132. *Some Derivatives of Thioxanthen.*

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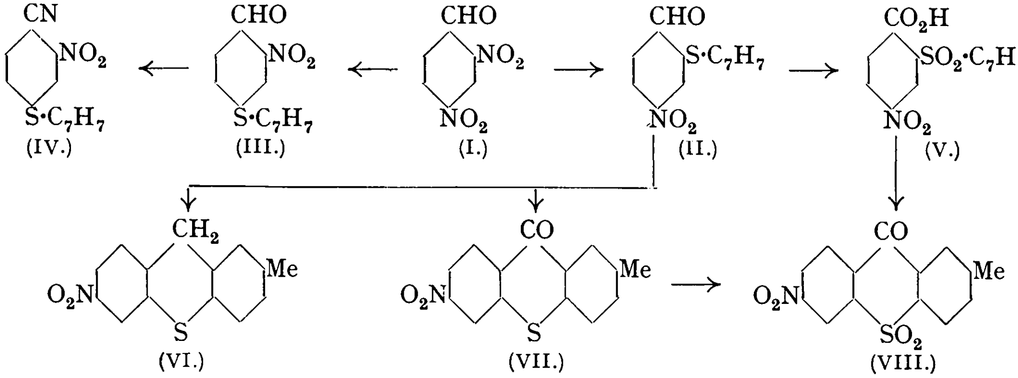
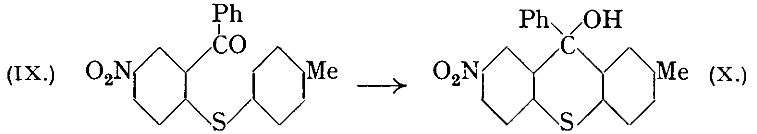
Benzaldehydes, substituted in the *o*-position by an arylthio-group, dissolve in concentrated sulphuric acid to give intensely red solutions, from which mixtures of the corresponding thioxanthen and thioxanthone are obtained by pouring into water. On the other hand, the thioxanthhydrol results from a similarly substituted benzophenone. The requisite carbonyl compounds are obtained by replacement of the chlorine atom in 2-chloro-5-nitro-benzaldehyde or -benzophenone, or of a nitro-group in 2 : 4-dinitrobenzaldehyde, in reaction with the sodium salts of thiophenols.

The replaceable character of the nitro-groups in 2 : 4-dinitrodiphenylsulphones (Loudon, J., 1936, 218) and in 2 : 4-dinitrobenzonitrile (Holmes and Loudon, J., 1940, 1521) suggested the use of 2 : 4-dinitrobenzaldehyde (I) as a source of diaryl sulphides containing an aldehydic function. Experiment showed that the aldehyde reacted with the sodium salts of thiols in the expected manner : for example, with thio-*p*-cresol and sodium hydroxide there was produced *4-nitro-2-(*p*-tolylthio)benzaldehyde* (II) together with a smaller amount of *2-nitro-4-(*p*-tolylthio)benzaldehyde* (III). These products were identified by conversion, *via* their *oximes*, into the known benzonitriles (*e.g.*, III → IV) (Holmes and Loudon, *loc. cit.*) and were further characterised by oxidation to the corresponding *sulphone-acids* (*e.g.*, II → V).



In contact with concentrated sulphuric acid diaryl sulphides containing an *o*-aldehydic group undergo what appears to be a general reaction resulting in the formation of thioxanthylium salts. This is apparent from the intense colour development which occurs as the solid dissolves and, in some cases at least, the reaction is complete almost as soon as dissolution at room temperature has been effected. Nevertheless, we have not been able to isolate thioxanthhydrols from the aldehydes, since on addition of the red solutions to ice-water there was produced in each case a mixture containing equivalent amounts of the *thioxanthen* and *thioxanthone* (*e.g.*, VI and VII). Oxidation of the products gave the *thioxanthone dioxides*; 6-*nitro*-2-*methylthioxanthone dioxide* (VIII) was independently synthesised by cyclisation of the acid (V), and 7-*nitro*-2-*methylthioxanthone* and its *dioxide* were similarly prepared by the alternative routes, *via* the respective *sulphides*, from 2-chloro-5-nitrobenzaldehyde and 2-chloro-5-nitrobenzoic acid.



