5 g.) were maintained at 120° for 5 hours. The product yielded only diphenimide and diphenamic acid. No condensation product was isolated from the product of interaction of diphenic acid and urea in the presence of phosphorus oxychloride.

(g) *With thiourea.* As for urea. The product was separated by crystallisation from acetic acid into *diphenoylthiourea* and the more soluble diphenimide. The former formed needles containing acetic acid of crystallisation, m. p. 231° (decomp.) (Found*: C, 51·9; H, 4·4; N, 14·0; S, 14·7. $C_{16}H_{14}O_2N_4S_2,C_2H_4O_2$ requires C, 51·7; H, 4·3; N, 13·4; S, 15·3%), insoluble in sodium bicarbonate solution but easily soluble in cold sodium hydroxide solution, from which it could be precipitated unchanged. On heating to the m. p., acetic acid and hydrogen sulphide were evolved; the residue on crystallisation from acetic acid furnished diphenimide.

No condensation product was isolated from the product of interaction of diphenic acid with thiourea in the presence of phosphorus oxychloride.

(h) *With* o-*aminophenol,* p-*aminophenol and salicylic acid.* After these compounds had been heated with diphenic anhydride and stannic chloride, fluorenone-4-carboxylic acid was the only crystalline material isolated from each of the products.

2 : 7-*Dinitrophenanthraquinone.*—Crude 2-nitrophenanthraquinone (30 g., obtained as a by-product in the preparation of 4-nitrophenanthraquinone) was refluxed for ½ hour with a mixture of fuming nitric acid (400 c.c.) and sulphuric acid (50 c.c.). The resultant solution was poured into water, and the precipitate filtered off, dried, and boiled with 2 l. of acetic acid to remove the more soluble 2 : 5-dinitrophenanthraquinone. The residual 2 : 7-dinitrophenanthraquinone crystallised readily from boiling nitrobenzene. Yield, 26·5 g.; m. p. 298°. On oxidation with potassium dichromate, 78·5 g. of this quinone gave 83·5 g. of purified 4 : 4′-dinitrodiphenic acid. The acid was readily converted into the anhydride by the method previously described (J., 1927, 1697).

Reactions of 4 : 4′-*Dinitrodiphenic Anhydride.*—(a) *With ammonia.* Powdered 4 : 4′-dinitrodiphenic anhydride rapidly dissolved in warm 15% ammonia solution to give 4 : 4′-*dinitrodiphenamic acid,* which, after recrystallisation from acetic acid, formed prisms, m. p. 237—239° (decomp.) (Found: equiv., 328. $C_{14}H_9O_7N_3$ requires equiv., 331).

(b) *With* m-*xylene.*—Powdered aluminium chloride (6 g.) was added to a suspension of 4 : 4′-dinitrodiphenic anhydride (6 g.) in *m*-xylene. After standing overnight, the mixture was decomposed with hydrochloric acid, the excess of xylene removed in steam, and the residue dissolved in sodium hydroxide solution, reprecipitated with hydrochloric acid, and purified by crystallisation from acetic acid. 4 : 4′-*Dinitro*-2-2″ : 4″-*dimethylbenzoyldiphenyl*-2′-*carboxylic acid* formed small prisms, m. p. 207° (Found*: C, 62·9; H, 3·9. $C_{22}H_{16}O_7N_2$ requires C, 62·9; H, 3·8%); warmed at 120° for ¼ hour with sulphuric acid, it yielded a sparingly soluble sulphonic acid.

(c) *With mesitylene.* As for *m*-xylene. 4 : 4′-*Dinitro*-2-2″ : 4″ : 6″-*trimethylbenzoyldiphenyl*-2′-*carboxylic acid* was separated from resinous acidic material by preparing its sparingly soluble sodium salt. The acid crystallised from acetic acid in needles, m. p. 183—185° (Found: equiv., 438. $C_{23}H_{18}O_7N_2$ requires equiv., 434). On heating with sulphuric acid at 100° for ¼ hour it gave 4 : 4′-dinitrodiphenic acid.

(d) *With quinaldine. Quino*-4 : 4′-*dinitrodiphenone,* obtained by heating 4 : 4′-dinitrodiphenic anhydride with quinaldine at 170—190° for 2 hours, crystallised from nitrobenzene in orange needles, m. p. above 300° (Found*: C, 65·6; H, 3·3. $C_{24}H_{13}O_6N_3$ requires C, 65·6; H, 3·3%).

(e) *With thiourea.* 4 : 4′-*Dinitrodiphenoylthiourea,* obtained by heating the anhydride with thiourea at 130—140° for 2 hours, crystallised from nitrobenzene in small, pale yellow needles, m. p. 239° (decomp.) (Found*: C, 43·7; H, 2·6; S, 13·7. $C_{16}H_{12}O_6N_6S_2$ requires C, 42·9; H, 2·6; S, 14·3%).

(f) *With ethylbenzene, phenol, or resorcinol.* No crystallisable material could be isolated from the products of interaction of the anhydride with phenol or resorcinol (both in presence of stannic chloride) or ethylbenzene (in presence of aluminium chloride).

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