

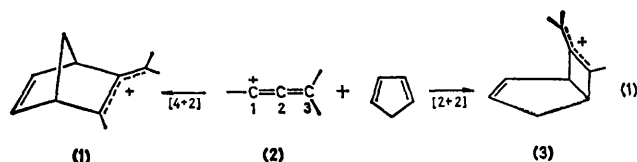
[2+2]-Cycloaddition of a Stabilised Vinyl Cation with Cyclopentadiene; X-Ray Crystal Structure of the 2:1 Addition Product

By HERBERT MAYR,* EBERHARD WILHELM, and CLAUS KALIBA

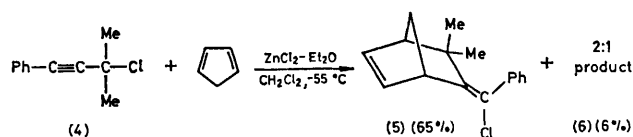
(Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg,
Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany)

Summary Lewis acid-catalysed reaction of 1,1-dimethyl-3-phenylprop-2-ynyl chloride with cyclopentadiene yields a 2:1 addition product *via* [2+2]-cycloaddition of an intermediate allenyl cation.

ACCORDING to Woodward and Hoffmann, vinyl cations are ' $\pi 2_a$ -components *par excellence*' for concerted [$\pi 2_s + \pi 2_a$]-cycloadditions.¹ In agreement with this concept, four-membered rings are formed from vinyl cations and alkynes² or alkenes.³ We now find that cyclopentadiene also undergoes [2+2]-cycloadditions with vinyl cations of type (2), even though the formation of less-strained products [equation (1)] seems to be feasible with 1,3-dienes.



We reported recently that $ZnCl_2$ -catalysed reactions of propargyl chlorides with cyclopentadiene yield bicyclic vinyl chlorides. These arise from initial attack of cyclopentadiene at C-3 of the intermediate allenyl cations (2).⁴ Allyl chlorides derived from (1) and (3) were not detected, in accord with our postulate that Lewis acid-catalysed addition reactions yield 1:1 products only if the adducts dissociate faster than the products.⁵ If allenyl cations (2) undergo vinyl cation type cycloadditions [equation (1)], the resulting allyl cations (1) and (3) are predicted⁵ to react with further cyclopentadiene to give higher addition products, since allyl chlorides solvolyse faster than their precursor propargyl chlorides.⁶



In fact, in addition to the previously reported 1:1 product (5),⁴ the reaction of (4) with cyclopentadiene afforded a fraction of high molecular weight from which the 2:1 product 4-chloro-2,2-dimethyl-7-phenylpentacyclo-

[6.3.1^{1,8}.1³.6.0^{1,7}.0^{6,12}]tridec-10-ene (6) (m.p. 106.5–108.0 °C) was isolated chromatographically. N.m.r. spectra show two vinylic carbon and hydrogen atoms, in accord with a variety of structures arising from two cycloaddition processes and a π -cyclization. Conclusive structural evidence was obtained from X-ray analysis.

Crystal data: (6), $C_{21}H_{23}Cl$, monoclinic, space group $P2_1/n$, $a = 8.187(2)$, $b = 15.405(3)$, $c = 25.826(4)$ Å, $\beta = 91.38(3)^\circ$, $Z = 8$. A total of 9056 reflections was measured on a Hilger & Watts Y290 diffractometer using Mo- K_α radiation. Averaging of symmetrically equivalent measurements yielded 3052 independent reflections. As $Z = 8$, there are two molecules in the asymmetric unit. The structure was solved automatically with the program system 'CRYSTAN'⁷ and refined by the block-diagonal least-squares method. The final R was 0.08 for 2253 reflections with $\theta \leq 18^\circ$.† The two molecules in the asymmetric unit are enantiomers. There are no significant geometrical differences between these two molecules.‡

