The Diels–Alder Addition of Dimethyl Vinylphosphonates to Cyclopentadienes: Stereochemistry of the Reaction using Nuclear Magnetic Resonance Spectroscopy

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Summary The configurations of the adducts of dimethyl vinylphosphonate with cyclopentadiene, hexachlorocyclopentadiene, dimethoxytetrachlorocyclopentadiene, and pentachlorocyclopentadiene are established by n.m.r.

DIELS–ALDER additions of vinylphosphonates to various cyclic dienes have been reported by several authors.[1,2] However, the stereochemistry of the reaction has not been fully elucidated, mostly due to the difficult separation of isomers.[2] In all reported examples, the adducts have only been characterized as mixtures. We report here preliminary results concerning the Diels–Alder addition of dimethyl vinylphosphonate, (I), to several cyclopentadienes. In all the cases, the isomers have been separated and characterized.

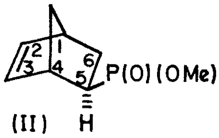
As expected from the usual behaviour of cyclopentadiene,[3] reaction with (I) leads to a mixture of isomers (II) and (III) in a 1·2 : 1 ratio,† separable by column chromatography. Their configurations follow from the examination of their n.m.r. spectra: as was shown by one of us,[4] the ^{31}P does not couple with the 4-H bridgehead proton in the *endo*-isomer (III) (90° dihedral angle relationship).

Addition of dimethyl vinylphosphonate to hexachlorocyclopentadiene gives only one compound, the *endo*-isomer (IV), in accordance with Alder's *endo*-rule.[3] The structure of this adduct has been proved by its total conversion (by sodium in MeOH–THF, a slight modification of a known procedure[5]) into the corresponding *endo*-cyclopentadiene-adduct (III).

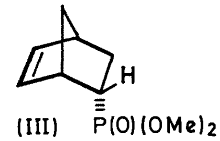
Similarly, treatment of 5,5-dimethoxytetrachlorocyclopenta-1,3-diene with (I) gives only one product, (V). The structure (V) is supported by the "*endo*-rule" and by the fact that the pattern displayed by the three ring protons in the n.m.r. spectrum is superimposable with the one shown by

$CH_2{=}CHP(O)(OMe)_2$

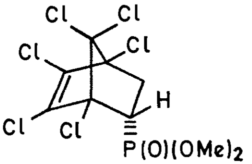
(I)



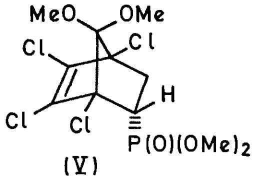
(II)



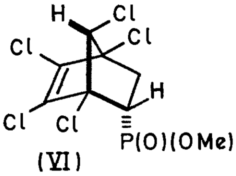
(III)



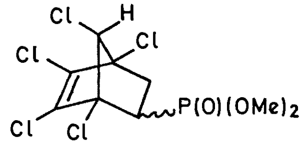
(IV)



(V)



(VI)



(VII)

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† A result quite comparable with the 1 : 1 ratio described by Daniewski and Griffin (ref. 2) for the reaction of $CH_2{=}CHP(O)(OEt)_2$ with cyclopentadiene.

‡ In compound (VII) the proton α to the phosphorus appears at higher field than the corresponding proton in compound (VI). It is known that *endo*-protons are usually more shielded than *exo*-protons (*cf.* ref. 7 and references cited therein). A third compound, tentatively assigned the *syn–endo* configuration, has been isolated in appreciable amount.

the corresponding protons in compound (IV). These results agree with those of Williamson,[6] concerning the adducts of hexachlorocyclopentadiene with various dienophiles. In all cases, only the *endo*-isomer was formed. A statement that the Diels–Alder addition of diethyl vinylphosphonate to hexachlorocyclopentadiene leads to both *endo*- and *exo*-isomers[2] is, therefore, probably incorrect.

The reaction of (I) with 1,2,3,4,5-pentachlorocyclopenta-1,3-diene leads to two compounds in the ratio 2 : 1. The respective structures (VI) and (VII) are assigned on the following basis. The n.m.r. of the major isomer (VI) shows a low-field proton (C*H*Cl, d of d) with two long-range **W**-type couplings; one with 6*n*-H [^4J (7–H, 6*n*-H) 1·5 Hz] the other with the phosphorus[4] [^4J (P, 7-H) 3·9 Hz as proved by phosphorus decoupling experiments]. Only structure (VI) is compatible with such a spectrum.

Part of the structure of compound (VII) may be deduced from the n.m.r. The 7-H appears as a sharp singlet (no long-range coupling) compatible with 7-*anti*-H. The configuration at the carbon bearing the dimethylphosphono-group is uncertain although the pattern displayed by the three ring protons, very different from the one observed in the case of the *endo*-compounds (IV), (V), and (VI) would suggest that the $(MeO)_2P(O)$ group is *exo*.‡ The formation of the predominant *anti-endo* compound (VI), although surprising, has precedent in a recent work by Williamson and Col.[7]

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[1] E. C. Ladd, U. S. P. 2,611,784/1952; *Chem. Abs.*, 1953, **47**, 9355 and U.S.P. 2,622,096/1952; *Chem. Abs.*, 1953, **47**, 9344; A. N. Pudovik, G. E. Yastrebova, V. I. Nikitina, and Yu. Yu. Samitov, *Zhur. obshchei Khim.*, 1968, **38**, 292; *Chem. Abs.*, 1968, **69**, 106815j.

[2] W. M. Daniewski and C. E. Griffin, *J. Org. Chem.*, 1966, **31**, 3236.

[3] J. Sauer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 16.

[4] C. Benezra, *Tetrahedron Letters*, 1969, 4471.

[5] P. G. Gassman and P. G. Pape, *J. Org. Chem.*, 1964, **29**, 160.

[6] K. L. Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 516.

[7] K. L. Williamson, Y.-F. Li Hsu, R. Lacko, and C. H. Youn, *J. Amer. Chem. Soc.*, 1969, **91**, 6129.