83. *Photochemical Reactions. Part XV.* (a) *Photopolymerisation of Coumarins and Related Substances.* (b) *Photo-addition and -reduction Processes of Aromatic Ketones.*

By Alexander Schönberg, Nazih Latif, Radwan Moubasher, and (in part) William Ibrahim Awad.

(*a*) 3-Phenylcoumarin forms a photodimer analogous to that from coumarin; the constitution of the latter dimer is therefore (I*a*) and not (II). Photodimers of 3-phenyl*iso*coumarin and benzylidenephthalide were obtained (cf. IV and III). These dimers gave the monomers when heated.

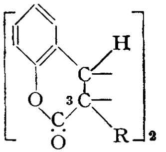
(*b*) From 2 : 7-dimethylphenanthraquinone with stilbene and from phenanthraquinone with 1 : 2-di-4′-pyridylethylene, 3 : 4-diphenyl- and 3-phenyl-*iso*coumarin and 1 : 3-diphenyl*iso*chromen, the photo-products (V), (VI), (VIII), (VII), and (IX) respectively were obtained.

o-Dibenzoylbenzene in *iso*propyl alcohol yielded a photoproduct which, when heated, gave 1 : 3-diphenyl*iso*benzofuran (XI). Phenanthraquinone monoxime and monoimine on photoreduction yielded diphenanthro-oxazine (XIII); with aromatic aldehydes in the presence of light the oxime yielded products which gave 2-arylphenanthro-oxazoles (X) on heating.

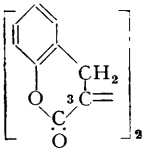
In connection with the constitution of the photoreduction product of triketoindane (XIV) the constitution of a substance erroneously described (Gabriel and Leupold, *Ber.*, 1898, **31**, 1159) as (XVII) is proved to be (XXI).

Photopolymerisations.—(a) *Coumarins.* Formulæ (I*a*) and (II) have been discussed for the product obtained when a solution of coumarin in alcohol or a suspension of the solid in water is exposed to sunlight (Ciamician and Silber, *Ber.*, 1902, **35**, 4130; 1903, **36**, 4266; De Jong, *Rec. Trav. chim.*, 1924, **43**, 318). Formula (II) is still widely used (cf. Richter and Anschütz, " Chemie der Kohlenstoffverbindungen," Vol. II, 2nd half, p. 515, 12th edn., 1935). Fischer has given to the photodimer of umbelliferone methyl ether a formula analogous to (II) (*Arch. Pharm.*, 1941, **279**, 306), but its correctness was questioned by Wessely and Flaichinger (*Ber.*, 1942, **75**, 971).

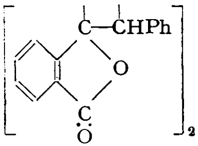
Photodimerisation of coumarin and its derivatives with the formation of (II) or its analogues is possible only when the hydrogen in the position 3 is unsubstituted. We found, however, that 3-phenylcoumarin in sunlight is easily converted in excellent yield into a similar *photodimer*; therefore, the dimers must be *cyclo*butane derivatives (I), a conception which is favoured by regeneration of the monomer when the photodimer of coumarin or of 3-phenylcoumarin is heated.



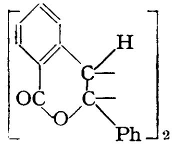
(I; *a*, R = H; *b*, R = Ph.)



(II.)

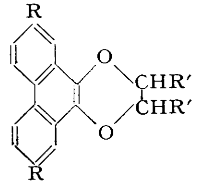


(III.)

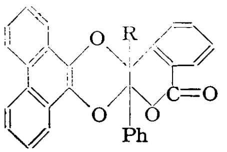


(IV.)

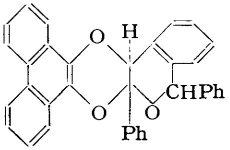
(b) *Benzylidenephthalide and* 3-*phenyl*iso*coumarin.* Both these substances form *photodimers* (III and IV, respectively) under the action of sunlight; when heated, the products regenerate the monomers.



