A Diene Synthesis with 2,3-Dichloro-5,6-dicyanobenzoquinone—an *X*-ray Study

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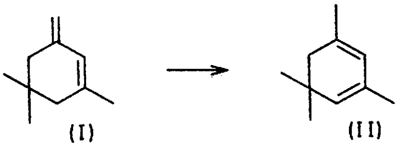
Summary 1,5,5-Trimethyl-3-methylenecyclohexene isomerises to 1,1,3,5-tetramethylcyclohexa-2,4-diene during the Diels–Alder reaction with DDQ; the side of the quinone molecule to which addition occurs and the stereochemistry of the adduct formed have been established by *X*-ray structure analysis.

2,3-DICHLORO-5,6-DICYANOBENZOQUINONE (DDQ) has been widely used as a dehydrogenating agent[1] but few examples of its use in diene synthesis are recorded. Addition of DDQ to 1,5,5-trimethyl-3-methylenecyclohexene was reported by Braude *et al.*[2] in 1961, but these authors were unable to establish to which side of the quinone molecule addition takes place. An *X*-ray structure analysis on the addition product has solved this problem, which was difficult to resolve by chemical and spectroscopic methods.

1,5,5-Trimethyl-3-methylenecyclohexene, prepared and first correctly characterised by Wheeler,[3] would not be expected to form the stable, crystalline adduct reported[2] which we obtained (80%) chromatographically pure (t.l.c.) after one recrystallisation. Data obtained for the diene (I) [λ_{max} (EtOH) 236 nm. (ϵ 10,320) with no maximum near 260 nm.] agreed well with reported values,[3] and the n.m.r. spectrum in CCl_4 showed a two-proton singlet at τ 5·41 p.p.m. attributable to the exocyclic methylene group. The structure of the adduct is consistent with the addition of

DDQ to 1,1,3,5-cyclohexa-2,4-diene (II) which probably forms during the reaction by the isomerisation following:



The adduct $C_{18}H_{16}Cl_2N_2O_2$ recrystallises from ethanol as rectangular prisms in the monoclinic space group $P2_1/n$ with $a = 9{\cdot}06 \pm 0{\cdot}03$, $b = 16{\cdot}10 \pm 0{\cdot}01$, $c = 12{\cdot}00 \pm 0{\cdot}01$ Å, $\beta = 96{\cdot}8° \pm 0{\cdot}1°$, $U = 1740$ Å^3, $D_c = 1{\cdot}39$ for $Z = 4$, $D_m = 1{\cdot}40$, $M = 363{\cdot}2$. Crystals of the optimum size (0·6 mm.) were used, and 955 reflections were obtained from Weissenberg photographs using Cu-K_α radiation.

The structure was solved by a reiterative sign determination process using a program[4] for centrosymmetric structures. The sign of 291 reflections with normalised structure amplitudes $|E| > 1{\cdot}1$ were determined, and a Fourier synthesis based on these reflections revealed all the atoms in the asymmetric unit. The two chlorine atoms were also found from a three-dimensional Patterson synthesis, and a Fourier synthesis phased on these atoms confirmed the structure. Refinement by the full-matrix least-squares method[5] with isotropic temperature parameters gave R as 0·18 which decreased to 0·13 (present value) on giving all atoms anisotropic temperature parameters. Certain atoms have marked anisotropic vibrations.

Addition of the diene occurs on the least hindered and most activated side of the quinone (see Figure), and the molecule has the expected stable *endo*-orientation.[6] Bond lengths are close to reported values[7] with the exception of bond C(4a)–C(8a) which is unexpectedly long. The dihydroquinone ring is distorted, probably because of a short intramolecular contact (3·00 Å) between O(4) and the methyl group C(11).

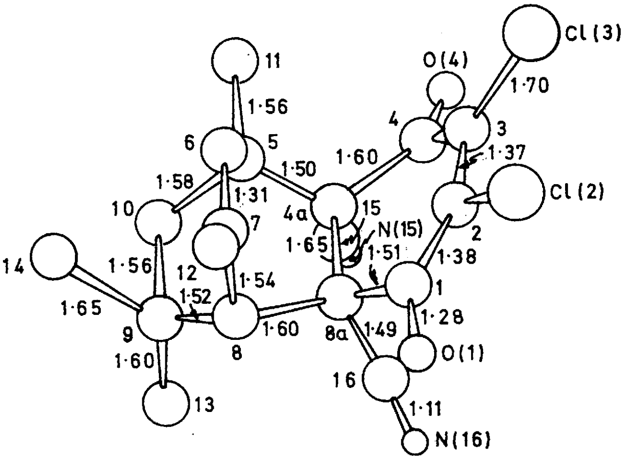


FIGURE. *Structure of the addition product projected on to a unit-cell plane. Carbon atoms are represented by numbers only; other elements have chemical symbols.*

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[2] E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *J. Chem. Soc.*, 1960, 3124.
[3] O. H. Wheeler, *J. Org. Chem.*, 1955, **20**, 1672.
[4] Centro-symmetric symbolic addition programme, O. J. R. Hodder, C. K. Prout, and J. S. Rollett, 1968.
[5] Autocode structure analysis programme, O. J. R. Hodder and J. S. Rollett, 1968.
[6] A. S. Onishchenko, "Diene Synthesis," Israel Program for Scientific Translations, Jerusalem, 1964, p. 37, and references therein.
[7] "Tables of Interatomic Distances," *Chem. Soc. Special Publ.*, *Nos.* 11 and 18, 1958 and 1965.