CCXXVIII.—*The Action of Diazonium Salts on Pyrones and their Parent Substances. Part I.*

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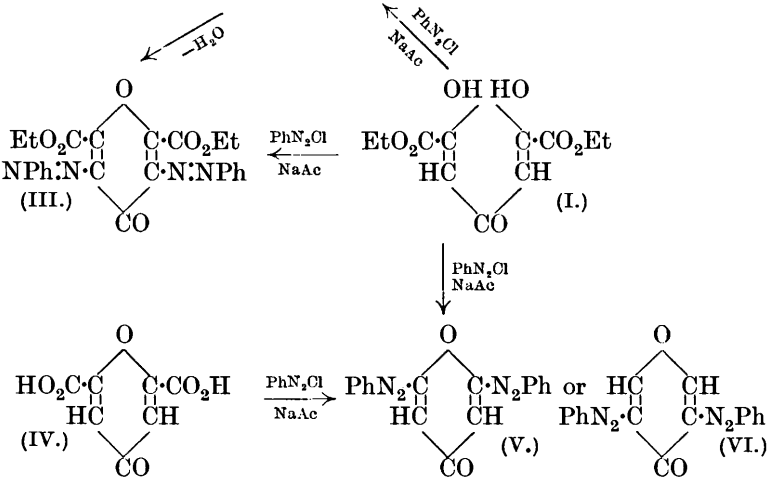
In connexion with the unsettled question of the constitution of mixed aliphatic aromatic azo-compounds, evidence in favour of the azo-structure has now been obtained, since ethyl acetonedioxalate (I), on treatment with benzenediazonium chloride in presence of sodium acetate, yields a mixture of *ethyl dibenzeneazoacetonedioxalate* (II) and *ethyl dibenzeneazochelidonate* (III). The former, on boiling with alcohol, loses water, ethyl dibenzeneazochelidonate being formed, with an ease that suggests the azo-structure.

$CO_2Et{\cdot}CO{\cdot}CH(N_2Ph){\cdot}CO{\cdot}CH(N_2Ph){\cdot}CO{\cdot}CO_2Et$ (II.)



Chelidonic acid (IV) reacts with benzenediazonium chloride to give an azopyrone (V or VI), formula (V) being the more probable because this substance could not be obtained by hydrolysis of the ester (III). The azopyrone was also formed to some extent during

the reaction between benzenediazonium chloride and ethyl acetonedioxalate. The replacement of carboxyl by azo-groups has been observed in other cases (compare Japp and Klingeman, J., 1888, **53**, 519; Bamberger, *Ber.*, 1892, **25**, 3547).

In the presence of sodium acetate, benzenediazonium chloride reacts with 2 : 6-dimethylpyrone and with diacetylacetone to give 3-*benzeneazo*-2 : 6-*dimethylpyrone* and 3 : 5-*dibenzeneazo*-2 : 6-*dimethylpyrone*, respectively.

EXPERIMENTAL.

Ethyl Dibenzeneazoacetonedioxalate (II).—Ethyl acetonedioxalate (prepared by Claisen's method, *Ber.*, 1891, **24**, 111, which gives a better yield than Willstätter's, *Ber.*, 1904, **37**, 3734) (7·8 g.) was added to an aqueous solution of benzenediazonium chloride (from aniline, 5 g., and hydrochloric acid, 13 c.c.). Addition of alcohol (59 c.c.) and much sodium acetate produced a heavy, red precipitate, which was filtered off and thoroughly washed by grinding with water; the aqueous-alcoholic filtrate slowly deposited a chocolate-coloured substance. The red product was crystallised from 80% alcohol and then from benzene–light petroleum (40% benzene), large, dark red prisms, m. p. 130°, soluble in organic solvents, being obtained (Found: C, 59·2; N, 12·0. $C_{23}H_{22}O_7N_2$ requires C, 59·2; N, 12·0%).

Ethyl Dibenzeneazochelidonate (III).—When the red precipitate formed by diluting the alcoholic filtrate from the crystallisation of the foregoing substance with water was crystallised from benzene–light petroleum, red needles were obtained, m. p. 117°, of a substance which was identical with that formed when ethyl dibenzeneazoacetonedioxalate was boiled with alcohol and the product crystallised (Found: C, 61·4; H, 4·5; N, 12·5. $C_{23}H_{20}O_6N_4$ requires C, 61·6; H, 4·5; N, 12·5%). It was readily soluble in organic solvents.

2 : 6-*Dibenzeneazopyrone*.—The chocolate-brown substance mentioned above crystallised from alcohol in chocolate-brown prisms, m. p. 131°, which were soluble in the common organic solvents (Found: N, 18·4. $C_{17}H_{12}O_2N_4$ requires N, 18·4%).

Action of Benzenediazonium Chloride on Chelidonic Acid.—Chelidonic acid (3 g.), obtained by repeatedly evaporating ethyl acetonedioxalate with concentrated hydrochloric acid (Claisen, *loc. cit.*), was added to a solution of benzenediazonium chloride (aniline, 5 g.; hydrochloric acid, 13 c.c.; water, 30 c.c.: sodium nitrite, 5 g.; water, 15 c.c.). The brown precipitate obtained on addition of an excess of sodium acetate crystallised from alcohol in chocolate-brown prisms, m. p. 131° (Found: C, 67·1; H, 3·6; N, 18·4%). A mixed-melting point proved this substance to be 2 : 6-dibenzeneazopyrone (above).

3-*Benzeneazo*-2 : 6-*dimethylpyrone*.—A solution of benzenediazonium chloride at 0° (aniline, 13 g.; hydrochloric acid, 26 c.c.; water, 60 c.c.: sodium nitrite, 13 g.; water, 30 c.c.) was treated with dimethyl pyrone (6 g.) and then with sodium acetate. After 2 days, the tarry product was filtered off and extracted several times with light petroleum–benzene (90% light petroleum); the *pyrone* obtained from the extract crystallised from light petroleum–benzene in yellow leaflets, m. p. 92° (Found : N, 12·5. $C_{13}H_{12}O_2N_2$ requires N, 12·3%).

3 : 5-*Dibenzeneazo*-2 : 6-*dimethylpyrone*.—To a solution of benzenediazonium chloride (aniline, 4·3 g.; hydrochloric acid, 9 c.c.; water, 20 c.c. : sodium nitrite, 4·3 g., in water, 10 c.c., was added until a blue colour was obtained on starch–iodide paper), diacetylacetone (2·5 g., prepared by boiling dimethylpyrone with baryta, acidifying the solution, and extracting it with ether; *Annalen*, 1890, **251**, 256) was added, followed by sodium acetate. The solution became yellow and then a light red substance was slowly precipitated. After 12 hours, this was filtered off, washed with cold water, and crystallised from benzene, from which it separated in light red needles, m. p. 150° (Found : N, 16·8. $C_{19}H_{16}O_2N_4$ requires N, 16·9%). It was soluble in organic solvents, but insoluble in water.

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