681. *Some Photochemical Reactions between Quinones and Hydrocarbons.*

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The photochemical dehydrogenations of *p*-xylene, cumene, and tetralin by means of phenanthraquinone, chloranil, and 1 : 4-naphthaquinone have been examined. A study of the reaction products shows that the hydrogen abstraction is homolytic.

In a previous paper (*J.*, 1953, 238) we suggested that the photochemical addition of benzaldehyde to the oxygen atoms of phenanthraquinone was a chain reaction promoted by the activation of the quinone to a diradical which was capable of abstracting a hydrogen atom from the aldehyde molecule. Since it had previously been suggested (Waters, *Ann. Reports*, 1945, **42**, 155; *Trans. Faraday Soc.*, 1946, **42**, 184; Dost and Van Nes, *Rec. Trav. chim.*, 1951, **70**, 403; 1952, **71**, 857) that the high-temperature thermal dehydrogenations of hydroaromatic substances by means of quinones involve a similar hydrogen-atom transfer, $Q + H{-}R \longrightarrow H{-}Q\cdot + \cdot R$, we decided to obtain further support for this reaction mechanism by investigating corresponding photochemical reactions at room temperature.

Benrath and von Meyer (*J. prakt. Chem.*, 1914, **89**, 258) had previously shown that phenanthraquinone reacted with *o*- and *p*-xylenes, and with ψ-cumene, on prolonged exposure to sunlight to give their phenanthrenediol monoethers, structurally similar to the phenanthrenediol monobenzoate discussed in our previous paper (*loc. cit.*). From corresponding reactions with *m*-xylene, mesitylene, and *p*-cymene however they isolated only phenanthraquinhydrone and did not discover the natures of the products derived from the hydrocarbons. Schönberg and Mustapha (*J.*, 1944, 67; 1945, 657) observed the production of tetra-arylethanes from diarylmethanes on irradiation in sunlight with *p*-benzoquinone, phenanthraquinone, and anthraquinone, but obtained no evidence of addition of diarylmethyl radicals to quinone molecules.

We have now examined the reactions which occur when solutions of phenanthraquinone, chloranil, and 1 : 4-naphthaquinone in *p*-xylene, cumene, and tetralin are exposed, in the absence of air, to the radiation from a 500-w Hanovia mercury-in-quartz lamp and have been able to identify each of the reaction products which are tabulated below.

Products of photochemical dehydrogenations of hydrocarbons.

Hydrocarbon	Phenanthraquinone	Chloranil	1 : 4-Naphthaquinone
p-Xylene	9-Hydroxy-10-*p*-methylbenzyloxyphenanthrene, 33% 1 : 2-Di-*p*-tolylethane, 2%	Tetrachloroquinol, 6% 2 : 3 : 5 : 6-Tetrachloro-4-*p*-methylbenzyloxyphenol, 90% Hydrogen chloride	1 : 4-Dihydroxynaphthalene, 65% 1 : 2-Di-*p*-tolylethane, 8%
Cumene	Phenanthraquinhydrone, 85% α-Methylstyrene 2 : 3-Dimethyl-2 : 3-diphenylbutane, 3%	Tetrachloroquinol, 63% α-Methylstyrene Hydrogen chloride	1 : 4-Dihydroxynaphthalene, 40% α-Methylstyrene
Tetralin	Phenanthraquinhydrone, 18% 1 : 2-Dihydronaphthalene, 50%	Tetrachloroquinol, 55% 1 : 2-Dihydronaphthalene, 21%	1 : 4-Dihydroxynaphthalene, 52% 1 : 2-Dihydronaphthalene, 10%

From the reaction of *p*-xylene with *p*-benzoquinone only quinhydrone could be isolated.