(V; R = Me, R′ = Ph.)
(VI; R = H, R′ = C_5H_4N.)



(VII; R = H.)
(VIII; R = Ph.)

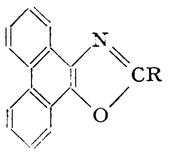


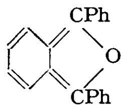
(IX.)

Photoaddition Reactions.—We have continued the investigations on the action of phenanthraquinone on ethylenes (Schönberg, Mustafa, and their co-workers, *J.*, 1944, 387; 1945, 551; 1948, 2126) and have studied the action of 2 : 7-dimethylphenanthraquinone on stilbene and of phenanthraquinone on 1 : 2-di-4′-pyridylethylene, 3 : 4-diphenyl- and 3-phenyl-*iso*coumarin, and 1 : 3-diphenyl*iso*chromen. In all cases colourless or almost colourless addition *products* (V)—(IX) were obtained, some of which, *e.g.*, (VII) and (VIII), regenerated the starting materials when heated.

Phenanthraquinone Monoxime and Aromatic Aldehydes.—The oxime and benzaldehyde do not react in benzene in the dark; in sunlight, however, a product was formed which on heating yielded 2-phenylphenanthro-oxazole (X; R = Ph); in the case of anisaldehyde 2-p-*methoxyphenylphenanthro-oxazole* (X; R = C_6H_4·OMe-*p*) was obtained. These reactions are similar to the photo-formation of 2-arylphenanthro-oxazoles by the action of aromatic aldehydes on phenanthraquinoneimine (Schönberg and Awad, *J.*, 1945, 197).

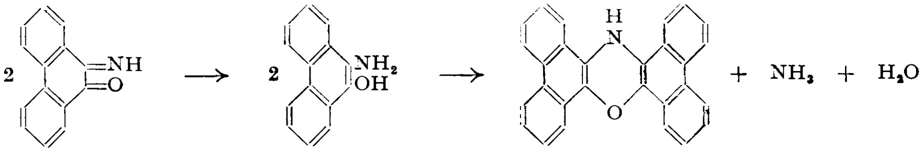
(X.)





(XI.)

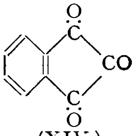
Photoreductions.—Very little is known about the photoreduction of *o*-diketones, *o*-quinone oximes or imines. When *o*-dibenzoylbenzene was exposed to sunlight in *iso*propyl alcohol, a yellow crystalline product was obtained which, when heated, gave 1 : 3-diphenyl*iso*benzofuran (XI) in good yield. Phenanthraquinone monoxime or imine (XII) in *iso*propyl alcohol in sunlight gave diphenanthro-oxazine (XIII) in good yield, probably by way of 10-aminophenanthr-9-ol.

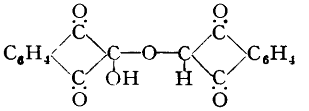


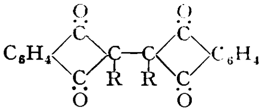
(XII.) (XIII.)

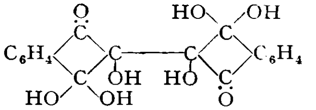
Previously it was shown (Schönberg and Moubasher, *J.*, 1944, 366) that when triketoindane (XIV) in *iso*propyl alcohol was exposed to sunlight and the reaction product crystallised from a mixture containing water, a compound known as hydrindantin was formed, which previously had been obtained by Ruhemann (*J.*, 1911, **99**, 797) by reduction of ninhydrin (the hydrate of

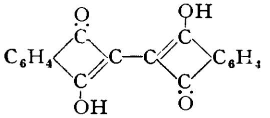
XIV) in the absence of light. Ruhemann believed that hydrindantin was (XV + $2H_2O$), but recently Schönberg and Moubasher (*J.*, 1949, 212) showed that the reactions of this compound do not accord with (XV + $2H_2O$), but do accord with (XVIII). However, there was one obstacle to the new formula: Gabriel and Leupold (*loc. cit.*) described a deep-yellow compound obtained


(XIV.)


