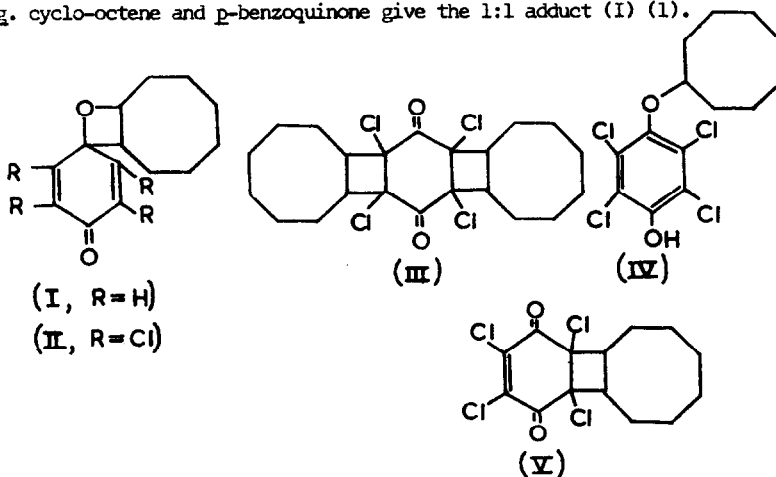


1:1- AND 2:1-PHOTOADDITION OF CYCLO-OCTENE AND
CYCLO-OCTA-1,5-DIENE TO CHLORANIL

By D. Bryce-Smith and A. Gilbert
(Chemistry Department, The University, Reading, England)

(Received 29 September 1964)

We recently reported that various mono-olefins and unconjugated polyolefins readily form spiro-oxetans by photoaddition to *p*-quinones, e.g. cyclo-octene and *p*-benzoquinone give the 1:1 adduct (I) (1).



Apart from dimerisation reactions (2), no definite example is known of the formation of a cyclobutane by 1,2-photoaddition of a *p*-quinone to an ethylenic bond (for a possible unestablished example see ref.2a).

We report now that irradiation of cyclo-octene and an excess of chloranil in benzene gives the expected oxetan (II) as the main product. On the other hand, the use of equivalent proportions of the reactants or, particularly, an excess of cyclo-octene gives a new

2:1 adduct having structure (III).

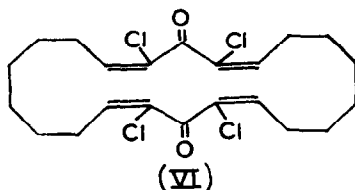
Thus irradiation of a solution of cyclo-octene (300 ml.) and chloranil (20 g.) in benzene (150 ml.) in a borosilicate glass flask at 30° for 64 hr. (Hanovia S-500 medium pressure mercury lamp) gave 4.8 g. of the colourless crystalline ether-insoluble 2:1-adduct (III), m.p. 235°, and 4.4 g. of the 1:1-adduct (II) as an orange-yellow oil, b.p. 189-191°/0.05 mm.: 14 g. of unchanged chloranil was recovered.

The evidence for structure (II) for the 1:1-adduct is as follows. The infrared spectrum showed a carbonyl stretching frequency at 1675 cm.⁻¹ consistent with the presence of conjugated carbonyl, and also a strong peak at 965 cm.⁻¹ which seems to be diagnostic for oxetans (3) and has been observed in the spectrum of each member of two series of spiro-oxetans. (1,4) The ultra-violet spectrum showed λ_{\max} 262 m μ ($\epsilon=6,500$) consistent with the dienone chromophore. Catalytic hydrogenation of the 1:1-adduct using 10% Pd on C consumed 1.0 mol. of hydrogen and gave a phenol (IV), m.p. 190°. This phenol was shown to be monohydric by the formation of a mono- α -naphthylurethane, m.p. 194-195°. This evidence excludes the alternative structure (V) for the 1:1-adduct.

Structure (III) for the 2:1-adduct is based on the following evidence. The infrared spectrum showed unconjugated carbonyl absorption at 1720 cm.⁻¹, and no significant peaks in the 965 cm.⁻¹ region. Its ultraviolet spectrum in cyclohexane had λ_{\max} 295 m μ ($\epsilon=45$), and no other peak at wavelengths longer than 210 m μ , in agreement with the unconjugated structure (III). The parent peak in the mass spectrum was at $m/e = 466$ (calc. $M = 466$), and peaks corresponding to the loss of one, two, three, and four chlorines were present.

It was considered probable that the 2:1-adduct (III) would be capable of valence-bond isomerisation to the C₂₂ macrocyclic

compound (VI), and preliminary work indicates that this is so. In refluxing tetralin, the 2:1-adduct forms a deep yellow air-sensitive oil. The ultraviolet spectrum has λ_{\max} 246 m μ (ϵ -20,000), which is



consistent with the presence of two electronically isolated dienone chromophores. The infrared spectrum differs substantially in general from that of the precursor (III). The carbonyl stretching frequency is shifted to 1677 cm^{-1} , as required by the conjugated structure (VI). This new approach to the synthesis of macrocyclic compounds is now under detailed investigation.

Cyclo-octa-1,5-diene shows closely parallel behaviour to that of cyclo-octene in all the reactions here reported.

This work has been carried out during the tenure of a D.S.I.R. Studentship (by A. Gilbert).

REFERENCES

1. D. Bryce-Smith and A. Gilbert, Proc.chem.Soc., 87 (1964).
2. (a) R.C. Cookson, D.A. Cox and J. Hudec, J.chem.Soc., 4499 (1961), [cf. R.C. Cookson and J. Hudec, Proc.chem.Soc., 11 (1959)]; (b) W. Flaig, J.C. Salfeld and A. Llanos, Angew.Chem., 72, 110 (1960); (c) D. Bryce-Smith and A. Gilbert, J.chem.Soc., 2428, (1964).
3. R. Guepet, J. Seyden-Penne, P. Pigonial and P. Chabrier, Bull.Soc.Chim. France, 2081 (1961).
4. S. Searle, E.F. Lutz and M. Tamres, J.Amer.Chem.Soc., 82, 2932 (1960).