262. *Reaction with Diazomethane and its Derivatives. Part III.* Action of Diazo-compounds on 2-Arylideneindane-1 : 3-diones and Methyleneanthrone.*

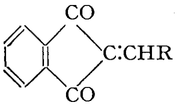
By Ahmed Mustafa and Mustafa Kamal Hilmy.

2-Arylideneindane-1 : 3-diones (listed in the Table) react with ethereal diazomethane, in the presence or absence of methyl alcohol, to yield colourless or almost colourless substances, believed to be furanoindenones (II).

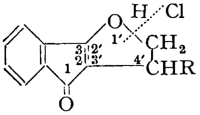
Methyleneanthrone (IV) reacts readily with diazomethane and its derivatives to form colourless crystals, believed to be *cyclo*propane derivatives (VI).

A NUMBER of the intensely coloured 2-arylideneindane-1 : 3-diones (I) (cf. the Table) react with ethereal diazomethane solution, in the presence or absence of methyl alcohol, giving the furanoindenones (II), which, except for the pale yellow nitro-compounds (II; R = $C_6H_4{\cdot}NO_2$-*m* and -*p*) are colourless or substantially colourless. The reaction mechanism is believed to be similar to that proposed for *o*-hydroxyanils (Schönberg, Mustafa, and Hilmy, *J.*, 1947, 1045; Schönberg and Awad, *J.*, 1950, 72). It is improbable that the products are *cyclo*propane derivatives (III), since (II; R = $C_6H_4{\cdot}OMe$-*p*) gives only a monoxime, does not give phthalic acid on treatment with alkali, and is thermostable at 160° for half an hour. There is of course a greater tendency to form a five-membered than a three-membered ring (strain theory).

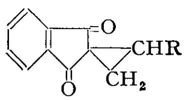
With alcoholic hydrochloric acid (II; R = $C_6H_4{\cdot}OMe$-*p*) gives a colourless product whence it is regenerated by pyridine; this product gives a ferric chloride colour and has one active hydrogen atom; it may be the furanoindanone 1′-oxonium salt or may be formed by addition of HCl across by 2 : 3-bond or by fission as indicated by the dotted line in (II). Hydrobromic acid in cold acetic acid leads to a similar product. Enols can be formed in each case.



(I)

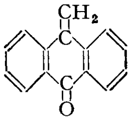


(II)

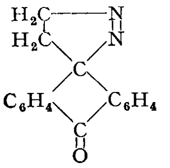


(III)

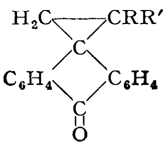
Methyleneanthrone (IV) reacts readily with ethereal diazomethane in the presence of methyl alcohol, with strong evolution of gas, to give colourless product (VI; R = R′ = H), probably by way of (V). For a similar formation of a *cyclo*propane ring, compare the action of diazomethane on 9-methylenefluorene (Wieland and Probst, *Annalen*, 1937, **530**, 277). The product (VI; R = R′ = H) is crystalline, whereas 9-ethylideneanthrone is an unstable red oil, b. p. 245—247°/20 mm. (Julian, Cole, and Wood, *J. Amer. Chem. Soc.*, 1935, **57**, 2508); it reacts with one mol. of phenylmagnesium bromide to give the carbinol and on oxidation with chromic acid gives anthraquinone.



(IV)



(V)



(VI)

With diazoethane, (IV) similarly yields (VI; R = Me, R′ = H), and with diphenyldiazomethane (VI; R = R′ = Ph).

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* The paper by Mustafa (*J.*, 1949, 256) is regarded as Part I and that by Mustafa and Hilmy (*J.*, 1951, 3254) as Part II.

EXPERIMENTAL

Action of Diazomethane on 2-*Arylideneindane*-1 : 3-*diones* (I). The dione (1 g.) in methyl alcohol (2 c.c.) was treated with ethereal diazomethane (from methylnitrosourea, 8 g.), and the mixture was left for 48 hours at 0°. The methyl alcohol and ether were evaporated off, and the residue was worked-up as follows (D denotes the deposit formed during the reaction, and R the residue obtained on evaporation of the reaction mixture) :

(*a*) R was dissolved in light petroleum (b. p. 60—80°), and the solution was allowed to evaporate slowly; the crystals which separated were recrystallised from the same solvent.

(*b*) R was washed with cold ethyl alcohol and crystallised from light petroleum (b. p. 80—100°).

(*c*) D was recrystallised from benzene–light petroleum (b. p. 30—50°); it was difficultly soluble in ethyl alcohol.

(*d*) D was washed repeatedly with ethyl alcohol; it was difficultly soluble in hot alcohol and light petroleum (b. p. 60—80°) and crystallised from benzene–light petroleum (b. p. 30—50°).

(*e*) R was treated with cold absolute ethyl alcohol, and crystallised from the same solvent.

(*f*) R was extracted with hot ethyl alcohol and the extract allowed to evaporate slowly; the crystals which separated were recrystallised from light petroleum (b. p. 60—80°).

