230. *Reactions in Sunlight of Certain Diketones with Ethylenes and Aromatic Aldehydes. Photopolymerisation of 9-Anthraldehyde.*

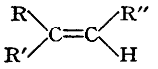
By Ahmed Mustafa.

Phenanthraquinone reacts in sunlight with the unsaturated compounds (I*b*—III*c*, IV—V*b*) to give the photo-products (VII—IX*c*, X—XI*b*), respectively; similarly, retenequinone with (III*d*) and (VI) forms (XII) and (XIII), respectively, and the photo-product from *pp*′-dianisil and (I*a*) has the structure (XIV) (see Table I).

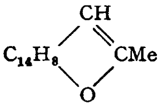
The photo-reaction between phenanthraquinone and 2-formylquinoline or 9-anthraldehyde to give (XV*a*) and (XV*b*), and that between retenequinone or chrysoquinone and 9-anthraldehyde, giving (XVI) and (XVII), respectively, are described (see Table II).

(*c*) A solution of 9-anthraldehyde in benzene, on exposure to sunlight, gives the dimer $(C_{15}H_{10}O)_2$.

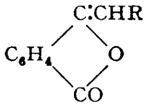
The work on the action of certain unsaturated compounds on phenanthraquinone to form derivatives of phenanthro-1 : 4-dioxen (Schönberg and Mustafa, *Chem. Reviews*, 1947, **40**, 181; Mustafa and Islam, *J.*, 1949, S 81; Mustafa, *ibid.*, p. S 83) has now been extended (see Table I, reaction A).



(I*a*; R = R″ = Ph, R′ = H.)
(I*b*; R = R′ = CH_2Ph, R″ = Ph.)

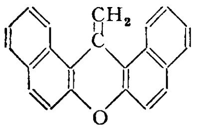


(II.) *

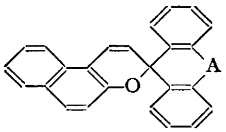


(III*a*; R = Me.)
(III*b*; R = Et.)
(III*c*; R = C_5H_{11}.)
(III*d*; R = Ph.)

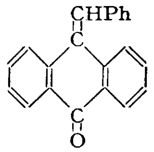
* Here and elsewhere, $C_{14}H_8$ = 9 : 10-phenanthrylene.



(IV.)

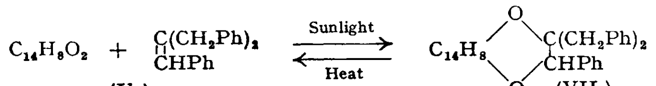


(V*a*; A = O.) (V*b*; A = S.)



(VI.)

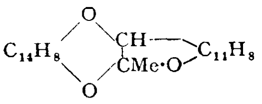
Phenanthraquinone has been allowed to react with the unsaturated compounds (I*b*), (II), (III*a*, *b*, and *c*), (IV), and (V*a* and *b*); also retenequinone with (III*d*) and (VI); and *pp*′-dianisil with (I*a*). We believe that the products are in all cases cyclic diethers formed by addition across the double bond (for the products in each particular case see Tables I and III, and the formulæ and Reaction A). These constitutions are based on the facts that the products are colourless or almost colourless, in contrast to the deep colour of the original quinones, and that heating decomposes the products into their generators, except that (III*b*) and (III*c*) were not obtained from (IX*b*) and (IX*c*), probably because of their thermolability.



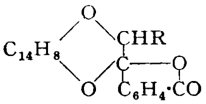
(I*b*.) (VII.) (Reaction A)

The velocities of the reactions between olefins and *o*-quinones differ. In general, the velocity with which benzil and *pp'*-dianisil react is much less than that of phenanthraquinone, retenequinone, and chrysoquinone. Triketoindane (Schönberg, Mustafa, *et al.*, *J.*, 1948, 2126) reacts moderately rapidly.

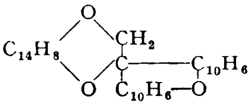
Recently, Mustafa (*loc. cit.*) described a number of photo-reactions between retenequinone and aromatic aldehydes. A similar reaction (Mustafa, *Nature*, 1950, **166**, 108) has been carried out with 2-formylquinoline or 9-anthraldehyde and phenanthraquinone (see Reaction B), and with 9-anthraldehyde and retenequinone or chrysoquinone. The addition products (Table II) were the hydroxymethylene ethers (orthocarboxylates) (XV*a* and *b*), (XVI), and (XVII).



