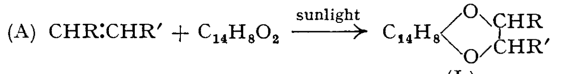
145. *Photochemical Reactions in Sunlight. Part X.* (a) *Reaction of Ethylenes with Phenanthraquinone and with Benzil.* (b) *A New Type of Photochemical Equilibrium.*

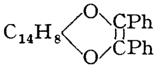
By Alexander Schönberg and Ahmed Mustafa.

(*a*) The reactions of phenanthraquinone with *pp*′-dimethoxystilbene, αα-diphenyl-Δ^{α}-propylene, α-stilbazole, and β-chlorostilbene, and of benzil with αα-diphenylethylene and stilbene are described (schemes A and B).

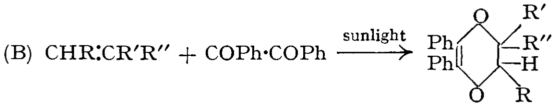
(*b*) The reversible photochemical reaction between xanthen and thioxanthone to yield (IV) is a new type of photochemical equilibrium (C). On pyrolysis, thioxanthone and xanthen are obtained from 9-xanthylthioxanthhydrol (IV), and xanthone and xanthen from 9-hydroxydixanthyl. ααββ-Tetraphenylethyl alcohol is more thermostable than (IV) or 9-hydroxydixanthyl.

(a) *Reaction of Ethylenes with Phenanthraquinone and with Benzil.*—Recently, we have shown (J., 1944, 387) that phenanthraquinone reacts with unsaturated compounds to form derivatives of phenanthro-1 : 4-dioxan (I; R = R′ = H) (A). This reaction was carried out with stryene, stilbene, αα-diphenylethylene, and triphenylethylene. We have now performed the same reaction with *pp*′-dimethoxystilbene, αα-diphenyl-Δ^{α}-propylene, and α-stilbazole, $CHPh{:}CH{\cdot}C_5H_4N$. The products are colourless or nearly so, and decompose at high temperatures with formation of phenanthraquinone and the corresponding ethylene.


(I.)


(II.)

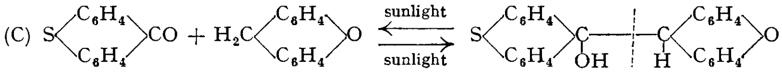
When phenanthraquinone was treated with β-chlorostilbene a mixture was first obtained, but on prolonged exposure, 2 : 3-diphenylphenanthro-9′ : 10′-1 : 4-dioxen (II) was obtained, hydrogen chloride being evolved. It is believed that an intermediate addition product analogous to (I) was formed.


(III.)

Benzil reacts with ethylenes similarly to phenanthraquinone, but more slowly (B). The reaction products obtained from benzil and stilbene, and from benzil and αα-diphenylethylene yielded benzil on pyrolysis, stilbene being isolated in addition from the former pyrolysis. Both photo-products, on prolonged action with concentrated sulphuric acid, gave benzil.

Parallel to the photo-experiments here described, control experiments in the dark were carried out, but showed lack of reaction in all cases.

(b) *A New Type of Photochemical Equilibrium.*—We recently showed (J., **1944**, 67) that xanthen reacts in sunlight with aromatic ketones, *e.g.*, xanthone or benzophenone, in accordance with the scheme : $COR_2 + CH_2R'_2 \xrightarrow{\text{sunlight}} CR_2(OH){\cdot}CHR'_2$, but no indication was found that the reaction was reversible. When the yellow thioxanthone was allowed to react with xanthen, both dissolved in benzene, the reaction product (IV) was formed in small yield, and attempts to increase the yield by prolonged illumination were unsuccessful. This failure is due to a photo-equilibrium reaction (C).


(IV.)

When 9-xanthylthioxanthhydrol (IV) was suspended in benzene and exposed to sunlight, it partly dissolved, and xanthen and thioxanthone were isolated from the solution ; moreover, (IV) was stable in the dark.