(*g*) R was extracted several times with hot light petroleum (b. p. 60—80°) and the extract was allowed to evaporate slowly; the crystals which separated were recrystallised from the same solvent.

(*h*) R was crystallised from light petroleum (b. p. 80—100°).

(*i*) R was extracted several times with hot light petroleum (b. p. 80—100°); the crystals which separated were recrystallised from the same solvent.

The *products* are recorded in the Table. All gave a violet colour in concentrated sulphuric acid; this changed to green in (*a*) and (*b*).

4′-*Substituted furano*(3′ : 2′-2 : 3)*indenones* (II).

			Yield,	Found, %				Required, %		
Ref.*	R	M. p.	%	C	H	N	Formula	C	H	N
a	Ph [1]	91—92°	40	82·1	4·8	—	$C_{17}H_{12}O_2$	82·2	4·8	—
b	*p*-MeO·C_6H_4 [2]	119	85	77·6	5·1	—	$C_{18}H_{14}O_3$ [4]	77·7	5·0	—
c	*m*-NO_2·C_6H_4 [2]	162—163	80	69·6	3·6	4·5	$C_{17}H_{11}O_4N$	69·6	3·7	4·8
d	*p*-NO_2·C_6H_4 [2]	168	82	69·6	3·8	4·4	$C_{17}H_{11}O_4N$ [5]	69·6	3·7	4·8
e	*p*-NMe_2·C_6H_4 [2]	102—103	50	78·2	5·9	4·8	$C_{19}H_{17}O_2N$	78·3	5·8	4·8
f	*p*-NEt_2·C_6H_4	75	30	78·7	6·7	4·5	$C_{21}H_{21}O_2N$	79·0	6·6	4·4
g	*p*-C_6H_4Cl [3]	92	40	72·0	3·9	—	$C_{17}H_{11}O_2Cl$ [6]	72·2	3·9	—
h	3 : 4-CH_2O_2:C_6H_3 [3]	110	70	74·0	4·0	—	$C_{18}H_{12}O_4$	74·0	4·1	—
i	2-Furyl [2]	126	50	75·3	4·3	—	$C_{15}H_{10}O_3$	75·6	4·2	—

* Cf. above.

[1] Wislicenus and Kotzle, *Annalen*, 1889, **252**, 73. [2] Petrow, Saper, and Sturgeon, *J.*, 1949, 2134. [3] Ionescu, *Bull. Soc. chim.*, 1930, **47**, 210. [4] Found : *M* (micro-Rast), 275. Reqd. : *M*, 278. [5] Found : *M* (micro-Rast), 290. Reqd. : *M*, 293. [6] Found : Cl, 12·5. Reqd. : Cl, 12·6%.

2-p-*Diethylaminobenzylideneindane*-1 : 3-*dione*.—Indane-1 : 3-dione (Teeters and Shriner, *J. Amer. Chem. Soc.*, 1933, **55**, 3026) (0·1 mole) and *p*-diethylaminobenzaldehyde (0·1 mole) were fused together at 130—140° (bath-temp.) for ½ hour. Water-vapour was vigorously evolved, the melt solidified on cooling, and the product was isolated by crystallisation from ethyl alcohol as violet red crystals (82%), m. p. 145° (Found : C, 78·5; H, 6·0; N, 4·4. $C_{20}H_{19}O_2N$ requires C, 78·7; H, 6·2; N, 4·6%).

Action of Hydroxylamine on (II; R = *p*-MeO·C_6H_4).—To a solution of the dione (0·4 g.) and hydroxylamine hydrochloride (0·55 g.) in ethyl alcohol (10 c.c.) was added a solution of potassium hydroxide (0·7 g.) in water (1 c.c.) (cf. Kohler, *J. Amer. Chem. Soc.*, 1919, **41**, 1254, 1261). The mixture was refluxed for 3 hours, poured into cold water, neutralised with dilute hydrochloric acid, and extracted with ether. The ethereal solution was washed with water, dried (Na_2SO_4), and evaporated, giving an oily residue. This was dissolved in hot ethyl alcohol, and on slow evaporation gave almost colourless crystals, m. p. 163—164°, from ethyl alcohol (Found : C, 73·4; H, 5·0; N, 4·4. $C_{18}H_{15}O_3N$ requires C, 73·7; H, 5·1; N, 4·8%).

Action of Hydrochloric Acid on (II; R = *p*-MeO·C_6H_4).—To a solution of 4′-*p*-methoxyphenylfurano(3′ : 2′-2 : 3)indenone in ethyl alcohol (10 c.c.), hydrochloric acid (5 c.c.; *d* 1·18) was added. The mixture was refluxed for 2 hours and then poured into ice-cold water. The oil, that separated, was washed several times with small amounts of cold ethyl alcohol, then becoming solid; it readily crystallised from benzene as colourless crystals, m. p. 110—111° (Found: C, 68·7; H, 4·7; Cl, 11·0; active H, 0·27. $C_{18}H_{15}O_3Cl$ requires C, 68·8; H, 4·8; Cl, 11·1; active H, 0·3%). The *substance* is easily soluble in light petroleum (b. p. 80—100°), hot ethyl alcohol, or hot benzene, and gave a violet colour in concentrated sulphuric acid. An alcoholic solution gave a reddish-violet colour when treated with alcoholic ferric chloride at 60°.

