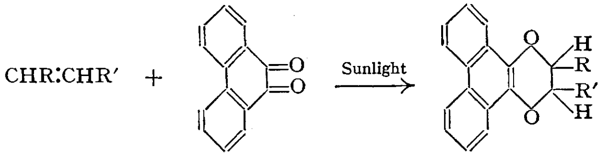
103. *Photochemical Reactions. Part VIII. Reaction of Ethylenes with Phenanthraquinone.*

By ALEXANDER SCHÖNBERG and AHMED MUSTAFA.

The reactions of phenanthraquinone with styrene, stilbene, αα-diphenylethylene, and triphenylethylene in sunlight are described. The products are probably derivatives of 2 : 3-dihydro-1 : 4-dioxan.

PHOTOCHEMICAL reactions of unsaturated compounds involving the double linkages are known (Berthelot and Gaudechon, *Compt. rend.*, 1910, **150**, 1169; Stobbe, *Ber.*, 1914, **47**, 2701; Ciamician and Silber, *Ber.*, 1902, **35**, 4129), but so far as we are aware the following reaction is without analogy. Under the influence of sunlight, phenanthraquinone reacts readily with styrene, stilbene, αα-diphenylethylene and triphenylethylene, giving probably derivatives of 2 : 3-dihydro-1 : 4-dioxan; *e.g.*,



In all four cases experiments carried out in the dark gave negative results. The photo-products are colourless, and decompose at high temperatures, yielding phenanthraquinone; stilbene and triphenylethylene also have been isolated in the two respective cases. The four photo-products, when treated with sulphuric acid, all yield phenanthraquinone.

EXPERIMENTAL.

The photo-experiments were carried out in sealed Monax glass tubes (Schlenk tubes) in an atmosphere of carbon dioxide (comp. Part VII, this vol., p. 67).

Photo-reaction between Phenanthraquinone and Stilbene.—Phenanthraquinone (1 g.) and stilbene (0·9 g.) in benzene (thiophen-free) (50 c.c.) were exposed to sunlight for 9 days in August, the phenanthraquinone then having dissolved. The benzene was driven off in a vacuum, and the residue washed with cold absolute ethyl alcohol and extracted with hot petroleum (b. p. 100—150°) (phenanthraquinone being difficultly soluble). On cooling (if necessary after concentration), almost colourless crystals were obtained; recrystallised from petroleum (b. p. 100—150°) or xylene, these gave colourless needles, m. p. about 260° (to a red melt) (Found : C, 86·2; H, 5·3. $C_{28}H_{20}O_2$ requires C, 86·5; H, 5·1%). The yield was about 70%.

The *product* (0·5 g.) was treated with concentrated sulphuric acid (3 c.c.) at room temperature and kept overnight. The solution, initially violet and finally brown, was poured on ice, filtered, neutralised with sodium carbonate, and extracted with ether. The extract was dried (anhydrous sodium sulphate) and distilled, leaving phenanthraquinone, identified by mixed m. p.

Thermal decomposition. The photo-product was heated in a stream of carbon dioxide in a tube about 25 cm. high at a bath temperature of about 270°. Red-brown fumes were formed and after ½ hour orange drops collected on the walls. After 48 hours, these solidified, forming a mixture of orange and almost colourless crystals. Extraction with hot light petroleum (b. p. 30—50°) removed stilbene, leaving an orange residue of phenanthraquinone. Both products were identified by mixed m. p. determinations after recrystallisation from alcohol.

Photo-reaction between Phenanthraquinone and Triphenylethylene.—Phenanthraquinone (1 g.) and triphenylethylene (2·4 g.) in benzene (25 c.c.) were exposed for 4 days in September. The oily residue remaining after removal of the benzene in a vacuum was repeatedly washed with petroleum (b. p. 80—90°) and with absolute ethyl alcohol. Both washings gave, on concentration, colourless crystals, m. p. about 225° (decomp.) after recrystallisation from petroleum (b. p. 80—90°) (Found : C, 87·8; H, 5·2. $C_{34}H_{24}O_2$ requires C, 87·8; H, 5·1%). The *product*, when treated with sulphuric acid, gave an olive-green colour after a few minutes.

Thermal decomposition. This was carried out for ½ hour at about 235° (bath temp.) as described above. The mixture of orange crystals of phenanthraquinone and almost colourless crystals of triphenylethylene was separated by means of hot light petroleum (b. p. 30—50°).

Photo-reaction between Phenanthraquinone and Styrene.—Phenanthraquinone (1 g.) and freshly distilled styrene (2 c.c.) in benzene (50 c.c.) were exposed for 4 days in October. After removal of the benzene, the residue was treated with light petroleum (b. p. 30—50°); on concentration, the extract gave almost colourless crystals, m. p. about 130° (decomp.) after washing with ether (Found : C, 84·2; H, 5·2. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%). The *product*, when treated with sulphuric acid, gave a violet colour after a few minutes. At a bath temperature of about 310° it yielded phenanthraquinone.

Photo-reaction between Phenanthraquinone and αα-Diphenylethylene.—Phenanthraquinone (1 g.) and freshly distilled αα-diphenylethylene (1·5 c.c.) in benzene (50 c.c.) were exposed for 16 days in October/November. After the usual treatment, light petroleum (b. p. 30—50°) extracted from the residue a crystalline solid. This was washed with hot ether and recrystallised from petroleum (b. p. 100—150°), giving colourless crystals, m. p. 202—203° (orange melt) (Found : C, 86·4; H, 5·4. $C_{28}H_{20}O_2$ requires C, 86·5; H, 5·1%). The *product* gave no initial coloration with sulphuric acid at the ordinary temperature, but an orange colour was observed immediately at 100°. At a bath temperature of about 230° it decomposed, yielding phenanthraquinone,

FOUAD I UNIVERSITY, ABBASIA, CAIRO. [*Received, March* 20*th*, 1944.]