When the *keto-sulphide* (IX), obtained from 2-chloro-5-nitrobenzophenone and thio-*p*-cresol, was treated with concentrated sulphuric acid, the product had the expected properties of the *thioxanthhydrol* (X). It gave a coloured salt with dry hydrogen chloride in ether, formed a deep red, crystalline *chloride-ferrichloride*, was readily reduced to the corresponding *thioxanthen* by heating with alcoholic hydrochloric acid, and formed an *ethyl* ether when warmed in alcohol containing a trace of acid but crystallised unchanged from the pure solvent. Its formation recalls the production of xanthhydrols and thioxanthhydrols (Reilly and Drumm, J., 1930, 455; *Proc. Roy. Irish Acad.*, 1930, **39**, 515) from diaryl ethers and thio-ethers respectively in the Friedel–Crafts reaction with benzoyl chloride, and we have confirmed the efficacy of aluminium chloride as condensing agent also for the reaction (IX) → (X). Analogous cyclisations using sulphuric acid have been effected by Decker and co-workers (*Annalen*, 1906, **348**, 231, 238) on 1-phenoxy- and 1-phenylthio-anthraquinones, but the conditions described are much more severe than those required in the present case.

Preliminary experiments have shown that oxy-ethers undergo cyclisations similar to those of the thio-ethers and other applications of the process will be investigated.

EXPERIMENTAL.

4-*Nitro*-2-(p-*tolylthio*)*benzaldehyde* (II).—2 : 4-Dinitrobenzaldehyde (7·6 g.) in alcohol (35 c.c.) was cooled in ice and treated, with shaking and in small quantities at a time, with an ice-cold solution of thio-*p*-cresol (5·6 g.) and sodium hydroxide (1·6 g.) in alcohol (20 c.c.) and water (3 c.c.). The intense red colour which developed was allowed to fade to an orange-yellow after each addition and a small piece of ice was added to the reaction mixture from time to time. Towards the end of the operation the product began to separate and when the addition was completed the whole was set aside for 1—2 hours. Crystallisation from acetic acid (mother-liquor preserved; see below) gave (II) in slender yellow needles, m. p. 147° (Found : C, 61·6; H, 4·1; N, 5·2. $C_{14}H_{11}O_3NS$ requires C, 61·5; H, 4·0; N, 5·1%). It formed an *oxime*, m. p. 164° (Found : N, 9·8. $C_{14}H_{12}O_3N_2S$ requires N, 9·7%), from which 4-nitro-2-*p*-tolylthiobenzonitrile, m. p. and mixed m. p. 155—156° (Holmes and Loudon, *loc. cit.*), was obtained by heating for 2 hours with acetic anhydride.

2-*Nitro*-4-(p-*tolylthio*)*benzaldehyde* (III).—When the acetic mother-liquor from (II) was moderately diluted with water and set aside for some days there slowly separated a mixture of yellow feathery needles, identified as (II), together with compact hexagonal prisms or plates of a much lighter colour. The latter were roughly separated by hand and were recrystallised from acetic acid–alcohol, yielding needles, m. p. 109°, depressed by admixture with (II) (Found : C, 61·8; H, 4·0; N, 5·0. $C_{14}H_{11}O_3NS$ requires C, 61·5; H, 4·0; N, 5·1%). The *oxime*, formed in the usual way, had m. p. 108° after crystallisation from benzene–ligroin (Found : N, 10·0. $C_{14}H_{12}O_3N_2S$ requires N, 9·7%) and, on dehydration, gave 2-nitro-4-*p*-tolylthiobenzonitrile, m. p. and mixed m. p. with an authentic specimen 116°.

4-*Nitro*-2-(β-*naphthylthio*)*benzaldehyde* was obtained when thio-β-naphthol was used in the process described for (II), with the addition of dioxan to promote solubility. The precipitate formed in the course of the reaction consisted almost entirely of β-naphthyl disulphide, which was removed, and the required product obtained by diluting the mother-liquor with water. After repeated crystallisation from acetic acid, it formed matted orange needles, m. p. 156—157° (Found : C, 66·1; H, 3·7. $C_{17}H_{11}O_3NS$ requires C, 66·0; H, 3·6%), but no isomeric substance could be isolated in a pure condition.