The product was boiled with pyridine for a few minutes and then poured into cold water and extracted with ether, and the extract washed with dilute cold hydrochloric acid, then with water, dried (Na_2SO_4), and evaporated. The resultant almost colourless crystals proved to be (II; R = *p*-MeO·C_6H_4) (m. p. and mixed m. p. and colour reaction with sulphuric acid).

Action of Hydrobromic Acid on (II; R = *p*-MeO·C_6H_4).—A saturated solution of dry hydrogen bromide in acetic acid (10 c.c.) was added to the dione (0·5 g.), and the reaction mixture was kept overnight at room temperature. It was then poured into ice-cold water, the brownish semi-solid *substance* that separated crystallised from benzene as pale yellow crystals, m. p. 177—178° [Found: C, 60·0; H, 4·0; Br, 22·1%; *M* (micro-Rast), 348. $C_{18}H_{15}O_3Br$ requires C, 60·1; H, 4·2; Br, 22·3%; *M*, 358·9]. This material is soluble in aqueous potassium hydroxide and gives a violet colour in concentrated sulphuric acid.

Reaction of Methyleneanthrone with Diazomethane.—Methyleneanthrone (1 g.) in methyl alcohol (2 c.c.) was treated with ethereal diazomethane solution as described for the 2-arylidene-1 : 3-indanediones. The crystals that separated recrystallised from benzene–light petroleum (b. p. 40—60°) in colourless crystals (VI), m. p. 152° (Found: C, 87·2; H, 5·4. $C_{16}H_{12}O$ requires C, 87·3; H, 5·5%) *Anthrone*-9-spirocyclo*propane* (VI; R = R′ = H) gives a yellow colour with a green fluorescene in concentrated sulphuric acid. Evaporation of the ethereal mother-liquor gave further quantity. The total yield is almost quantitative.

Action of phenylmagnesium bromide on (VI; R = R′ = H). To a Grignard solution of phenylmagnesium bromide [from magnesium (0·9 g.), bromobenzene (9 g.), and ether (50 c.c.)], dry benzene (30 c.c.) was added, and the mixture treated gradually with the foregoing spiran (powdered) (1 g.). The mixture was refluxed for 2 hours, set aside overnight, poured into aqueous ammonium chloride, and extracted with ether, and the extract dried (Na_2SO_4) and evaporated. Solid 10-*phenylanthranol*-9-spirocyclo*propane* that separated was washed twice with light petroleum (b. p. 40—60°) and crystallised from benzene as colourless crystals, m. p. 185—186° (Found: C, 88·4; H, 6·1; active H, 0·32. $C_{22}H_{18}O$ requires C, 88·6; H, 6·1; active H, 0·34%). This compound gives a dark brown colour with sulphuric acid and its benzene solution acquires a blue-violet fluorescene.

Oxidation. The anthrone-spiran (1 g.), in glacial acetic acid (20 c.c.), was treated on the boiling water-bath with chromic acid (2 g.) for 5 hours. The cooled mixture was poured into ice-cold water, and the separated solid was filtered off, washed thoroughly with water, and crystallised from xylene, in pale yellow crystals, m. p. 278°; it was identified as anthraquinone by its m. p. and mixed m. p. and colour reaction with zinc dust and aqueous ammonia.

Reaction of Methyleneanthrone with Diazoethane.—The oily residue after the excess of the ethereal diazoethane (Werner, *J.*, 1919, **115**, 1093) had been removed solidified on long storage and then was crystallised from ethyl alcohol, forming colourless crystals, m. p. 82° (Found: C, 87·1; H, 5·8. $C_{17}H_{14}O$ requires C, 87·2; H, 5·9%). 2′-*Methylanthrone*-9-spiro-1′-cyclo*propane* (VI; R = Me, R′ = H) is easily soluble in benzene or hot alcohol and gives a green colour with concentrated sulphuric acid.

Reaction of Methyleneanthrone with Diphenyldiazomethane.—The anthrone (1 g.) in benzene (20 c.c.) was treated with diphenyldiazomethane (Staudinger and Gaule, *Ber.*, 1916, **49**, 1897) [prepared from benzophenone hydrazone (1·2 g.) and yellow mercuric oxide (3 g.) suspended in benzene 50 c.c.]. The mixture was refluxed for 30 minutes. The deep red colour faded. The benzene was evaporated off, and the solid residue was washed with cold ether, followed by hot light petroleum (b. p. 50—60°), and finally crystallised from benzene as colourless crystals, m. p. 206° (yellow-orange melt) [Found: C, 90·1; H, 5·2%; *M* (Rast), 365. $C_{28}H_{20}O$ requires C, 90·3; H, 5·4%; *M*, 372]. 2′ : 2′-*Diphenylanthrone*-9-spiro-1′-cyclo*propane* is soluble in hot benzene, but difficultly soluble in cold ethyl alcohol, and gives an orange colour with concentrated sulphuric acid.

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