(VIII.)

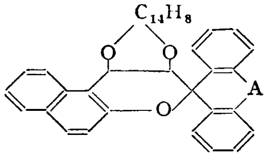


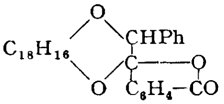
(IX*a*; R = Me.) (IX*b*; R = Et.)
(IX*c*; R = C_5H_{11}.)



(X.)

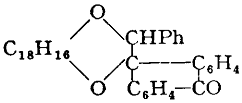
(XI*a*; A = O.)
(XI*b*; A = S.)

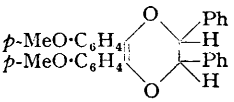




(XII.) *

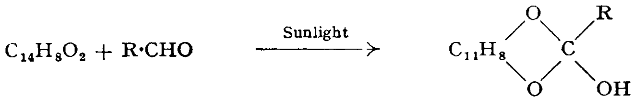
(XIII.) *





(XIV.)

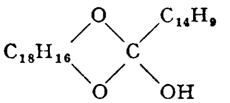
* In these formulæ, $C_{18}H_{16}$ = 1-methyl-7-*iso*propylphenanthrene residue.

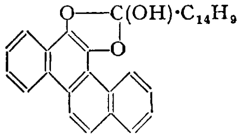


(Reaction B)

(XV*a*; R = 2-quinolyl.) (XV*b*; R = 9-anthryl.)

(XVI.)





(XVII.)

When a benzene solution of 9-anthraldehyde was exposed to sunlight (cf. Mustafa, *loc. cit.*, and the photopolymerisation of benzaldehyde in sunlight, Ciamician and Silber, *Ber.*, 1903, **36**, 1575), an almost colourless photo-dimer $(C_{15}H_{10}O)_2$ was formed. Its constitution is based on (i) its lack of colour, (ii) its regeneration of 9-anthraldehyde when heated at 270°, and (iii) its molecular weight.

EXPERIMENTAL.

All reactions were in solution unless otherwise stated. The benzene (30 c.c. for each experiment) was free from toluene (cf. Mustafa, *loc. cit.*) and thiophen and had been dried over sodium. The reaction mixtures were placed in a 25-cm. Schlenk tube (Schlenk and Thal, *Ber.*, 1913, **46**, 2655; Houben, " Die Methoden der Organischen Chemie," 2nd edn., Vol. IV, 960) of Pyrex glass, the air was displaced by dry carbon dioxide, and the tube sealed. Control experiments in the dark, but otherwise under identical conditions, showed no reaction (cf. Schönberg and Latif, *J. Amer. Chem. Soc.*, 1950, **72**, 4828).

Thermal Decomposition of the Addition Products (VII—XIV).—The addition products, when heated at 270° (bath-temp.) [except (XI*a*) which was at 300° (bath-temp.)] in a stream of dry carbon dioxide for ½ hour, decomposed into their generators which were separated as follows: (*a*) In the case of (VII), (VIII), (IX*a*), (X), and (XII—XIV), the contents of the tube were treated with hot ligroin (b. p. 70—80°); the part which went into solution proved to be the corresponding ethylene, and the insoluble part, after crystallisation from boiling ethyl alcohol, proved to be the corresponding 1 : 2-diketone. (*b*) With

(XI*a*) and (XI*b*), the contents of the tube were treated with hot ethyl alcohol; the soluble part was phenanthraquinone and the insoluble part, after crystallisation from benzene, proved to be the ethylene derivative.

The thermal decomposition products were identified in all the cases by m. p. and mixed m. p. determinations and colour reaction with sulphuric acid.

Photopolymerisation of 9-Anthraldehyde.—A solution of 9-anthraldehyde (Fieser and Hartwell, *loc. cit.*) (1 g.) in benzene (25 c.c.) was exposed to sunlight for 4 days (June). The crystals that separated were filtered off, washed with light petroleum (b. p. 30—50°), and crystallised from benzene, forming almost colourless crystals, m. p. 250° (decomp.; yellow melt) [Found: C, 87·6; H, 4·8%; *M* (micro-Rast), 402. $C_{30}H_{20}O_2$ requires C, 87·4; H, 4·8%; *M*, 412]. The photo-*dimer* gave a deep red colour

TABLE I.