(XV.)

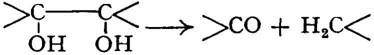

(XVI; R = H.)
(XVII; R = OH.)


(XVIII.)

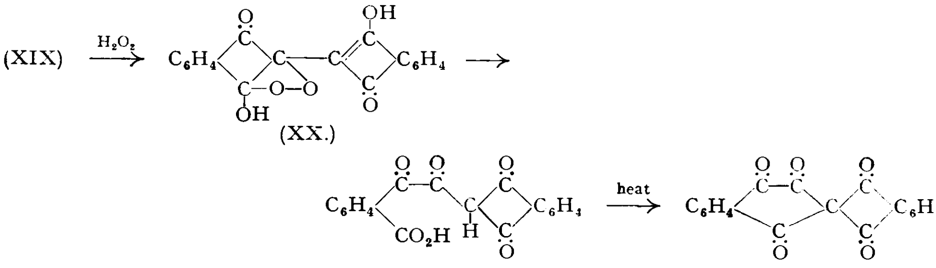

(XIX.)

by the action of alkaline hydrogen peroxide on the violet bisindane-1 : 3-dionyl. This yellow compound for which Gabriel and Leupold advanced formula (XVII) cannot be transformed into hydrindantin by the action of water. For the violet compound Gabriel and Leupold erroneously advanced formula (XVI); it has in reality formula (XIX) (cf. Schönberg and Moubasher, *J.*, 1944, 366).

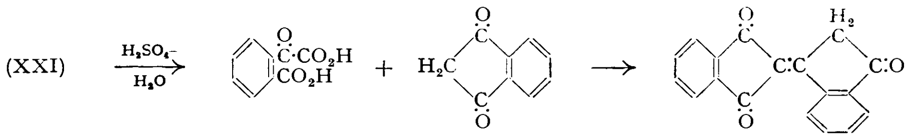
Gabriel and Leupold's oxidation scheme (XVI) ⟶ (XVII) has to be replaced by (XIX) ⟶ (XX) ⟶ (XXI). Formula (XXI) but not (XVII) is in agreement with the deep-yellow colour of the compound and its solubility in sodium hydrogen carbonate solution with evolution of carbon dioxide and its vigorous reaction with diazomethane. *o*-(1 : 3-Diketoindanyl-2-glyoxyloyl)benzoic acid (XXI) on pyrolysis yields indane-1 : 3-dione-2-*spiro*-2′-(1′ : 3′ : 4′-triketo-1′ : 2′ : 3′ : 4′-tetrahydronaphthalene) (XXII) (cf. Radulescu, *Zentr.*, 1923, III, 1081).

If formula (XVI) were correct, then, on heating, (XVII) should decompose according to the scheme:  $>\underset{OH}{C}-\underset{OH}{C}< \longrightarrow >CO + H_2C<$ (cf. Schönberg and Mustafa, *J.*, 1944, 305).

Formula (XXI) explains readily the nature of the product actually obtained by pyrolysis, namely (XXII). The hypothetical change (XVII) ⟶ (XXII) can take place only in consequence of a pinacolin rearrangement; however, such rearrangement is not effected by pyrolysis alone, but by heating the pinacols with acids, etc.


(XX.)
(XXI.)
(XXII.)

Acid hydrolysis of (XXI) yields phthalonic acid (XXIII) and 2-(3-ketoindan-1-ylidene)-indane-1 : 3-dione (XXV), which is believed to be formed from the primary product (indane-1 : 3-dione) (XXIV) by autocondensation (cf. Wislicenus and Kötzle, *Annalen*, 1889, **252**, 79).


(XXIII.)
(XXIV.)
(XXV.)

EXPERIMENTAL.

The photochemical reactions were carried out in Pyrex glass tubes, the air having been displaced by dry carbon dioxide and the tube sealed. " AnalaR " benzene which had been dried over sodium was used.