As can be said of the results of Schönberg and Mustapha, the isolation of hydrocarbon dimers, R–R ($Me{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}Me$ and $Ph{\cdot}CMe_2{\cdot}CMe_2Ph$) gives clear evidence that free hydrocarbon radicals, R•, must have been formed from both *p*-xylene and cumene, and so substantiates the homolytic mechanism for quinone dehydrogenation. Correspondingly phenanthraquinhydrone and quinhydrone can be regarded as the dimers of the semiquinone radicals HQ•. It may be noted that only from the reactions involving *p*-xylene was it possible to isolate any combination products of the unlike radicals R• and HQ•. Whereas the *p*-methylbenzyl radical, $Me{\cdot}C_6H_4{\cdot}CH_2{\cdot}$, which cannot easily yield a stable olefin by the loss of a hydrogen atom, does preponderatingly form the cross combination product, R•QH, with semiquinone radicals, both the αα-dimethylbenzyl and the α-tetralyl radical seem to react by hydrogen loss rather than by addition, *e.g.*

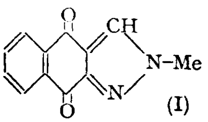
$$Ph{\cdot}CMe_2{\cdot} + {\cdot}Q\text{–}H \longrightarrow Ph{\cdot}CMe{:}CH_2 + H\text{–}Q\text{–}H.$$

However Criegee (*Ber.*, 1936, **69**, 2758), who obtained quinol monoethers by warming *cyclo*hexene and tetralin with dichloroquinizarinquinone, found that the addition products were unstable at high temperatures and similarly yielded mixtures of olefins and quinols (cf. Ziegler and Deparade, *Annalen*, 1950, **567**, 128), but it can be doubted whether this thermal decomposition would occur so readily under our reaction conditions. Since quinol monoethers were not formed extensively except from the reaction between *p*-xylene and chloranil it is unlikely that these photochemical dehydrogenations involve long reaction chains of the type, $R{\cdot} + Q \longrightarrow R\text{–}Q$: $R\text{–}Q{\cdot} + H\text{–}R \longrightarrow R\text{–}Q\text{–}H + {\cdot}R$, postulated for the much easier photochemical reactions between aldehydes and quinones.

The formation of some hydrogen chloride from the reactions involving chloranil apparently indicates that some of the photochemically produced radicals must be active enough to attack nuclear chlorine.

It may be noted that the infra-red spectrum of 9-hydroxy-10-*p*-methylbenzyloxyphenanthrene shows absorption bands indicative of both H–O and C=O bonds, in confirmation of the keto–enol tautomerism suggested for it by Benrath and von Meyer (*loc. cit.*). Our failure to effect any reaction of it with diazomethane indicates that the ketonic form predominates. In contrast, the corresponding *p*-methylbenzyl ether of tetrachloroquinol exhibits no ketonic properties.

Attention may also be directed to the fact that the methylation of 1 : 4-dihydroxynaphthalene with an ethereal solution of diazomethane yields 1-methylnaphthaquinono-(2′ : 3′-3 : 4)pyrazole (I). This is also obtained by the action of diazomethane on the naphthaquinono(2′ : 3′-3 : 4)pyrazole itself, though Fieser and Peters (*J. Amer. Chem. Soc.*, 1931, **53**, 4081) found that methylation with methyl sulphate produced the isomeric α-methyl derivative (cf. Auwers and Düesberg, *Ber.*, 1920, **53**, 1179).



(I)

Experimental

The photochemical reactions were carried out by shaking the reactants mechanically in thin-walled soft-glass bulbs, sealed under nitrogen, in the radiation from a 500-w mercury-in-quartz Hanovia lamp placed about 25 cm. away.

Irradiations with Cumene.—Commercial cumene was purified by shaking it with portions of 98% sulphuric acid until the acid layer was not discoloured, washing it with water, dilute sodium carbonate and water again, drying ($CaCl_2$) and fractionating it. The distillate, b. p. 149—152°, was then hydrogenated for 2 hr. at 80°/60 atm., Raney nickel being used. The product on refractionation gave 95% of material, b. p. 151—152°.

(a) *With phenanthraquinone.* The quinone (2 g.) in cumene (35 ml.) was irradiated for 20 days. The blackish phenanthraquinhydrone (1·7 g.; m. p. 165—169°) which separated gave a green colour with alkali and phenanthraquinone when boiled with alcohol. Reductive acetylation with zinc dust and acetic anhydride gave 9 : 10-diacetoxyphenanthrene, m. p. and mixed m. p. 202°. After evaporation of excess of cumene, the residue was chromatographed on alumina. The first eluates, ligroin being used, yielded 2 : 3-dimethyl-2 : 3-diphenylbutane (0·1 g.), needles (from ethanol), m. p. 118—119° which was unchanged after admixture with an authentic specimen (Kharasch and Urry, *J. Org. Chem.*, 1948, **13**, 108) (Found: C, 90·3; H, 9·0. Calc. for $C_{18}H_{22}$: C, 90·8; H, 9·2%).