It is believed that the first step in the photo-dissociation of the carbinol is the formation of two free radicals (see broken line) which are stabilised by disproportionation. The fact that (IV) is colourless, whereas thioxanthone is yellow is in agreement with the constitution shown above. At 270°, (IV) decomposes into its generators, showing that the ethane linkage in the carbinol is weak. In this respect (IV) is similar to 9-hydroxydixanthyl (IV; but with O instead of S) which, on pyrolysis, yields xanthone and xanthen, in contrast to ααββ-tetraphenylethyl alcohol, which is much more thermostable.

EXPERIMENTAL.

The benzene was thiophen-free and dried over sodium. The photochemical reactions were carried out in a Pyrex-glass tube, the air having been displaced by dry carbon dioxide, and the tube sealed.

(a) *Photo-reaction between Phenanthraquinone and* pp′-*Dimethoxystilbene.*—Phenanthraquinone (1 g.) and *pp*′-dimethoxystilbene (Elbs, *J. pr. Chem.*, 1893, **47**, 68) (1·1 g.) in benzene (50 c.c.) were exposed to sunlight for 17 days (November), the phenanthraquinone gradually dissolving completely. The benzene was evaporated off in a vacuum, and the residual dark oil extracted with ether. The solvent was evaporated, and the oily residue was washed with light petroleum (b. p. 90—100°), followed by hot absolute ethyl alcohol, and finally extracted with hot light petroleum (b. p. 90—100°). The extract, on slow evaporation in a vacuum, gave almost colourless crystals, which recrystallised from light petroleum (b. p. 100—150°) in colourless crystals, m. p. 194° (orange melt) (Found : C, 80·3; H, 5·6. $C_{30}H_{24}O_4$ requires C, 80·3; H, 5·3%). 2 : 3-*Dianisylphenanthro*-9′ : 10′-1 : 4-*dioxan* (I; R = R′ = *p*-$C_6H_4{\cdot}OMe$) when treated with sulphuric acid gave a green and then a violet colour; it was soluble in hot absolute ethyl alcohol.

Thermal decomposition. The foregoing product was heated at about 270° (bath temp.) in a stream of dry carbon dioxide (the height of the decomposition tube being about 25 cm.) during ½ hr.; red-brown fumes were evolved, and an orange liquid collected on the walls of the tube. After 24 hours, this solidified to a mixture of orange and almost colourless crystals; extraction with hot light petroleum (b. p. 90—100°) left a residue of phenanthraquinone (identified, after recrystallisation from alcohol, by m. p., mixed m. p., and colour reaction with sulphuric acid). The extract was concentrated, and the resulting crystals, recrystallised from ethyl alcohol, proved to be *pp*′-dimethoxystilbene.

Photo-reaction between Phenanthraquinone and αα-Diphenyl-Δ^{α}-propylene.—Phenanthraquinone (1 g.) and the propylene (Klages, *Ber.*, 1902, **35**, 2647) (2·4 g.) in 25 c.c. of benzene were exposed to sunlight for 11 days (January), the phenanthraquinone dissolving as before and the orange colour fading to pale yellow. The crystals that separated were filtered off, washed with light petroleum (b. p. 30—50°), and recrystallised from xylene, forming colourless crystals, m. p. 233° (decomp.; orange melt) (Found: C, 86·1; H, 5·7. $C_{29}H_{22}O_2$ requires C, 86·5; H, 5·5%). 3 : 3-*Diphenyl*-2-*methylphenanthro*-9′ : 10′-1 : 4-*dioxan* gave no colour with sulphuric acid at room temperature, but a brown colour at 100°; when heated as described above, it yielded its generators, which were separated by means of hot light petroleum (b. p. 30—50°), in which the hydrocarbon is soluble.