Photopolymerisations.—Coumarin (cf. Ciamician and Silber, *Ber.*, 1914, **47**, 642). Powdered coumarin (3 g.), suspended in water (100 c.c.) in a stoppered 1-l. flask, was exposed to sunlight during October. The solid was filtered off, dried, and extracted several times with ether in which the photodimer was slightly soluble. The dimer recrystallised from glacial acetic acid in almost colourless crystals, m. p. *ca.* 260° (decomp.) (*ca.* 10% yield).

The photodimer was heated under water-pump vacuum at 290° (bath) in a Pyrex test-tube for 1 hour. Oily drops of coumarin (m. p. and mixed m. p.) which accumulated on the upper parts of the reaction vessel solidified after being allowed to cool in a vacuum.

3-*Phenylcoumarin.* 3-Phenylcoumarin (1 g.) (Meerwein *et al.*, *J. pr. Chem.*, 1939, **152**, 253) in benzene (25 c.c.) was exposed to sunlight during October. Crystals separated gradually, were filtered off, and were washed with ether. A further quantity of the crude photodimer was obtained on concentration of the benzene filtrate, addition of a few drops of ether, and cooling. The crude product was dissolved in the least amount of hot benzene, filtered hot, and left to cool slowly; to the still warm solution, a few drops of ether were added. The *photodimer* (I*b*) slowly separated in colourless crystals, m. p. *ca.* 242° (*ca.* 90%) (Found : C, 81·1; H, 4·7. $C_{30}H_{20}O_4$ requires C, 81·1; H, 4·5%).

Thermal decomposition was carried out as above by heating the material for 1 hour in a boiling ethyl phthalate bath. The oily droplets of 3-phenylcoumarin (m. p. and mixed m. p.) which accumulated at the upper parts of the reaction vessel solidified on cooling in a vacuum and were recrystallised from ethyl alcohol.

3-*Phenyl*iso*coumarin.* 3-Phenyl*iso*coumarin (1 g.) (Gabriel, *Ber.*, 1885, **18**, 2445) in benzene (30 c.c.) was exposed to sunlight for 25 days (November) and the crystals which separated were filtered off and washed several times with ether. A further quantity of the crude product was obtained on concentrating the benzene filtrate and allowing it to cool slowly to room temperature. The *photodimer* (IV) recrystallised from benzene in colourless crystals, m. p. 254° (yield almost quantitative) (Found : C, 80·7; H, 4·7. $C_{30}H_{20}O_4$ requires C, 81·1; H, 4·5%).

The photodimer was heated as described previously at 300° for 30 minutes and then left to cool in a vacuum, and the crystals of 3-phenyl*iso*coumarin (m. p. and mixed m. p.), which formed on the upper parts of the vessel, recrystallised from dilute alcohol.

Benzylidenephthalide. Benzylidenephthalide (*ca.* 1·5 g.) (Gabriel, *Org. Synth.*, Vol. XIII, 10) in benzene (25 c.c.) were exposed to sunlight for 10 days (January). The small amount of colourless crystals which separated was filtered off. The benzene filtrate was concentrated, left to cool slowly, and, while still warm treated with a few drops of ether. On cooling in ice, a colourless crystalline solid separated out, having m. p. *ca.* 206°. For purification, the *dimer* was treated again similarly with benzene–ether and then had m. p. 202—215° [Found : C, 81·6; H, 4·3%; *M* (Rast), 507. $C_{30}H_{20}O_4$ requires C, 81·1; H, 4·5%; *M*, 445].

The photodimer was heated at 260° for 40 minutes under reduced pressure. Oily drops of benzylidenephthalide (m. p. and mixed m. p.) which accumulated on the upper parts of the reaction vessel solidified on cooling slowly under reduced pressure. They were recrystallised from benzene.

