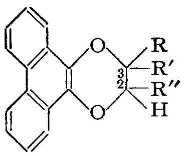
428. *Photochemical Reactions. Part XIII.* (a) *Photochemical Reactions of Ethylenes with Phenanthraquinone and with* 1 : 2 : 3-*Triketones.* (b) *Dimerisation Reactions in Sunlight.*

By Alexander Schönberg, Ahmed Mustafa, Mohamed Zaki Barakat, Nazih Latif, Radwan Moubasher, and Akila Mustafa (Mrs. Said).

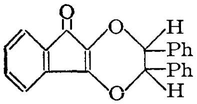
(*a*) Photochemical reactions of phenanthraquinone and *p*-methylstilbene, α-ethylstilbene, and 1-phenyl-2-β-naphthylethylene yield the substances (I*a*), (I*b*), and (I*c*), respectively. Similar reactions were carried out with triketoindane and stilbene and with *peri*naphthindane-7 : 8 : 9-trione (III) and stilbene, yielding the substances (II) and (IV), respectively.

(*b*) Photochemical polymerisation of α-naphthaquinone yields the colourless dimer (V); 1 : 2-benzanthracene yields the photo-dimer (VII). The bearing of this experiment on biological experiments with carcinogenic substances is stressed. The dimer (VIII) of 1 : 3-diphenylbenz*iso*furan, so far only obtained by a photo-process, was synthesised by a dark method.

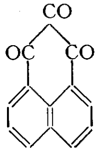
(*a*) The work on the action of stilbenes on phenanthraquinones (Schönberg and Mustafa, *Chem. Reviews*, 1947, **40**, 181; *J.*, 1944, 387; 1945, 551; 1947, 997) has been continued, and phenanthraquinone has been allowed to react in sunlight with *p*-methylstilbene, α-ethylstilbene, and 1-phenyl-2-β-naphthylethylene. The reaction products,*, 3-*phenyl*-2-p-*tolyl*- (I*a*) 2 : 3-*diphenyl*-3-*ethyl*- (I*b*), and 3-*phenyl*-2-β-*naphthylphenanthro*(9′ : 10′ : 5 : 6)*dioxen* (I*c*), are colourless or almost colourless substances which, when heated, decompose into their generators. So far, photo-addition reactions of this type have been carried out with 1 : 2-diketones (*o*-quinones), but only now it has been found † that the reaction can be carried out also with 1 : 2 : 3-triketones; thus triketoindane and *peri*naphthindane-7 : 8 : 9-trione (III) gave with stilbene the photo-addition products 1′-*keto*-2 : 3-*diphenylindeno*(2′ : 3′ : 5 : 6)*dioxen* (II) and 9′-*keto*-2 : 3-*diphenyl*peri*naphthindeno*(7′ : 8′ : 5 : 6)*dioxen* (IV). Their constitution is based on the fact that they are almost colourless, in contrast to the initial triketones which are dark red, and on the fact that the photo-addition products decompose on heating, with the re-formation of stilbene.



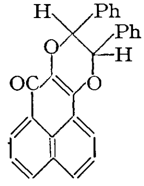
(I*a*; R = H, R′ = Ph, R″ = *p*-C_6H_4Me.)
(I*b*; R = Et, R′ = R″ = Ph.)
(I*c*; R = H, R′ = Ph, R″ = β-$C_{10}H_7$.)



(II.)



(III.)



(IV.)

The scope of the photo-reaction between ethylenes and 1 : 2-diketones or 1 : 2 : 3-triketones may be seen from the following lists which give the names of the substances so far found active.

Ethylenes. Styrene, 1 : 1-diphenylethylene, stilbene, *p*-methylstilbene, *pp*′-dimethoxystilbene, α-ethylstilbene, 1 : 1-diphenylprop-1-ene, 1 : 1-di-(*p*-diphenylyl)-2-methylethylene, 1 : 1-dixenylethylene, 1 : 1-di-*p*-methoxyphenyl-2-methylethylene, α-stilbazole, β-chlorostilbene, 9-benzylidenexanthen, 9-benzylidenethioxanthen, benzylidenephthalide, methyleneanthrone, triphenylethylene, 1-phenyl-2-β-naphthylethylene, and diphenylketen.

Ketones. Benzil, phenanthraquinone, retenequinone, triketoindane, and *peri*naphthindane-7 : 8 : 9-trione.

Phenanthraquinone reacts with all the ethylenes mentioned above, and stilbene with all those in the second list.

