64. *Some Decompositions of Triphenylphenylazomethane in Presence of Quinones.*

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The reaction of triphenylphenylazomethane with *p*-benzoquinone to give 2-phenyl-1 : 4-benzoquinone and quinol bistriphenylmethyl ether has been confirmed. 1 : 4-Naphthaquinone gives 2-phenyl-1 : 4-naphthaquinone, but there is no significant attack on phenanthraquinone, chloranil, toluquinone, or 2 : 5-diethoxy-1 : 4-benzoquinone. The reaction may be heterolytic.

Wieland (*Annalen*, 1934, **514**, 157) reported that the decomposition of triphenylphenylazomethane in a benzene solution of *p*-benzoquinone yields quinhydrone, 2-phenylbenzoquinone, and quinol bistriphenylmethyl ether :

$$2\text{Ph}\cdot\text{N:N}\cdot\text{CPh}_3 + 5\text{C}_6\text{H}_4\text{O}_2 \longrightarrow \text{Ph}_3\text{C}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CPh}_3 + 2\text{Ph}\cdot\text{C}_6\text{H}_3\text{O}_2 + (\text{C}_6\text{H}_6\text{O}_2,\text{C}_6\text{H}_4\text{O}_2)$$

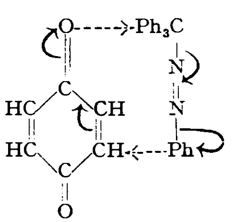
In this reaction the active phenyl radical substitutes hydrogen in the quinone nucleus and the displaced hydrogen reduces a portion of the quinone, whilst the less active triphenylmethyl radicals add to the oxygen atoms of the quinone. Nuclear substitution of quinones by free radicals can also be effected by the use of diacyl peroxides (Fieser and Oxford, *J. Amer. Chem. Soc.*, 1942, **64**, 2060; Fieser and Turner, *ibid.*, 1947, **69**, 2338) and may be involved in the reactions between quinones and aromatic diazo-compounds (Kvalnes, *ibid.*, 1934, **56**, 2478). Bickel and Waters (*J.*, 1950, 1764), however, found that the feebly active 2-cyano-2-propyl and 2-carbomethoxy-2-propyl radicals react with *p*-benzoquinone to form only the mono- and di-ethers of quinol. Since different free radicals appear to react in different ways with quinones it was decided to check and extend Wieland's observations.

Wieland's reaction yielded a small amount of diphenyl in addition to the substances described by him, indicating that the reaction between phenyl radicals and the solvent described by Hey (*J.*, 1934, 1966) proceeds concurrently with the attack on the quinone. Phenyl ethers of quinol were searched for but could not be detected.

From each of the decompositions, under nitrogen, of benzene solutions of triphenylphenylazomethane in the presence of chloranil, *p*-toluquinone, 2 : 5-diethoxy-1 : 4-benzoquinone, and 9 : 10-phenanthraquinone about 10—15% of the phenyl radicals generated by the azo-compound were recovered as diphenyl; 30—50% of the triphenylmethyl radicals were recovered as triphenylmethyl peroxide, indicating that they had remained largely unchanged until oxygen was admitted in working up the reaction product, for, unlike Hey who performed the decompositions in solution with no other solutes present, we did not continue the heating of our reaction mixture until the destruction of triphenylmethyl was complete. No derivatives of any of these quinones could be isolated; recoveries of unchanged material ranged from 50 to 90% even when the azo-compound was used in excess.

On account of the low solubilities of these quinones in benzene these reactions had to be conducted in dilute solution; this would favour reactions of the free radicals with the solvent, but nevertheless *p*-benzoquinone itself was attacked at a comparable molar concentration. All these quinones are readily attacked, on oxygen, by 2-cyano-2-propyl radicals (Lopez Aparicio and Waters, *J.*, 1952, 4666).

