

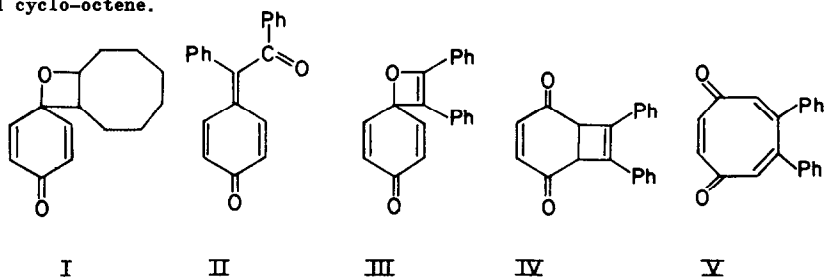
A Photoadduct of p-Benzoquinone and Diphenylacetylene

By D. Bryce-Smith, G.I. Fray and A. Gilbert

(Chemistry Department, The University,
Reading, England)

(Received 15 June 1964)

The photoaddition of p-quinones to olefins has recently been reported as a widely-applicable reaction.¹ The products in general are spiro-oxetanes, e.g. the adduct (I) is formed in virtually quantitative yield from p-benzoquinone and cyclo-octene.

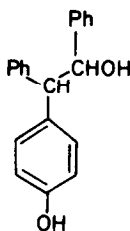


Chloranil forms oxetanes, but addition to its ethylenic bonds can also occur.² We now report that diphenylacetylene readily forms a photo-adduct with p-benzoquinone having the fuchsone-like structure (II). Feasible alternative structures such as (IV) and (V) derived from addition to an ethylenic bond in the quinone have been ruled out.

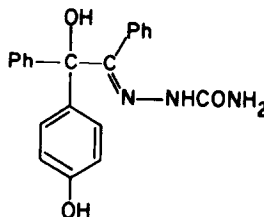
In a typical experiment, a solution of p-benzoquinone (5.0g.) and diphenylacetylene (12.0g.) in benzene (180 ml.) was irradiated under air in a borosilicate glass flask for 18 hr. at 38-42° at a distance of 12 cm. from an Hanovia S-500 medium pressure mercury lamp. The adduct (II), 1'-phenyl-1'-benzoyl-1-methylenecyclohexa-2,5-dien-4-one, (7.9 g., 60% yield) formed yellow hexagonal plates, m.p. 104°: much of the starting materials remained, and the true yield was probably almost quantitative. Found: C, 83.9; H, 4.9; M (mass spectrum), 286.

Calc. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9; \bar{M} , 286. This adduct was also readily prepared in sunlight in high yields. The ultraviolet spectrum had $\lambda_{\text{max.}}$ (ϵ) 207 $m\mu$ (14,200), 244.5 $m\mu$ (14,500), 301 $m\mu$ (13,750) (shoulder), and 332 $m\mu$ (16,650). This rules out structures (III) and (IV). Structure (IV) was also inconsistent with the n.m.r. spectrum (proton ratios 2:10:2, bands centered at τ 2.8, 3.3, and 3.8 respectively).

Catalytic hydrogenation of the adduct (Adams catalyst, or 10% Pd on C) led to the consumption of only 2 mol. of hydrogen (no discontinuity at the 1-mol. stage), and the quantitative formation of the phenol (VI), m.p. 190°, having the correct elemental analysis.



(VI)



(VII)

Structure (V) for the adduct was thereby eliminated. Structure (VI) for the hydrogenated product was established by its typical phenolic reactions (solubility in aqueous NaOH, and formation of an orange dye with benzenediazonium chloride), the formation of a diphenylurethane, m.p. 96°, with phenyl isocyanate, and the n.m.r. spectrum (proton ratios 1:2:10:2:1:1:1 at τ values 1.95, 2.67, 2.83, 3.24, 4.48, 5.78, and 5.97 respectively, assigned to phenolic OH, aromatic H, aromatic H, aromatic H, >C-H , >C-H , and aliphatic OH: the first and last peaks were absent from the spectrum in D_2O , and from the spectrum of

the diacetate, m.p. 122°).

The adduct (II) reacted with semicarbazide in the pH range 7.5 -10 to form the colourless phenol (VII), m.p. 193°, which gave yellow solutions at pH > 10. The adduct (II) was fairly stable to cold aqueous and alcoholic potassium hydroxide, but was rapidly decomposed by ethanolic HCl to give benzoic acid and p-hydroxybenzoic acid. Oxidation with KMnO_4 in refluxing acetone gave benzil (mixed m.p. and infrared spectrum) and benzoic acid. The adduct (II) is thermally very stable, and distilled unchanged from a bath at 350°.

The formation of the adduct can be rationalised in terms of an unstable intermediate oxetene (III). Oxetenes have been postulated as intermediates in the addition of dec-5-yne to certain aldehydes and ketones.³ Investigation of the mechanism and scope of the present reaction is continuing.

We thank Drs. J. B. Davis and D. A. Wilson for valuable assistance with the n.m.r. spectra, and for preparing the diacetate of compound (VI), D.S.I.R. for a maintenance grant (to A. G.), Esso Research Ltd. for laboratory facilities, and Professor Howard Zimmerman for suggesting the synchronous publication of his and our work in this area.

References

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