Photoreactions.—2 : 7-*Dimethylphenanthraquinone and stilbene.* 2 : 7-Dimethylphenanthraquinone (0·5 g.) (Lieberman, *Ber.*, 1911, **44**, 1453) and stilbene (0·4 g.) in benzene (20 c.c.) were exposed to sunlight for one week in May. The benzene solution was then filtered and concentrated almost to dryness, and a small amount of hot acetone was added, followed by a few drops of methyl alcohol. A yellow solid separated on cooling (in the ice-chest) and was recrystallised from xylene. The addition *product* (V) formed almost colourless crystals which decomposed at about 258° to an orange-brown melt. It gave no colour with cold concentrated sulphuric acid, but on gentle warming a violet colour was observed (Found : C, 86·0; H, 5·3. $C_{30}H_{24}O_2$ requires C, 86·5; H, 5·7%).

Phenanthraquinone and 1 : 2-*di*-4′-*pyridylethylene.* Phenanthraquinone (1 g., 1 mol.), and 1 : 3-di-4′-pyridylethylene (1 mol.) in benzene (30 c.c.) were exposed to sunlight in November. After 7 days, the crystals which separated were filtered off and washed with hot acetone, in which the initial components were soluble. The colouless residue of the *adduct* (VI) obtained was washed with 5% sodium hydroxide solution, then with alcohol, and lastly with ether, and decomposed at *ca.* 187° to an orange melt (Found : C, 79·4; H, 4·6; N, 7·7. $C_{26}H_{18}O_2N_2$ requires C, 80·0; H, 4·6; N, 7·2%).

Phenanthraquinone and 3 : 4-*diphenyl*iso*coumarin.* Phenanthraquinone (0·7 g.) and 3 : 4-diphenyl*iso*coumarin (1 g.) (Koelsch and Le Claire, *J. Amer. Chem. Soc.*, 1943, **65**, 754) were exposed to sunlight in benzene (50 c.c.) for 20 days (December). The benzene solution was filtered, concentrated, and left to cool slowly, almost colourless crystals of the addition *product* (VIII) separating. These recrystallised from benzene in colourless crystals which decomposed at *ca.* 267° to a reddish brown melt. They gave no colour reaction with concentrated sulphuric acid, and were insoluble in cold or warm sodium hydroxide solution (*ca.* 5%) (Found : C, 83·1; H, 4·7. $C_{35}H_{22}O_4$ requires C, 83·0; H, 4·3%).

(VIII) was heated under reduced pressure (water-pump vacuum) at 300° (bath temperature) for 15 minutes in a test tube and then allowed to cool in a vacuum. The crystals formed on the upper parts of the reaction vessel were extracted with cold benzene, the benzene extract was evaporated to dryness, and the residue dissolved in the least amount of hot methyl alcohol and allowed to cool slowly. The crystals which separated proved to be 3 : 4-diphenyl*iso*coumarin. The orange crystals left undissolved after benzene extraction were recrystallised from boiling benzene and proved to be phenanthraquinone (m. p. and mixed m. p.).

Phenanthraquinone and 3-*phenyl*iso*coumarin.* Phenanthraquinone (1 g.) and 3-phenyl*iso*coumarin (1·1 g.) in benzene (30 c.c.) were exposed to sunlight for 2 days (May). A heavy crystalline deposit of *adduct* (VII) began to separate after a few hours. This was filtered off and recrystallised from xylene in almost colourless crystals decomposing to a reddish-brown melt at about 270° and giving no colour reaction in sulphuric acid (Found : C, 80·8; H, 4·3. $C_{29}H_{18}O_4$ requires C, 80·9; H, 4·2%).

(VII) was heated as was (VIII). The crystals formed on the upper parts of the reaction vessel were extracted several times with cold methyl alcohol; uniform orange crystals melting at 195° were left and gave, with concentrated sulphuric acid, the olive-green colour reaction of phenanthraquinone. On concentration of the methyl-alcoholic extract, crystals which separated out proved to be 3-phenyl*iso*coumarin (m. p. and mixed m.p.).