However, the decomposition of triphenylphenylazomethane in a benzene solution of 1 : 4-naphthaquinone does also lead to the formation of a quinhydrone, substantially that of unsubstituted naphthaquinone, and also of some 2-phenyl-1 : 4-naphthaquinone. Triphenylmethane and triphenylmethyl peroxide have also been isolated, but no definite evidence of the formation of a triphenylmethyl ether has been obtained. It may be significant that 1 : 4-naphthaquinone is easily alkylated in the nucleus by diacyl peroxides and that it is the only quinone with which direct nuclear attack by 2-cyano-2-propyl radicals has been observed (Lopez Aparicio and Waters, *loc. cit.*). From our experiments it was noticeable that nuclear phenylation occurs only when a portion of the quinone is reduced to quinhydrone. This reduction may be an essential feature of the reaction mechanism, and the results would then be consistent with the view that a bimolecular heterolytic reaction between triphenylphenylazomethane and quinone accompanies the unimolecular homolysis of the azo-compound. This leads to nuclear phenylation and cationoid triphenylmethyl attack on oxygen, not necessarily on the same quinone molecule.



The scheme resembles that used for explaining the Thiele acetylation of quinones, and it may be noted that the inactive quinones do not readily undergo this acetylation reaction. An analogous heterolytic decomposition of an unsymmetrical diacyl peroxide has been described by Leffler (*J. Amer. Chem. Soc.*, 1950, **72**, 67). This heterolytic reaction may become evident only when a sufficiently reactive catioenoid system is available to allow the bimolecular process to proceed much more rapidly than the normal homolysis.

EXPERIMENTAL

The decomposition of triphenylphenylazomethane in the presence of *p*-benzoquinone was carried out in benzene solution under nitrogen at 70° as described by Wieland (*loc. cit.*). From 6·3 g. (0·018 mole) of azo-compound, 5·4 g. of benzoquinone (0·05 mole) and 50 c.c. of benzene there were obtained, in three experiments, 0·77, 0·82, and 0·80 g. of quinhydrone, m. p. 110°, and 1·77, 1·85, and 1·83 g. of quinol bistriphenylmethyl ether, m. p. 230—233° (decomp.) (Schmidlin, *Ber.*, 1910, **43**, 1300, gives m. p. 235°; Wieland gives 230°) (Found: C, 88·8; H, 5·5. Calc. for $C_{44}H_{34}O_2$: C, 88·8; H, 5·8%). In a separate experiment the crude product was steam-distilled after the solvent and quinhydrone had been removed. Unchanged benzoquinone (0·86 g.) was recovered, together with an oil (0·22 g.) which was nitrated at 100° with nitric acid–acetic acid, yielding 4-nitrodiphenyl, m. p. and mixed m. p. 110—112°. Attempts to separate other reaction products by chromatographic methods were not successful. In a later experiment half the above quantities of solids were allowed to interact in 250 c.c. of benzene, whereupon in spite of this ten-fold dilution there were obtained 0·37 g. of quinhydrone, 0·04 g. of 2-phenyl-*p*-benzoquinone, and 0·8 g. of the quinol diether.

Decomposition of Triphenylphenylazomethane in Presence of 1 : 4-*Naphthaquinone*.—Freshly prepared 1 : 4-naphthaquinone (4·54 g., 0·029 mole) was dissolved in dry benzene (25 c.c.) and heated to 70° under oxygen-free nitrogen, and a solution of the azo-compound (4·0 g., 0·0115 mole) in benzene was added in small portions during 30 min. so as to minimise radical–radical interactions. The colour of the solution changed from yellow to dark brown as the reaction proceeded and, on cooling, purple-blue crystals (0·3 g.) separated. After being washed with benzene these had m. p. 162° (decomp.) [the quinhydrone of 1 : 4-naphthaquinone has m. p. 175° (decomp.); that of 2-phenylnaphthaquinone has m. p. 136°]. This quinhydrone in ether was shaken with acid aqueous ferric chloride; the ethereal layer on evaporation then gave semi-crystalline material, which after recrystallisation from ethanol gave 1 : 4-naphthaquinone, m. p. and mixed m. p. 124—125°. Another portion was reductively acetylated and yielded colourless needles of 1 : 4-diacetoxynaphthalene, m. p. and mixed m. p. 128—130°.