(Reaction A).

(For names of products, see Table III.)

Diketone, and wt. (g.).	Ethylenic compd., and wt. (g.).	Time of irradiation, days.	Number, m. p., and colour with H_2SO_4 of addition product.	Recrystn. solvent.	Formula of product.	Analysis of product.			
						Found, %.		Reqd., %.	
						C.	H.	C.	H.
Phenanthraquinone (1·0)	2-Benzyl-1 : 3-diphenylpropene (I*b*) [a] (1·4)	40 (Jan.–Feb.)	VII, 220°, olive-green	(See footnotes 1, 2)	$C_{36}H_{28}O_2$	87·4	5·6	87·4	5·7
Phenanthraquinone (1·3)	5-Methylphenanthro-(9′ : 10′-1 : 2)-furan (II) [b] (1·4)	60 (Mar.–April)	VIII, >260°, olive-green	Xylene *	$C_{31}H_{20}O_3$	84·3	4·2	84·5	4·5 †
Phenanthraquinone (1·0)	Ethylidenephthalide (III*a*) (0·8)	4 (Mar.)	IX*a*, 240°, olive-green at 100°	Xylene [2]	$C_{24}H_{16}O_4$	78·2	4·2	78·3	4·3
Phenanthraquinone (1·0)	*n*-Propylidenephthalide (III*b*) (0·8)	7 (Mar.)	IX*b*, 210°, olive-green at 100°	Benzene [2]	$C_{25}H_{18}O_4$	78·6	4·5	78·5	4·7
Phenanthraquinone (1·0)	*n*-Hexylidenephthalide (III*c*) (1·0)	4 (Mar.)	IX*c*, 240°, olive-green at 100°	Benzene–petrol (b. p. 30—50°) [2]	$C_{28}H_{24}O_4$	78·9	5·6	79·3	5·6
Phenanthraquinone (1·0)	9-Methylene-1 : 2-7 : 8-dibenzoxanthen (IV) [c] (1·4)	7 (June)	X, 226°, deep violet	Xylene	$C_{36}H_{22}O_3$	85·8	4·2	86·1	4·4
Phenanthraquinone (1·0)	β-Naphthoxantho*spiro*pyran (V*a*) [d] (1·7)	25 (July)	XI*a*, >250°, brown changing to violet	Benzene	$C_{39}H_{24}O_4$	83·9	4·3	84·1	4·3 ‡
Phenanthraquinone (1·0)	β-Naphthothiaxantho*spiro*pyran (V*b*) [e] (1·8)	7 (Mar.)	XI*b*, 254° olive-green at 100°	Xylene [2]	$C_{39}H_{24}O_3S$	81·6	4·2	81·8	4·2 §
Retenequinone (1·0)	Benzylidenephthalide (III*d*) [f] (0·8)	20 (May)	XII, 212°, olive-green at 100°	Benzene [2]	$C_{33}H_{26}O_4$	81·1	4·9	81·5	5·3
Retenequinone (1·0)	9-Benzylideneanthrone (VI) [g] (1·1)	50 (May–June)	XIII, 230°, red-violet	Benzene [2]	$C_{39}H_{30}O_3$	85·5	5·3	85·7	5·5
pp′-Dianisil (1·0)	Stilbene (I*a*) (0·7)	*ca.* 90 (May–July)	(XIV) 258°, orange-yellow	Xylene	$C_{30}H_{26}O_4$	79·8	5·6	80·0	5·8

References: [a] Orechov and Grinberg, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1713; [b] Japp and Klingemann, *Ber.*, 1888, **21**, 2932; [c] Wizinger and Al-Atter, *Helv. Chim. Acta*, 1947, **30**, 189; [d] Irving, *J.*, 1929, 1093; [e] Mustafa, *J.*, 1949, 2295; [f] Gabriel, *Org. Synth.*, Vol. XIII, 10; [g] Cook, *J.*, 1926, 2160.

[1] The benzene solution was evaporated, and the residual oil solidified when washed with cold light petroleum (b. p. 40—60°) and with absolute ethyl alcohol and crystallised from benzene–light petroleum (b.p. 30—50°). [2] Yield almost quantitative.

* After being washed with hot ethanol. † *M* (micro-Rast), 428 (required, 440). ‡ *M* (micro-Rast), 540 (required, 556). § S, 5·1 (required, S, 5·6%).