The presence of α-methylstyrene was established by Tiffeneau's method (*Ann. Chim. Phys.*, 1907, **10**, 165). The cumene distillate (25 ml.) was stirred vigorously for 2 hr. with 1% aqueous neutral potassium permanganate (200 ml.) at 0°. The solution was decolorised (SO_2) and extracted with ether, and the dried extract was fractionated. The final 3 ml. when warmed with dinitrophenylhydrazine in aqueous alcohol yielded acetophenone dinitrophenylhydrazone, m. p. an mixed m. p. 237°. The purified cumene used for the irradiation gave no similar reaction.

(b) *With chloranil.* The quinone (2 g.) in cumene (35 ml.) was irradiated for 30 days. When the bulb was broken hydrogen chloride escaped. The solid which had separated (1·3 g.) proved to be tetrachloroquinol (m. p. and mixed m. p. 236°; dibenzoate, m. p. and mixed m. p. 238°). After evaporation of the cumene the small residue (0·5 g.) was fractionated through alumina but gave no pure products. Permanganate oxidation, as above, of the cumene distillate established the presence of α-methylstyrene.

The hydrogen chloride formed in another experiment was estimated after absorption in water. The amount corresponded to the abstraction of one chlorine atom from about 25% of the chloranil.

(c) *With* 1 : 4-*naphthaquinone.* The quinone (2 g.) in cumene (35 ml.) was irradiated for 21 days. The blackish solid which separated (0·85 g.), when rubbed with benzene gave 1 : 4-dihydroxynaphthalene (0·5 g.; needles, m. p. and mixed m. p. 191°, from toluene; dibenzoate, m. p. and mixed m. p. 169°). The filtrate on evaporation gave naphthaquinhydrone (0·1 g.) which on reductive acetylation yielded 1 : 4-diacetoxynaphthalene, m. p. 128°. Permanganate oxidation of the cumene established the presence of α-methylstyrene.

Irradiations with Tetralin.—The tetralin, which had been fractionated through a 50-plate column (by Imperial Chemicals Limited, Billingham), was shaken with 98% sulphuric acid, sodium hydrogen carbonate solution, and water, and then refractionated over sodium: it had b. p. 206°.

(a) *With phenanthraquinone.* The quinone (2 g.) in tetralin (50 ml.) was irradiated for 18 days. Phenanthraquinhydrone separated (0·35 g.) and was identified as above. Evaporation of the tetralin left an amorphous residue. Bromination of the distillate with 10% solution of bromine in chloroform at 0° until the colour no longer faded rapidly (about 0·4 ml. of bromine required) and subsequent removal of solvents yielded 1 : 2-dibromo-1 : 2 : 3 : 4-tetrahydronaphthalene (0·7 g.; m. p. and mixed m. p. 71° after crystallisation from ligroin) (Found: Br, 55·1. Calc. for $C_{10}H_{10}Br_2$: Br, 55·2%).

(b) *With chloranil.* The quinone (2 g.) in tetralin (50 ml.) was irradiated for 39 days. When the bulb was broken hydrogen chloride escaped. Separated tetrachloroquinol (1 g.) was identified as above and more (0·15 g.) was obtained by evaporation of the solvent. On bromination this distillate gave dibromotetralin (0·5 g.).

(c) *With* 1 : 4-*naphthaquinone.* The quinone (2 g.) in tetralin (30 ml.) was irradiated for 21 days. Dihydroxynaphthalene (1·05 g.) separated and was identified as above. The filtrate on evaporation and bromination gave dibromotetralin (0·3 g.).