The filtrate from the quinhydrone was evaporated almost to dryness and the residue was extracted with hot light petroleum (b. p. 60—80°; 70 c.c.). This solution was concentrated to 20 c.c., diluted with an equal volume of ethanol, and set aside, whereupon colourless crystals (0·05 g.) separated. On crystallisation from benzene–light petroleum (1 : 1) these proved to be bistriphenylmethyl peroxide, m. p. and mixed m. p. 186° (decomp.). Identity was confirmed by comparison of its infra-red spectrum with that of an authentic specimen prepared from triphenylmethyl chloride.

The filtrate from the peroxide was treated with twice its volume of ethanol and set aside. Yellow needles (0·32 g.) separated which after crystallisation from ethanol proved to be 2-phenyl-1 : 4-naphthaquinone, m. p. and mixed m. p. 110° (Found: C, 82·1; H, 4·30. Calc. for $C_{16}H_{10}O_2$: C, 82·2; H, 4·3%).

In a second experiment the quinhydrone (0·28 g.) was removed as described above and the solution was then concentrated to 20 c.c. and cooled. A brown solid (0·32 g.) separated, which after crystallisation from ethanol proved to be unchanged naphthaquinone, m. p. and mixed m. p. 124°. The remaining liquid was evaporated to dryness and then distilled in steam, yielding 0·06 g. of triphenylmethane, m. p. and mixed m. p. 92°.

In a third experiment the solution, after removal of the quinhydrone, was diluted with light petroleum (b. p. 60—80°) and passed down an alumina column. The first eluate yielded tetraphenylmethane (0·07 g.), m. p. and mixed m. p. 285°, and then followed triphenylmethane (0·26 g.), m. p. and mixed m. p. 94° (from ethanol). Extraction with benzene–light petroleum (3 : 1) gave 2-phenyl-1 : 4-naphthaquinone, m. p. and mixed m. p. 109° (from ethanol), but subsequent elution gave no pure products.

Decompositions in Presence of Other Quinones.—(*a*) A solution of the azo-compound (6 g.) in benzene (20 c.c.) was added in portions during 30 min. to a solution of chloranil (4·24 g., 1 mol.) in benzene kept at 70° under nitrogen. When gas evolution had ceased, the solution was boiled for 5 min. to complete the reaction. After evaporation of most of the benzene under nitrogen the remaining liquid was extracted with alkaline sodium dithionite solution to remove unchanged chloranil and then concentrated under nitrogen, yielding a mobile gum. Treatment of this with ether separated bistriphenylmethyl peroxide (1·3 g.). After crystallisation from benzene–light petroleum (b. p. 80—100°; 1 : 1) this had m. p. 186° (decomp.) and an infra-red spectrum identical with that of an authentic specimen (Found : C, 87·5; H, 5·8. Calc. for $C_{38}H_{30}O_2$: C, 88·0; H, 5·8%). The remaining gum was steam-distilled and yielded diphenyl (0·3 g.) which was identified as its 4-nitro-derivative, m. p. and mixed m. p. 112°. The total recovery of unchanged chloranil was 90%, and when the quantities of azo-compound and chloranil were changed to 3 g. and 1 g. respectively remained as high as 75%.

(*b*) From a similar reaction of 4 g. of azo-compound with 6 g. of phenanthraquinone in 350 c.c. of benzene, 5·5 g. of quinone were recovered together with 1·0 g. of bistriphenylmethyl peroxide and 0·25 g. of diphenyl.

(*c*) From 0·9 g. of toluquinone and 5 g. (2 mol.) of azo-compound there were recovered 0·44 g. of unchanged quinone, 1·8 g. of peroxide, and 0·25 g. of diphenyl. Chromatographic separation of other products was not successful.

(*d*) From 2·83 g. of 2 : 5-diethoxy-1 : 4-benzoquinone, m. p. 184° (Knoevenagel and Bückel, *Ber.*, 1901, **34**, 3994), and 2 g. of the azo-compound in 60 c.c. of benzene, 1·88 g. (67%) of unchanged quinone were recovered. Chromatography of the remainder led to the isolation of 0·06 g. of triphenylmethane and 0·87 of bistriphenylmethyl peroxide. From another experiment 0·09 g. of diphenyl was recovered by steam-distillation.

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