TABLE II.

(Reaction B).

(For names of products, see Table III.)

Quinone, and wt. (g.).	Aldehyde, and wt. (g.).	Time of irradiation, days.	Number, m. p., and colour with H_2SO_4 of addition product.	Recrystn. solvent.	Formula of product.	Analysis of product.			
						Found, %.		Reqd., %.	
						C.	H.	C.	H.
Phenanthraquinone (1·0)	2-Formylquinoline [a] (0·7)	3 (Dec.)	(XV*a*), 224°, olive-green	Xylene [1] *	$C_{24}H_{15}O_3N$	78·7	3·9	78·9	4·1 ‡
Phenanthraquinone (1·0)	9-Anthraldehyde [b] (1·0)	20 (Mar.)	(XV*b*), 228°, olive-green	Xylene [1]	$C_{29}H_{18}O_3$	84·1	4·3	84·1	4·3 §
Retenequinone (1·0)	9-Anthraldehyde [b] (0·8)	20 (Mar.)	(XVI), 187°, brownish-green	Benzene *	$C_{33}H_{26}O_3$	84·1	5·3	84·3	5·5
Chrysoquinone (1·0)	9-Anthraldehyde [b] (0·8)	20 (Mar.)	(XVII), 190°, violet-blue	Xylene [1] †	$C_{33}H_{20}O_3$	85·0	4·2	85·3	4·3

References : [a] Kaplan, *J. Amer. Chem. Soc.*, 1941, **63**, 2655; [b] Fieser and Hartwell, *Org. Synth.*, Vol. 20, p. 11.

[1] Yield almost quantitative.

* After being washed with hot ethanol. † After being washed with boiling acetone. ‡ Found: N, 3·5. Reqd. : N, 3·8%. § *M* (micro-Rast), 401 (required, 414).

TABLE III.

Formal names of products given in Tables I *and* II.

Number.	Name.
VII	5 : 5-Dibenzyl-6-phenylphenanthro(9′ : 10′-2 : 3)dioxen.
VIII	4 : 5-Dihydro-5-methyl-4 : 5-phenanthrylenedioxyphenanthro(9′ : 10′-2 : 3)furan.
IX*a*	6-Methylphenanthro(9′ : 10′-2 : 3)dioxen-5-*spiro*-3″-phthalide.
IX*b*	6-Ethylphenanthro(9′ : 10′-2 : 3)dioxen-5-*spiro*-3″-phthalide.
IX*c*	6-*n*-Pentylphenanthro(9′ : 10′-2 : 3)dioxen-5-*spiro*-3″-phthalide.
X	Phenanthro(9′ : 10′-2 : 3)dioxen-5-*spiro*-9″-(1″ : 2″-7″ : 8″-dibenzoxanthen).
XI*a*	4 : 5-Phenanthrylenedioxynaphtho(2′ : 1′-2 : 3)pyran-6-*spiro*-9″-xanthen.
XI*b*	4 : 5-Phenanthrylenedioxynaphtho(2′ : 1′-2 : 3)pyran-6-*spiro*-9″-thioxanthen.
XII	1′-Methyl-6-phenyl-7′-*iso*propylphenanthro(9′ : 10′-2 : 3)dioxen-5-*spiro*-3″-phthalide.
XIII	1′-Methyl-6-phenyl-7′-*iso*propylphenanthro(9′ : 10′-2 : 3)dioxen-5-*spiro*-9″-anthrone.
XIV	2 : 3-Di-*p*-methoxyphenyl-5 : 6-diphenyl-Δ^2-dioxen.
XV*a*	2-Hydroxy-2-2″-quinolylphenanthro(9′ : 10′-4 : 5)dioxole.
XV*b*	2-9″-Anthryl-2-hydroxyphenanthro(9′ : 10′-4 : 5)dioxole.
XVI	2-9″-Anthryl-2-hydroxy-1′-methyl-7′-*iso*propylphenanthro(9′ : 10′-4 : 5)dioxole.
XVII	2-9″-Anthryl-2-hydroxychryseno(1′ : 2′-4 : 5)dioxole.

with sulphuric acid, and was soluble in hot benzene or xylene and difficultly soluble in ethyl alcohol. When heated at 270° (bath-temp.), it afforded 9-anthraldehyde (m. p. and mixed m. p. and colour reaction with sulphuric acid).

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