(*b*) (i) When the benzene solution of the yellow α-naphthaquinone is exposed to sunlight, the colourless photo-*dimer* (V) is formed.‡ The constitution of (V) is based on the following facts. The lack of colour makes a quinonoid structure improbable. The substance is not phenolic, for it is insoluble in alkali and does not react with diazomethane; it decomposes on heating at 270°, quantitatively or nearly so, with regeneration of α-naphthaquinone. As the dimer is difficultly

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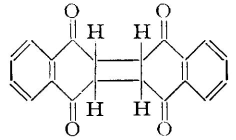
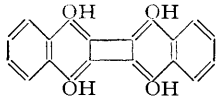
* These experiments were carried out by Nazih Latif.
† These experiments were carried out by R. Moubasher and Mrs. Said.
‡ These experiments were carried out by M. Z. Barakat.

soluble, no molecular-weight determination could be carried out. The assignment of a dimeric structure is based on the fact that 2-methyl-1 : 4-naphthaquinone gives, in sunlight, a photo-dimer (Madinaveitia, *Chem. Abs.*, 1935, **29**, 5438) which is soluble enough to allow of a molecular-weight determination. (V) is of interest because its hypothetical enolic form (VI) is related to diphenylene.

(V.)



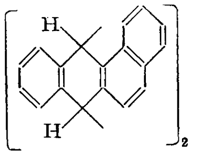


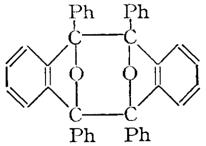
(VI.)

We were unable to prepare the photo-dimer of 2 : 3-dimethyl-1 : 4-naphthaquinone; the crystals were unchanged when exposed to sunlight, and no photo-reaction could be detected in their irradiated benzene solution.

(*b*) (ii) Very little is known about the photo-dimerisation of carcinogenic hydrocarbons. We found * that the weakly carcinogenic 1 : 2-benzanthracene (Shmuk and Guseva, *Chem. Abs.*, 1941, **35**, 3271) forms a difficultly soluble colourless photo-*dimer*, analogous to dianthracene, the photo-dimer of anthracene. The former dimer was obtained as a crystalline powder which is probably a mixture of isomers: whereas isomers are not possible for dianthracene, they are possible for di-1 : 2-benzanthracene (VII), which can be either an *s*- or an *as*-compound.

(VII.)





(VIII.)

The possibility of photo-dimerisation should not be overlooked when substances are tested for carcinogenic activity, where the material is applied externally. When 1 : 2-benzanthracene is tested, the animals should be kept in the dark to avoid photo-polymerisation of the material under investigation. A number of carcinogenic substances are now being investigated in this Department to discover whether they are changed † (formation of non-carcinogenic substances by the action of sunlight?). It is a remarkable fact that not only many carcinogenic hydrocarbons, but also a number of highly active carcinogenic compounds containing nitrogen, are derivatives of substances which undergo chemical reactions when their solutions are exposed to sunlight. Carcinogenic substances of this type are, *inter alia*, 4-dimethylaminoazobenzene (butter-yellow) and 2 : 3′-azotoluene, which are derivatives of azobenzene of which it is known that in solution the *cis*- and the *trans*-form are interconvertible in sunlight (Hartley, *J.*, 1938, 634). The carcinogenic derivatives of 4-aminostilbene (Haddow and Kon, *Brit. Med. Bull.*, 1947, **4**, 324) are derivatives of stilbene, which forms a dimer when its benzene solution is exposed to sunlight (Ciamician and Silber, *Ber.*, 1902, **35**, 4129).

(*b*) (iii) The photo-dimer (VIII) of 1 : 3-diphenyl*iso*benzfuran, obtained by the action of sunlight on the orange-yellow monomer (Guyot and Catel, *Bull. Soc. chim.*, 1906, **35**, 1127; Adams and Gold, *J. Amer. Chem. Soc.*, 1940, **62**, 2041), has not yet been obtained by a dark process. We found that when the monomer is heated at 270° in a sealed tube in dry carbon dioxide, and the melt is chilled in ice-water as quickly as possible, a good yield of (VIII) is obtained.

Parallel experiments were carried out with anthracene and α-naphthaquinone, but no dimerisation occurred.

EXPERIMENTAL.

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

Photo-reactions of Phenanthraquinone.—(i) *With* p-*methylstilbene.* Phenanthraquinone (1·09 g.) and *p*-methylstilbene (1 g.) (Meerwein *et al.*, *J. pr. Chem.*, 1939, **152**, 237) in benzene (50 c.c.) were exposed to sunlight for six days (October). Most of the benzene was then driven off; after some time,

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* These experiments were carried out by A. Mustafa.