Photo-reaction between Phenanthraquinone and α-Stilbazole.—Phenanthraquinone (1 g.) and α-stilbazole (Shaw and

Wagstaff, J., 1933, 77) (0·9 g.) in benzene (50 c.c.) were exposed to sunlight for 24 days (April—May), a dark brown solution resulting. The benzene was removed in a vacuum, and the crystalline residue washed with cold absolute ethyl alcohol, followed by acetone, and recrystallised from xylene, forming almost colourless crystals, m. p. 236—237° (red melt) (Found: C, 83·2; H, 5·2. $C_{27}H_{19}O_2N$ requires C, 83·3; H, 4·9%). 2-*Pyridino*-3-*phenylphenanthro*-9′ : 10′-1 : 4-*dioxan* (I; R′ = α-C_5H_4N; R = Ph) did not react with sulphuric acid; it was difficultly soluble in ether, acetone, and ethyl alcohol, but soluble in hot benzene or xylene. When heated as in the preceding cases, it yielded its generators, separated by means of hot light petroleum (b. p. 30—50°).

Photo-reaction between Phenanthraquinone and β-Chlorostilbene.—Phenanthraquinone (1 g.) and β-chlorostilbene (Sudborough, J., 1897, **71**, 220) (1·2 g.) in benzene (50 c.c.) were exposed to sunlight for 6 months (May—November); the phenanthraquinone had then dissolved, and the resulting crystals were filtered off and washed with light petroleum (b. p. 50—70°) and then repeatedly with cold acetone. The product crystallised from nitrobenzene in colourless needles with 1 mol. of solvent of crystallisation; m. p. above 320° (Found: C, 80·2; H, 4·5; N, 2·4. $C_{28}H_{18}O_2,C_6H_5O_2N$ requires C, 80·1; H, 4·5; N, 2·75%). 2 : 3-*Diphenylphenanthro*-1 : 4-*dioxan* (II; R = R′ = Ph) gave no colour with sulphuric acid at room temperature, but an olive-brown colour at 100°; it was difficultly soluble in benzene, light petroleum (b. p. 90—100°), acetone, and xylene. The formation of hydrogen chloride during the insolation was confirmed.

Photo-reaction between Benzil and αα-Diphenylethylene.—Benzil (1 g.) and αα-diphenylethylene (freshly distilled) (1·5 g.) in benzene (50 c.c.) were exposed to sunlight for 8 months (April—November), the solution becoming brownish-yellow. The benzene was expelled in a vacuum, and the oily residue crystallised on standing. This was washed successively with hot light petroleum (b. p. 30—50°), light petroleum (b. p. 50—70°), and with a small amount of hot absolute ethyl alcohol. The dried residue crystallised from hot light petroleum (b. p. 90—100°) in almost colourless crystals, m. p. 160° (yellow melt), giving a deep red coloration with sulphuric acid. 3 : 3 : 5 : 6-*Tetraphenyl*-1 : 4-*dioxan* (III; R′ = R″ = Ph, R = H) (Found: C, 85·9; H, 5·7. $C_{28}H_{22}O_2$ requires C, 86·1; H, 5·6%) is soluble in cold benzene, difficultly in cold ethyl alcohol and light petrolem (b. p. 30—50°).

Thermal decomposition. This was carried out as described above, and after 10 mins. drops of a yellow oil had collected on the walls of the tube. After 2 hours these solidified and were identified as benzil.

Action of sulphuric acid. 0·2 G. of the photo-product was treated with concentrated sulphuric acid (2 c.c.) at room temperature and set aside overnight, the solid dissolving. The solution was poured on ice, filtered, the filtrate neutralised with sodium carbonate, and extracted with ether, benzil being obtained.

Photo-reaction between Benzil and Stilbene.—Benzil (4 g.) and stlbene (3·6 g.) in benzene (50 c.c.) were exposed to sunlight for 5 months (July—December), both dissolving and being replaced by other crystals; these were filtered off, and recrystallised from benzene in almost colourless crystals of tetraphenyldioxen (III; R = R′ = Ph; R″ = H), m. p. 246° (yellow melt) (Found: C, 86·1; H, 5·8. Calc. for $C_{28}H_{22}O_2$: C, 86·1; H, 5·6%). The original mother-liquor afforded a further yield of this product. Tetraphenyldioxen is difficultly soluble in ethyl alcohol and cold benzene and soluble in hot benzene and xylene.