Irradiations with p-*Xylene.*—(a) *With phenanthraquinone* (*compare Benrath and von Meyer,* loc. cit.). The quinone (2 g.) in *p*-xylene (30 ml.) was irradiated for 18 days. After evaporation of the solvent, the residue was chromatographed on alumina. Ligroin eluted 1 : 2-di-*p*-tolylethane (0·2 g.), plates, m. p. 81°, from aqueous ethanol (Found : C, 90·9; H, 8·7. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%). The m. p. was not depressed by admixture with an authentic specimen prepared by persulphate oxidation of *p*-xylene (Moritz and Wolffenstein, *Ber.*, 1899, **32**, 433, 2531). Chloroform eluted a gum which when rubbed with alcohol gave 9-hydroxy-10-*p*-methylbenzyloxyphenanthrene (1 g.). This crystallised from alcohol or ligroin in pale yellow prisms, m. p. 128—129° (Found : C, 84·0; H, 5·7. Calc. for $C_{22}H_{18}O_2$: C, 84·1; H, 5·7%), and its infra-red spectrum showed characteristic bands at 2·88 μ for H–O stretching and at 5·96 μ for conjugated C=O stretching. The compound failed to react with an ethereal solution of diazomethane.

(b) *With chloranil.* The quinone (2 g.) in *p*-xylene (25 ml.) was irradiated for 40 days. When the bulb was broken hydrogen chloride escaped. The separated solid (0·12 g.) crystallised from acetic acid in needles, m. p. 236° undepressed by admixture with tetrachloroquinol. Evaporation of the *p*-xylene and treatment of the residue with ligroin gave 2 : 3 : 5 : 6-*tetrachloro*-4-p-*methylbenzyloxyphenol* (1·8 g.) which crystallised from acetic acid in needles, m. p. 125° (Found : C, 47·7; H, 2·8; Cl, 39·7. $C_{14}H_{10}O_2Cl_4$ requires C, 47·7; H, 2·8; Cl, 40·3%). It was soluble in cold alkali, gave no colour with alcoholic ferric chloride and no reaction with dinitrophenylhydrazine. The infra-red spectrum showed the characteristic H–O stretching band at 2·94 μ but no carbonyl band. The *acetate* crystallised from aqueous alcohol in needles, m. p. 106° (Found : C, 48·5; H, 3·1; Cl, 36·3. $C_{16}H_{12}O_3Cl_4$ requires C, 48·7; H, 3·1; Cl, 36·0%). Methylation of the monoether (0·4 g.) at 0° for 24 hr. with diazomethane (from 1 g. of nitrosomethylurea) gave 2 : 3 : 5 : 6-*tetrachloro*-4-p-*methylbenzyloxyphenylmethyl ether*, needles, m. p. 153° (from ethanol) (Found : C, 49·9; H, 3·2; Cl, 38·3. $C_{15}H_{12}O_2Cl_4$ requires C, 49·2; H, 3·3; Cl, 38·8%).

(c) *With* 1 : 4-*naphthaquinone.* The quinone (2 g.) in *p*-xylene (30 ml.) was irradiated for 16 days. 1 : 4-Dihydroxynaphthalene (1·2 g.) separated and was identified as above. After evaporation of the solvent the residue was methylated with diazomethane, and the product was fractionated on alumina. Ligroin eluted 1 : 2-di-*p*-tolylethane (0·05 g.), m. p. 81°, and following this chloroform eluted a gum which when rubbed with alcohol gave 1-*methylnaphthaquinono*(2′ : 3′-3 : 4)*pyrazole* (0·1 g.), small needles, m. p. 176°, from alcohol (Found : C, 68·0; H, 3·8; N, 13·2. $C_{12}H_8O_2N_2$ requires C, 67·9; H, 3·8; N, 13·2%). Its infra-red spectrum showed the characteristic band at 5·95 μ indicative of conjugated C=O, but no band indicative of N–H. The compound was insoluble in alkali. It was also obtained (i) by the action of diazomethane (from 4 g. of nitrosomethylurea) on 1 : 4-dihydroxynaphthalene (0·5 g.) in ether at 0° (yield 0·35 g.), and (ii) by the action of diazomethane on naphthaquinono-(2′ : 3′-3 : 4)-pyrazole (Fieser and Peters, *loc. cit.*) in dioxan–ether solution.

(d) *With* p-*benzoquinone.* The quinone (2 g.) in *p*-xylene (30 ml.) was irradiated for 9 days. Quinhydrone (1·1 g.) separated as a black solid which on reductive acetylation gave quinol diacetate, m. p. and mixed m. p. 122°. After evaporation of the *p*-xylene the residue gave no crystalline products.

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