† It was found that 5- and 4′-methylbenzanthracene furnish in sunlight colourless photo-products of high melting point, which at room temperature are less soluble in benzene than the initial materials. These two substances were kindly supplied by Professor Haddow and Professor Kon (The Chester Beatty Research Institute of the Royal Cancer Hospital, London), but lack of material made further investigation impossible.

crystals appeared which were recrystallised from ethyl acetate. The addition *product* (I*a*) formed colourless crystals, m. p. 247° (decomp.; orange melt) (Found: C, 86·2; H, 5·4. $C_{29}H_{22}O_2$ requires C, 86·5; H, 5·5%); it gave a violet colour reaction with concentrated sulphuric acid at room temperature after a few minutes, and was soluble in benzene, but difficulty soluble in light petroleum (b. p. 50—70°); on pyrolysis, phenanthraquinone and *p*-methylstilbene were obtained.

The foregoing product was heated at about 270° (bath temp.) in a stream of carbon dioxide (the height of the decomposition tube being 25 cm.) for 15 minutes. The product was allowed to cool in a stream of carbon dioxide, and after 24 hours the crystals formed on the upper parts of the reaction vessel were extracted with hot light petroleum (b. p. 50—70°); the residue proved to be phenanthraquinone. The petroleum extract was concentrated and the resulting crystals, recrystallised from methyl alcohol, proved to be *p*-methylstilbene (m. p. and mixed m. p.).

(ii) *With α-ethylstilbene.* Phenanthraquinone (0·9 g.) and α-ethylstilbene (0·7 g.) (Klages and Heilmann, *Ber.*, 1904, **37**, 1452) in 30 c.c. of benzene were exposed to sunlight for 13 days in December, the phenanthraquinone gradually dissolving completely. Then the contents of the tube were filtered, and the filtrate concentrated; a solid orange product (phenanthraquinone) appeared, which was filtered off. The filtrate was concentrated, and light petroleum (b. p. 50—70°) added until it became turbid. After 24 hours' standing, orange crystals of phenanthraquinone were formed; the filtrate from these, after addition of methyl alcohol and a few drops of acetone, yielded the photo-*product* (I*b*); colourless crystals, m. p. 169°, from light petroleum (b. p. 50—70°). When this was treated with concentrated sulphuric acid no colour occurred in the cold, but on being warmed on the water-bath, the acid became violet after a short time (Found: C, 86·7; H, 6·3. $C_{30}H_{24}O_2$ requires C, 86·6; H, 5·8%).

Thermal decomposition was carried out as described above for 30 minutes, and the products were α-ethylstilbene, which was purified by crystallisation from light petroleum (m. p. and mixed m. p.), and phenanthraquinone.

(iii) *With* 1-*phenyl*-2-*β-naphthylethylene.* Phenanthraquinone (0·4 g.) and 1-phenyl-2-β-naphthylethylene (0·4 g.) (Bergmann and Schapiro, *J. Org. Chem.*, 1947, **12**, 57) in benzene (30 c.c.) were exposed to sunlight for 15 days (April), the phenanthraquinone dissolving gradually. The contents of the tube were filtered and the filtrate concentrated. On addition of acetone, crystals were formed after some time in the ice-chest; the *product* (I*c*) recrystallised from chloroform-methyl alcohol as colourless crystals, m. p. 199° (orange melt) (Found: C, 87·6; H, 5·2. $C_{32}H_{22}O_2$ requires C, 87·6; H, 4·9%).

Thermal decomposition, as before, afforded phenanthraquinone and 1-phenyl-2-β-naphthylethylene (m. p. and mixed m. p.).

Photo-reactions of Stilbene.—(i) *With triketoindane.* Triketoindane (1 g.), stilbene (0·7 g.), and anhydrous sodium sulphate (0·5 g.) in benzene (25 c.c.) were exposed to sunlight for three weeks in February. The contents of the tube were filtered off, and the residue washed with water to remove sodium sulphate and unreacted triketone. The *product* (II) (0·6 g.) crystallised from benzene-petrol (b. p. 70—90°) as light yellow crystals, m. p. 210° (decomp.), easily soluble in benzene, difficultly soluble in cold alcohol and petrol, and not giving a colour reaction with 20% sodium hydroxide at room temperature, in contrast to the original ketone which gives an intense blue coloration with this reagent (Found: C, 80·4; H, 4·4. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%). Sodium sulphate was used in this experiment to retain any water which might enter the tube during sealing, as the ketone reacts rapidly with water to form the hydrate ("ninhydrin").

Pyrolysis of (II) was carried out in a test-tube in a bath at 220° for 20 minutes; after cooling, the colourless crystals which had formed on the upper part of the test tube proved to be stilbene (m. p. and mixed m. p.).

