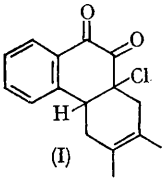
# The Reactions of 3-Chloro-1,2-naphthaquinone and Phenanthrene-9,10-diol with Dimethylbutadiene

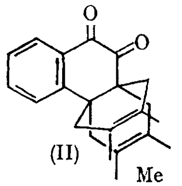
By M. F. ANSELL* and R. A. MURRAY

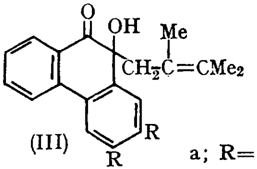
(*Department of Chemistry, Queen Mary College, Mile End Road, London E.*1)

THE reaction of 3-chloro-1,2-naphthaquinone and dimethylbutadiene has been reported by Fieser and Dunn[1] to give a 1 : 1 adduct, assigned structure (I), which may react with more diene to yield the "further reaction product" (A) which was assigned the structure (II). We have repeated these reactions obtaining the same products and have confirmed the structure of the 1 : 1 adduct.

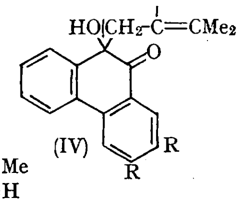
However, from its spectral properties the product (A) has either structure (IIIa) or (IVa) or is a mixture of compounds of these structures.

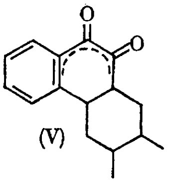

(I)

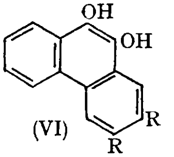

(II)


(III)

a; R=Me
b; R=H


(IV)


(V)


(VI)

The structure of the 1 : 1 adduct (I) is confirmed by its infrared spectrum which shows absorption at 1690 and 1745 cm.$^{-1}$ attributable to the presence of a conjugated and a non-conjugated carbonyl group and its n.m.r. spectrum ($CDCl_3$) which shows the presence of four aromatic protons ($\tau$ 1·9—2·9, multiplet), the 4a-proton (6·32, pair of doublets $|J|$ 6 and 12 c./sec.), four allylic protons (6·6—8·2, multiplet), and the 2- and 3-methyl groups (8·30 and 8·47, singlets). This adduct on heating with dimethylbutadiene yields the "further product" reported by Fieser and Dunn[1] which has the composition of a 1 : 2 adduct less the elements of hydrogen chloride. It cannot have the structure (II) as it exhibits OH absorption at 3490 and a conjugated carbonyl absorption at 1680 cm.$^{-1}$. Further its n.m.r. spectrum shows the presence of six aromatic protons ($\tau$ 2·15—2·85, multiplet), a hydroxy-proton (lost on deuteriation) (6·02), a methylene group (7·25 and 7·66, AB quartet $|J|$ 14 c./sec.), two aromatic methyl groups (7·63 and 7·70), two vinyl methyl groups (8·50), and another vinyl methyl group (8·72). These spectral data lead to the assignment of structure (IIIa) or (IVa) to the product. That the product is a mixture of both of these compounds is possible from its method of formation, which we consider involves the initial elimination of hydrogen chloride from the 1 : 1 adduct to give the dihydrodimethylphenanthraquinone (V) which undergoes an intra- or inter-molecular oxidation reduction to 2,3-dimethylphenanthrene-9,10-diol (VIa) followed by acid-catalysed addition of dimethylbutadiene.

The evidence for this route is that the adduct A when heated in chloroform solution in a sealed n.m.r. tube yields 2,3-dimethylphenanthrene-9,10-diol (VIa) (in the presence of air 2,3-dimethyl-9,10-phenanthraquinone is formed). This 9,10-diol when heated in chloroform solution with dimethylbutadiene in the presence of hydrogen chloride yields a product identical with the product A. Since this final addition may occur at either the 9- or the 10-position, and the dissymmetry of the molecule due to methyl groups at the 2- and the 3-positions is far removed from the reaction centre, we consider that compound A is a mixture of compounds (IIIa) and (IVa) which would have essentially identical n.m.r. and i.r. spectra.

We have found that the analogous acid-catalysed reaction of phenanthrene-9,10-diol (VIb) yields the adduct (IIIb) quantitatively. This compound, m.p. 91—94°, is identical with that obtained by Farid[2] from the photochemical reaction of 9,10-phenanthraquinone and tetramethylethylene. Although such hydroxy-phenanthrones have been previously prepared from phenanthraquinone by the use of Grignard reagents (*e.g.*, $PhCH_2MgBr$[3] or in our own hands $CH_2{=}CH{\cdot}CH_2MgBr$), base-catalysed reactions[4] (*e.g.*, with $MeNO_2$ + KOH) or photochemically,[2,3] as far as we are aware they have not been previously prepared by acid-catalysed reactions from phenanthrene-9,10-diol.

We thank the S.R.C. for a Research Studentship.

(*Received, September* 26*th*, 1968; *Com.* 1315.)

---

[1] L. F. Fieser and J. T. Dunn, *J. Amer. Chem. Soc.*, 1937, **59**, 1016, 1021.
[2] S. Farid and K. H. Scholz, *Chem. Comm.*, 1968, **412**; and personal communication.
[3] M. R. Rubin and P. Zwitkowits, *J. Org. Chem.*, 1964, **29**, 2362.
[4] A. I. Yakubovich, *J. prakt. Chem.*, 1935, **142**, 37.