5-*Nitro*-2-(p-*tolylthio*)*benzaldehyde*.—2-Chloro-5-nitrobenzaldehyde (2·4 g.) in warm alcohol was treated slowly with a hot aqueous alcoholic solution of thio-*p*-cresol (1·8 g.) and sodium hydroxide (0·6 g.). The reaction was completed by warming on the water-bath for 30 minutes; after cooling, the product was collected and crystallised from acetic acid, forming long yellow needles, m. p. 156° (Found : C, 61·7; H, 4·3. $C_{14}H_{11}O_3NS$ requires C, 61·5; H, 4·0%).

5-*Nitro*-2-(p-*tolylthio*)*benzophenone* (IX) was similarly obtained from 2-chloro-5-nitrobenzophenone, heating being continued for 1 hour. It formed dense, pale yellow cubes when slowly crystallised from alcohol–acetic acid and had m. p. 102° (Found : C, 68·7; H, 4·3. $C_{20}H_{15}O_3NS$ requires C, 68·8; H, 4·3%). Oxidation with hydrogen peroxide in acetic acid gave the corresponding *sulphone*, m. p. 184° (Found : C, 63·15; H, 4·3. $C_{20}H_{15}O_5NS$ requires C, 63·0; H, 3·9%), from which, and also from the chloro-ketone, there was obtained, by heating with piperidine, 5-*nitro*-2-*piperidinobenzophenone*, m. p. 102° (Found : N, 9·2. $C_{18}H_{18}O_3N_2$ requires N, 9·0%).

5-*Nitro*-2-(p-*tolylthio*)*benzoic acid* was similarly obtained from 2-chloro-5-nitrobenzoic acid, thio-*p*-cresol, and sodium hydroxide (2 mols.). After acidification the product was crystallised from acetic acid and had m. p. 253° (Found : C, 58·3; H, 3·7. $C_{14}H_{11}O_4NS$ requires C, 58·1; H, 3·8%).

4-*Nitro*-2-(p-*toluenesulphonyl*)*benzoic Acid* (V).—(*a*) The aldehyde (II) was oxidised by warming with hydrogen peroxide in acetic acid. (*b*) An aqueous solution of sodium 2-chloro-4-nitrobenzoate and sodium *p*-toluenesulphinate was heated with copper bronze at 130° for 3 hours. In each case after purification from alcohol, the product was obtained in colourless prisms, m. p. and mixed m. p. 217° (Found : C, 52·3; H, 3·3. $C_{14}H_{11}O_6NS$ requires C, 52·3; H, 3·4%).

2-*Nitro*-4-(p-*toluenesulphonyl*)*benzoic acid*, m. p. 191° after crystallisation from acetic acid, was obtained when the aldehyde (III) was oxidised with hydrogen peroxide in acetic acid (Found : C, 52·3; H, 3·3. $C_{14}H_{11}O_6NS$ requires C, 52·3; H, 3·4%).

6-*Nitro*-2-*methyl*-*thioxanthone* (VII) *and* -*thioxanthen* (VI).—The aldehyde (II) was shaken with concentrated sulphuric acid until a clear red solution was obtained. This was left for several hours and was then poured on ice. The solid was collected, washed with water, and dissolved in boiling acetic acid, from which on standing the *thioxanthone* (VII) separated, forming yellow leaflets, m. p. 276° (Found : C, 61·8; H, 3·7. $C_{14}H_9O_3NS$ requires C, 62·0; H, 3·3%). The mother-liquor on dilution with water gave the *thioxanthen* (VI), which crystallised from alcohol–acetic acid in plates, m. p. 155° (Found : C, 65·2; H, 4·5. $C_{14}H_{11}O_2NS$ requires C, 65·4; H, 4·3%).