The photo-product gave no coloration with sulphuric acid at room temperature, but a dark brown solution was obtained on heating, as noted by Madelung and Oberwegner (*Annalen*, 1936, **526**, 246; 1931, **490**, 235), who gave m. p. 245—247°. Prolonged action of sulphuric acid (as described above) afforded benzil.

Thermal decomposition. Thermal decomposition for 15 minutes at about 250° (bath temp.) afforded a yellow oil and an almost colourless sublimate. Extraction of these products with hot light petroleum (b. p. 30—50°) removed stilbene, leaving a pale yellow residue of benzil; both products were identified by mixed m. p. after recrystallisation from alcohol.

(b) *Photochemical Reaction between Xanthen and Thioxanthone.*—Equimolecular amounts of xanthen (1 g.) and thioxanthone (Davis and Smiles, J., 1910, **97**, 1296) in benzene (15 c.c.) were exposed to sunlight for 2 days (May). The solution acquired a green fluorescence and 9-*xanthylthioxanthhydrol* separated in colourless needles; it was filtered off, washed with benzene several times, and recrystallised from xylene; m. p. *ca.* 214° (Found: C, 79·45; H, 4·6; S, 7·2; active hydrogen, 0·26. $C_{26}H_{18}O_2S$ requires C, 79·2; H, 4·5; S, 8·1; active hydrogen, 0·25%). It is difficultly soluble in cold benzene, but soluble in hot light petroleum (b. p. 100—110°). It is not affected by acetyl chloride at 50° (6 hrs.).

Further action of sunlight. 9-Xanthylthioxanthhydrol (1 g.) was suspended in dry benzene (20 c.c.) and exposed to direct sunlight for 20 days (August—September). The solution became yellow with a green fluorescence, and the solid gradually dissolved, being replaced by another solid; this was collected, cystallised from xylene, and proved to be thioxanthone (m. p. and mixed m. p.; colour with sulphuric acid). The benzene mother-liquor was evaporated in a vacuum, and the residue steam-distilled; an ethereal extract of the distillate was dried (sodium sulphate) and the ether evaporated off. The colourless crystals obtained, recrystallised from methyl alcohol, were xanthen (m. p. and mixed m. p.).

In a parallel experiment, but with the reaction vessel covered with black paper, no reaction was detected.

Action of heat on 9-*xanthylthioxanthhydrol.*—2 G. of the hydrol were heated (bath temp. 270°) in a current of dry carbon dioxide for 30 mins. in a tube (A), 26 cm. high, connected by a bent tube to a similar tube (B) containing water, externally cooled. Rapid evolution of vapours was observed, which partly condensed in tube (B); this solid was collected, extracted with light petroleum (b. p. 30—50°), the extract evaporated, the solid crystallised from methyl alcohol, and identified as xanthen (m. p. and mixed m. p.). The substance in tube (A) was extracted as above to remove xanthen, and recrystallised from xylene; the product was thioxanthone (m. p., mixed m. p., and colour reaction with sulphuric acid).

Action of Heat on 9-*Hydroxydixanthyl.*—9-Hydroxydixanthyl (J., 1944, 67) (2 g.) was heated (bath temp. 270°) in the apparatus described above for 30 mins.; the vapours evolved condensed in tube (B), and this solid was steam-distilled, the ethereal extract of the distillate being dried over anhydrous sodium sulphate and evaporated in a vacuum; colourless crystals of xanthen (m. p. and mixed m. p.) were obtained. The solid in tube (A), on steam distillation, gave xanthen and xanthone, separated as described for xanthen and thioxanthone (above); xanthone was crystallised from hot absolute ethyl alcohol and identified by m. p., mixed m. p., and blue fluorescence with sulphuric acid.

Thermal Stability of ααββ-*Tetraphenylethyl Alcohol.*—The alcohol (Paternó and Chieffi, *Gazzetta*, 1909, **39**, II, 415) (0·5 g.) was heated (bath temp. 270°) in the apparatus described above for 30 minutes. The solid contents of tube (A) were washed with light petroleum (b. p. 30—50°), and 0·477 g. of the initial alcohol (m. p. and mixed m. p.) obtained.

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