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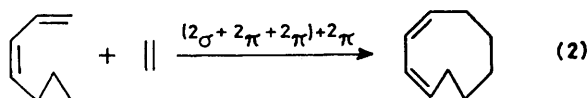
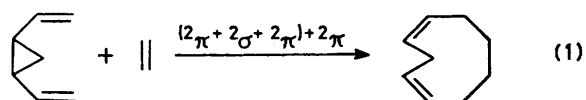
1,7-Cycloadditions of Dichlorodicyano-*p*-benzoquinone and Tetracyanoethylene to a Dienylcyclopropane

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Summary A novel $[(2\sigma + 2\pi + 2\pi) + 2\pi]$ cycloaddition is described.

THE recent report¹ of 1,7-cycloadditions of tetracyanoethylene (TCNE) to divinylcyclopropane systems represented by equation (1) prompts us to describe our related observations of the isoelectronic 1,7-cycloaddition represented by equation (2).

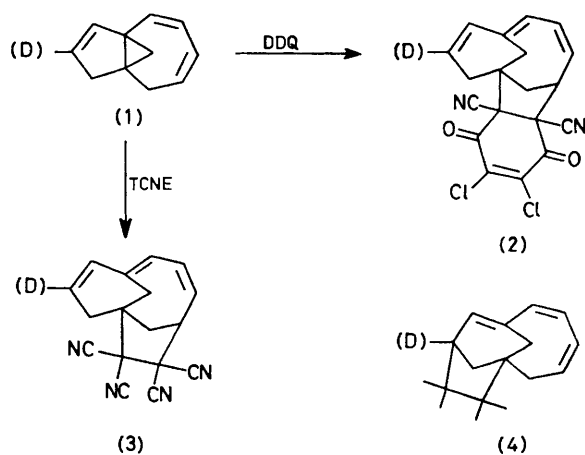


(The carbon skeleton only of each compound is presented.)

In the course of our work on the synthesis of 1,5-methano-[10]annulene,² we attempted to dehydrogenate tricyclo-[5.3.1.0^{1,7}]undeca-2,4,9-triene (1) with 1 equiv. of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). After 2 h at room temp. a 1:1 adduct (2) was isolated in 50% yield. An analogous adduct (3) was obtained in 87% yield from the reaction of (1) with TCNE (2 h; room temp.; tetrahydrofuran).

The structures of the cycloadducts (2) and (3) (stereochemistry unknown) followed from their ¹H n.m.r., i.r., u.v., and mass spectra and from deuterium labelling studies. In particular, the lack of high-field ¹H n.m.r. signals shows the

absence of cyclopropane ring protons. There appears instead a pair of doublets at δ 2.14 and 3.34 (*J* 15 Hz) for the hydrogen atoms which originated from the cyclopropane ring in (2) and a similar pattern at δ 2.30 and 2.90 (*J* 15 Hz) for those in (3). The presence of a conjugated triene in each



was apparent from their u.v. spectra [(2): λ_{max} (CH₂Cl₂) 288 nm (ϵ 7000); (3): λ_{max} (EtOH) 298 (ϵ 8600) and 208 nm (7900)]. A simple Diels-Alder reaction is thus excluded.

The isomeric ring system (4), which could have arisen *via* 1,5-cycloaddition (homo-Diels-Alder reaction), was eliminated as an alternative to (2) and (3) by repeating both cycloadditions on specifically labelled [9-²H₁]tricyclo-[5.3.1.0^{1,7}]undeca-2,4,9-triene. The ¹H n.m.r. spectra of the two labelled adducts [²H₁]- (2) and - (3) differ from those of

the unlabelled adducts only by the absence of one *vinyl*-H signal.

The 1,7-cycloaddition of electron-deficient alkenes to a 1-homo-hexatriene (equation 2) is thus established and complements the corresponding 1,7-cycloaddition to 3-homo-hexatrienes (equation 1).

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¹ S. Sarel and M. Langbeim, *J.C.S. Chem. Comm.*, 1977, 593.

² L. T. Scott and W. R. Brunsvold, *J. Amer. Chem. Soc.*, 1978, **100**, in the press.