6-*Nitro*-2-*methylthioxanthone Dioxide* (VIII).—(*a*) The thioxanthone (VII) or the thioxanthen (VI), dissolved in acetic acid at 100°, was oxidised with hydrogen peroxide. (*b*) A solution of (V) in nitrobenzene was heated on the water-bath with thionyl chloride, the excess of which was removed by distillation when the reaction was complete. Thereafter aluminium chloride was added, and heating continued for 2 hours. After addition of water the nitrobenzene was distilled in steam, and the residue purified from acetic acid. In each case the *dioxide* was obtained and had m. p. 238° (Found: C, 55·2; H, 3·1. $C_{14}H_9O_5NS$ requires C, 55·5; H, 3·0%).

6-*Nitro*-1 : 2-*benz-thioxanthone* and -*thioxanthen* were prepared from 4-nitro-2-(β-naphthylthio)benzaldehyde as in the previous case. The thioxanthone formed golden needles, m. p. 273°, from acetic acid (Found: C, 66·6; H, 3·0. $C_{17}H_9O_3NS$ requires C, 66·45; H, 2·9%), and the thioxanthen pale yellow, brittle needles, m. p. 168° (Found: C, 69·5; H, 3·7. $C_{17}H_{11}O_2NS$ requires C, 69·6; H, 3·75%).

7-*Nitro*-2-*methyl-thioxanthone* and -*thioxanthen*, from 5 nitro-2-(*p*-tolylthio)benzaldehyde, had m. p. 262° (Found: C, 61·5; H, 3·6. $C_{14}H_9O_3NS$ requires C, 62·0; H, 3·3%), and m. p. 146° (Found: C, 65·35; H, 4·8. $C_{14}H_{11}O_2NS$ requires C, 65·4; H, 4·3%), respectively. The thioxanthone was also prepared by dissolving 5-nitro-2-(*p*-tolylthio)benzoic acid in fuming sulphuric acid. Both samples gave the same *dioxide*, m. p. 287°, on oxidation (Found: C, 55·45; H, 2·6. $C_{14}H_9O_5NS$ requires C, 55·5; H, 3·0%).

7-*Nitro*-9-*phenyl*-2-*methylthioxanthhydrol* (X).—(*a*) The keto-sulphide (IX) was dissolved in cold concentrated sulphuric acid and the solid obtained by pouring into ice-water was washed with dilute sodium carbonate solution and then with water. (*b*) The ketone, aluminium chloride, and nitrobenzene in a stoppered flask were kept at room temperature for 3 days and after addition to ice-water and washing free of acid, the nitrobenzene was removed in steam. In each case the crude product, after drying, crystallised from benzene–ligroin in yellow prisms, m. p. 203° (Found: C, 68·5; H, 4·4. $C_{20}H_{15}O_3NS$ requires C, 68·8; H, 4·3%). When solutions of the thioxanthhydrol and ferric chloride in acetic acid, previously saturated with hydrogen chloride, were mixed there was formed a red precipitate of the *chloride-ferrichloride*. It crystallised from the same solvent and decomposed at 197—200° (Found: Fe, 11·0; Cl, 26·3. $C_{20}H_{14}O_2NClS,FeCl_3$ requires Fe, 10·5; Cl, 26·8%). An unstable red chloride, presumably a chloride hydrochloride, was formed by passing dry hydrogen chloride into a solution of (X) in ligroin and was converted by warming with alcohol into the *ethyl* ether, m. p. 151° (Found: C, 70·5; H, 5·4. $C_{22}H_{19}O_3NS$ requires C, 70·0; H, 5·05%), also formed when (X) was heated with alcohol containing a trace of sulphuric acid.

7-*Nitro*-9-*phenyl*-2-*methylthioxanthene*, m. p. 167° after crystallisation from alcohol, was obtained by heating a solution of (X) in alcohol saturated with dry hydrogen chloride (Found: C, 72·2; H, 4·5. $C_{20}H_{15}O_2NS$ requires C, 72·1; H, 4·5%).

Grateful acknowledgment is made to The Carnegie Trustees for a Teaching Fellowship held by one of us (J. D. L.) and to Mr. J. M. L. Cameron, who performed the micro-analyses.

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[*Received, August 5th*, 1941.]