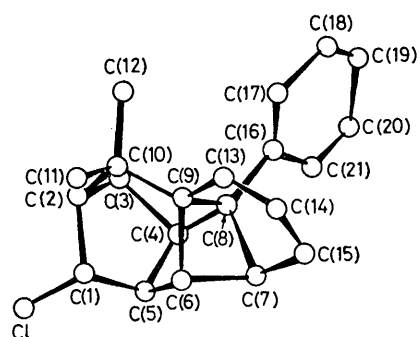
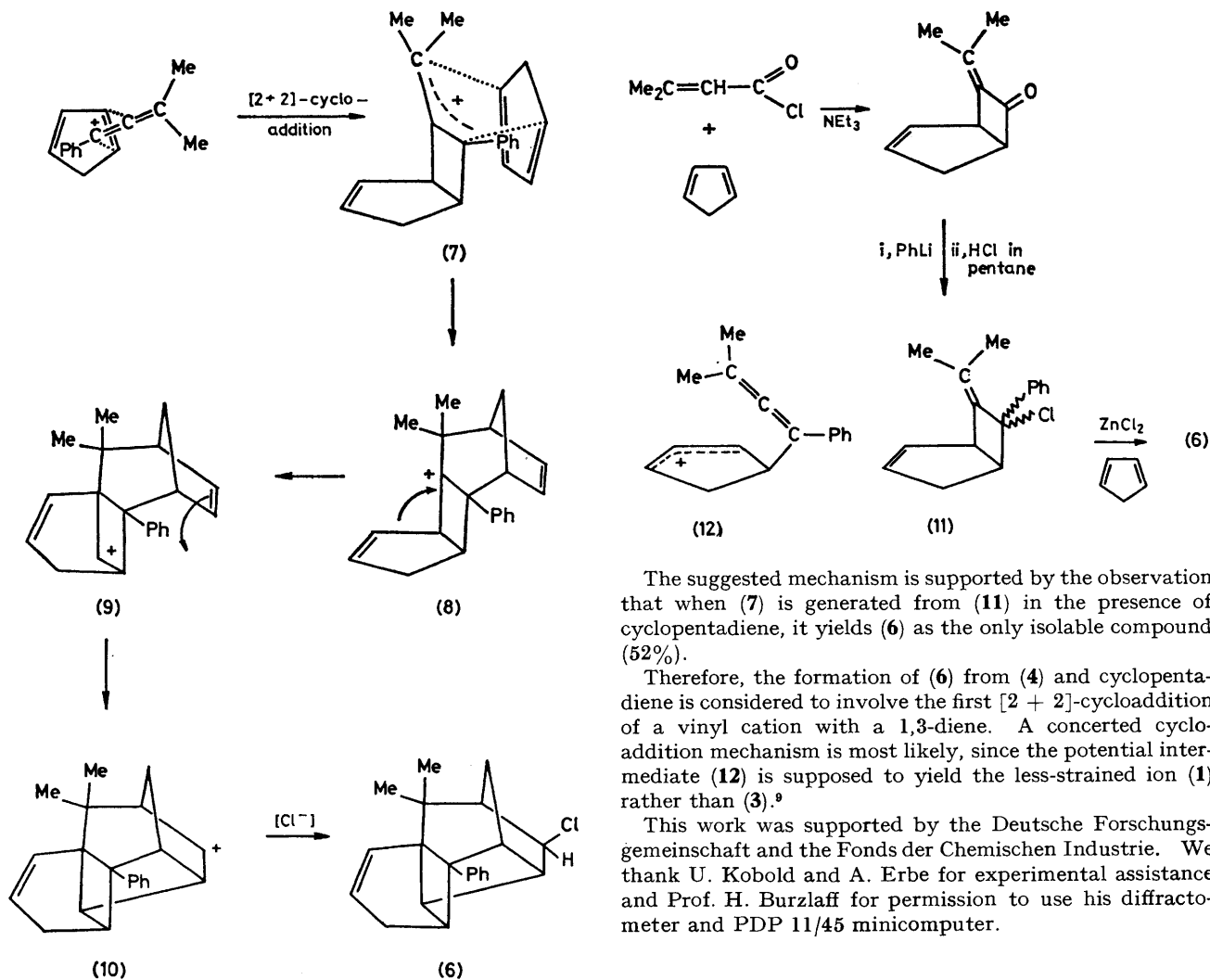


FIGURE. Molecular structure of $C_{21}H_{23}Cl$ (one enantiomer).

A reaction mechanism for the formation of (6) is suggested in the Scheme. [$\pi 2_s + \pi 2_a$]-Cycloaddition of the initially formed allenyl cation with cyclopentadiene yields allyl cation (7), which undergoes a [3+4]-cycloaddition⁸ with cyclopentadiene. A 1,2-alkyl shift and π -cyclisation afford carbenium ion (10), which is finally trapped by Cl^- to give (6).

† Data with $\theta > 18^\circ$, for which not all equivalents could be measured, were of poorer quality.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



SCHEME

(Received, 13th April 1981; Com. 429.)

¹ R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 781.² K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 933.³ G. Hammen and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 614; M. Hanack, I. Harder, and K.-R. Bofinger, *Tetrahedron Lett.*, 1981, 553.⁴ H. Mayr and I. K. Halberstadt, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 814; H. Mayr and F. Schütz, *Tetrahedron Lett.*, 1981, 925.⁵ H. Mayr, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 184.⁶ H. G. Richey, Jr., and J. M. Richey in 'Carbonium Ions,' Vol. II, eds. G. A. Olah and P. v. R. Schleyer, Wiley-Interscience, New York, 1970, p. 944.⁷ H. Burzlaff, R. Böhme, and M. Gomm, 'CRYSTAN - A Crystallographic Program System for Minicomputers,' Universität Erlangen-Nürnberg, 1977.⁸ H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 819.⁹ The exclusive formation of cyclobutanones from diphenylketen and 1,3-dienes has previously been considered an argument for a concerted cycloaddition mechanism: R. Huisgen and P. Otto, *Chem. Ber.*, 1969, **102**, 3475.