Phenanthraquinone and 1 : 3-*diphenyl*isochromen. Phenanthraquinone (0·25 g.) and 1 : 3-diphenyl*iso*chromen (0·3 g.) (Schmidlin and Bannus, *Ber.*, 1912, **45**, 3202) partly suspended in benzene (30 c.c.) were exposed to sunlight for one week (May). The benzene solution was filtered, concentrated to small volume, and treated with light petroleum (b. p. 60—80°), which caused precipitation. The supernatant fluid was decanted, and the residual *adduct* (IX) washed with cold alcohol and recrystallised from benzene–acetone. It recrystallised from xylene in colourless crystals, decomp. *ca.* 300° to a reddish-brown melt (Found : C, 85·4; H, 5·3. $C_{35}H_{24}O_3$ requires, C, 85·3; H, 4·9%).

Photoreductions.—o-*Dibenzoylbenzene.* *o*-Dibenzoylbenzene (1·3 g.) (Simonis and Remmert, *Ber.*, 1915, **48**, 206) in *iso*propyl alcohol (30 c.c.) was exposed to sunlight for 30 days (April). The yellow crystals formed were filtered off from the fluorescent benzene solution and recrystallised from chloroform in yellow needles m. p. *ca.* 160°. They gave no colour reaction with concentrated sulphuric acid (*o*-dibenzoylbenzene gives a red colour), but in chloroform solution a green fluorescence was noted. The photo-product was heated under reduced pressure (oil-pump vacuum) in a Pyrex test-tube at 200° (bath temperature) for 1 hour and then allowed to cool slowly in a vacuum. After 24 hours a crystalline mass appeared near the bottom of the reaction vessel (most of the material used) and some yellow crystals on the upper part, which was not in contact with the bath. The lower crystalline mass recrystallised from alcohol in yellow crystals which proved to be 1 : 3-diphenyl*iso*benzofuran (XI) (m. p. and mixed m. p.) (80% yield). Both the decomposition product and an authentic specimen gave a red colour with concentrated sulphuric acid, fugitive at room temperature. The decomposition product gave the brilliant green fluorescence described by Guyot and Catel (*Compt. rend.*, 1905, **140**, 1349).

*Phenanthraquinone monoxime.** The oxime (0·5 g.) in *iso*propyl alcohol (25 c.c.) was exposed to sunlight for a fortnight (June). The brown deposit was filtered off and crystallised from 2-methylnaphthalene in very small brown crystals showing a green lustre; on pulverisation a brown powder was produced. It gave the characteristic blue colour of diphenanthro-oxazine with concentrated sulphuric acid and had m. p. above 305° (Found : N, 4·0. Calc. for $C_{28}H_{17}ON$: N, 3·7%) (yield, almost quantitative).

Phenanthraquinone imine. The experiment was carried out as previously described and the product (almost quantitative yield) crystallised from 2-methylnaphthalene in very small brown crystals showing a green lustre, giving a brown powder on pulverisation and the characteristic blue colour with concentrated sulphuric acid, and having m. p. above 305° (Found : N, 4·2. Calc. for $C_{28}H_{17}ON$: N, 3·7%).

Photochemical Reaction between Aldehydes and Phenthraquinone Monoxime.—*With benzaldehyde.* Phenanthraquinone monoxime (0·5 g.) and benzaldehyde (1 g.) in benzene (25 c.c.) were exposed to sunlight for 15 days (May) (in a Monax glass vessel); a colourless deposit was formed which was filtered off. The solution was concentrated under reduced pressure and the product recrystallised from benzene in almost colourless crystals, m. p. 256° (decomp.) depending on the rate of heating.

In a parallel experiment in the absence of light phenanthraquinone monoxime was recovered unchanged almost quantitatively.

When the photo-product was heated in a boiling ethyl cinnamate bath (b. p. 271°) in a carbon dioxide atmosphere for ½ hour, a colourless crystalline sublimate was obtained which proved to be 2-phenylphenanthro-oxazole, m. p. 204° undepressed on admixture with an authentic specimen prepared according to Stein and Day (*J. Amer. Chem. Soc.*, 1942, **64**, 2567).