(ii) *With* peri*naphthindane*-7 : 8 : 9-*trione.* The triketone (III) (1 g.) and stilbene (1 g.), partly dissolved and partly suspended in benzene (25 c.c.), were exposed to sunlight for 10 days (May). The reaction *product* (IV) which separated was crystallised from benzene-petrol (b. p. 70—90°) and then from methyl alcohol; m. p. 220—222° (decomp.; dark red-brown melt); yield 0·9 g. The pale yellow product is soluble in benzene and difficultly soluble in cold methyl and ethyl alcohol; it gives an orange colour with concentrated sulphuric acid and no colour reaction with 20% sodium hydroxide in the cold, in contrast to (III) which gives a blue coloration with this reagent (Found: C, 83·1; H, 4·6. $C_{27}H_{18}O_3$ requires C, 83·1; H, 4·7%).

Thermal decomposition of (IV) was carried out as in the case of (II) and stilbene was identified by m. p. and mixed m. p.

Photo-dimerisation of α-Naphthaquinone.—The quinone (0·5 g.) in benzene (12 c.c.) was exposed to sunlight (mid-November to mid-December); colourless crystals began to form after a week, and at the end of the experiment these were filtered off, washed with a little cold benzene, and crystallised from excess of alcohol; m. p. 244—248° (decomp.; brown melt) (Found: C, 75·7; H, 4·1. $C_{20}H_{12}O_4$ requires C, 75·9; H, 3·8%); yield 0·2 g. A parallel experiment carried out in the dark gave a negative result. The *dimer* is very difficultly soluble in hot benzene and boiling ether. It is insoluble in concentrated or dilute aqueous sodium hydroxide solution, and gives no colour reaction with concentrated sulphuric acid and no reaction with diazomethane.

The thermal decomposition of (V) was carried out in a large test-tube through which a stream of dry carbon dioxide passed. The lower part was heated at 270° for 10 minutes. The resulting brown melt was cooled and crystallised from ethyl alcohol, and the product proved to be α-naphthaquinone (mixed m. p. and properties). No other product could be detected.

Effect of sunlight on solid α-naphthaquinone. Solid α-naphthaquinone was exposed to sunlight in a Monax glass tube for two months (July and August) but no change could be observed. In a parallel experiment 2-methyl-1 : 4-naphthaquinone was transformed into the photo-dimer.

Behaviour of 2 : 3-*Dimethyl*-1 : 4-*naphthaquinone in Sunlight.*—The quinone (Fieser and Oxford, *J. Amer. Chem. Soc.*, 1942, **64**, 2063) was found to be stable when exposed to sunlight in benzene solution or in the solid state. These experiments were carried out as described above.

Molecular Weight of the Photo-dimer of 2-*Methyl*-1 : 4-*naphthaquinone.*—A determination carried out by Rast's method gave *M*, 357 (Calc. for $C_{22}H_{16}O_4$: *M*, 344).

Polymerisation of 1 : 2-*Benzanthracene in Sunlight.*—This substance (1 g.) (Eastman–Kodak) was dissolved in dry benzene (20 c.c.) and exposed to sunlight (January). After 24 hours' exposure, the colourless microcrystalline photo-*dimer* was obtained, and was recrystallised from tetralin at 100°. It is easily soluble in boiling tetralin, difficultly soluble in benzene and carbon disulphide; m. p. 235° (Found: C, 94·4; H, 5·6. $C_{36}H_{24}$ requires C, 94·7; H, 5·3%).

The photo-dimer (0·5 g.) was heated at 270° (ethyl phthalate bath) for 10 minutes in dry carbon dioxide and allowed to cool. The solidified melt proved to be the monomer (m. p. and mixed m. p.).

Polymerisation of 1 : 3-*Diphenylbenz*iso*furan in the Dark.*—This substance (0·2 g.) (Guyot and Catel, *loc. cit.*), contained in a sealed Pyrex tube, was completely immersed in boiling ethyl phthalate (270°) for 30 minutes; the tube was then rapidly chilled in ice-water. The contents of the tube were washed with hot light petroleum (b. p. 50—70°) several times (to remove any unchanged substance), and the insoluble residue dissolved in hot acetic acid (12 c.c. of 99·6% acid containing 0·5 c.c. of water); on slow cooling, colourless crystals were obtained and proved to be (VIII) (Guyot and Catel, *loc. cit.*) (m. p. and mixed m. p. and comparison of the properties) (Found: C, 88·8; H, 5·5. Calc. for $C_{40}H_{28}O_2$: C, 88·9; H, 5·2%); yield *ca.* 80%. If in the above experiment the reaction tube was allowed to cool very slowly, no dimeric product could be detected.

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