With anisaldehyde. The oxime (0·5 g.) and aldehyde (1 g.) in benzene (25 c.c.) were exposed to sunlight (Monax glass vessel) for one week (April). The colourless deposit, recrystallised from absolute ethyl alcohol, had m. p. 244°, gave a yellowish-brown colour with concentrated sulphuric acid, and, when heated in an ethyl cinnamate bath, as described in the case of benzaldehyde, gave an almost colourless crystalline sublimate of 2-p-*methoxyphenylphenanthro-oxazole* (X; $R = C_6H_4{\cdot}OMe\text{-}p$), m. p. 178° (Found : C, 80·9; H, 4·7; N, 4·4. $C_{22}H_{15}O_2N$ requires C, 81·2; H, 4·6; N, 4·3%).

This oxazole was also prepared as follows : Equimolecular amounts of phenanthraquinone imine and anisaldehyde (freshly distilled), dissolved in absolute alcohol containing few drops of piperidine, were refluxed for 1 hour. On cooling (and if necessary concentration of the solution) a deposit was formed which, crystallised from alcohol, had m. p. 178°, not depressed on admixture with the substance obtained as above.

o-(1 : 3-*Diketoindanyl-2-glyoxyloyl*)*benzoic Acid* (XXI).†—(XXI) was prepared from bisindane-1 : 3-dionyl (XIX) according to the directions given by Gabriel and Leupold (*loc. cit.*) for the preparation of the supposed (XVII).

Pyrolysis was carried out in a boiling-tube, connected with a vacuum pump, the lower part being immersed in a bath at 250°; the heating was for 30 minutes. Crystals of (XXII) were formed on the cold parts of the reaction vessel; they recrystallised from acetic acid in orange needles, m. p. 222—225°, undepressed on admixture with an authentic sample (cf. *loc. cit.* and Radulescu, *loc. cit.*) (Found : C, 70·8; H, 2·7. Calc. for $C_{18}H_8O_5$: C, 71·0; H, 2·6%) (yield about 40%).

A suspension of (XXI) (0·5 g.) in dilute sulphuric acid (20 c.c. of concentrated acid in 100 c.c. of water) was heated on a water-bath for 3 hours. The reaction mixture was concentrated to about 50 c.c., whereupon a yellow substance (A) separated from the solution (B). (A) recrystallised from ethyl alcohol as pale yellow needles, m. p. 208° (brown melt), and was proved to be the 2-(3-ketoindan-1-ylidene)-

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* The experiments with phenanthraquinone monoxime and imine were carried out by William Ibrahim Awad.

† These experiments were carried out by Radwan Moubasher.

indane-1 : 3-dione (XXV) by m. p. and mixed m. p. determinations with an authentic specimen prepared according to Wislicenus and Kötzle (*loc. cit.*). It dissolved in concentrated sulphuric acid, giving an orange colour. (B) was heated for 30 minutes on the water-bath, allowed to cool and filtered; and the filtrate was extracted several times with ether, from which colourless crystals were then obtained; recrystallised from ether in colourless needles, m. p. 145° (decomp.), they proved to be phthalonic acid (XXIII) (m. p. and mixed m. p.).

Di-(2-hydroxy-1 : 3-diketoindan-2-yl) (XVII).—Hydrindantin (XVIII) (1 g.) was refluxed with oxalyl chloride (10 g.) for 10 minutes, with a calcium chloride safety tube. The reaction product was evaporated to dryness in a vacuum, moisture being excluded, and the residue crystallised from benzene (anhydrous); colourless crystals were obtained, having m. p. *ca.* 235° (decomp.). The *product* (XVII) gave an orange-yellow colour with concentrated sulphuric acid (Found: C, 66·9; H, 3·3. $C_{18}H_{10}O_6$ requires C, 67·1; H, 3·1%).

The product, suspended in ether, was shaken at room temperature with water for about 30 minutes; the solid was then collected and proved to be (XVIII). (XVII) and (XVIII) are decomposed by alkali with the formation of a blue solution, containing probably the salt of the enolic form of 2-hydroxyindane-1 : 3-dione and the hydrate of (XIV) (ninhydrin).

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