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Reaction of Norbornadiene with Butadiene Catalysed by Low-valent Cobalt, giving 5-Butadienylnorborn-2-ene

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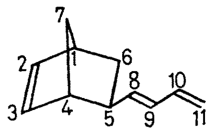
Summary Low-valent cobalt catalysts catalyse the reaction of norbornadiene with butadiene to form 5-butadienylnorborn-2-ene (I) with high specificity.

It was recently reported[1] that the reaction of norbornadiene with butadiene in presence of low-valent iron catalysts gave (II), (III) and (IV) together with norbornadiene dimers. Low-valent cobalt catalysts have now been found to direct the reaction towards specific formation of 5-butadienylnorborn-2-ene (I).

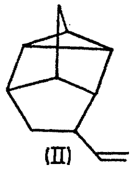
Norbornadiene (0·52 mole) and butadiene (0·54 mole) were heated in the presence of the catalysts prepared by the reduction of cobalt trisacetylacetonate (2·1 mmoles) with triethylaluminium (7·3 mmoles) in a stainless-steel autoclave at 40° for 4 h under nitrogen. The catalysts were killed by acetone (3 ml) and the mixture was steam-distilled to give 45·3 g of a crude oil. It gave on distillation a main fraction, b.p. 77·5° at 15 mm Hg, 40.4 g [51·5% of (I)], which was found to be gas-chromatographically homogeneous; other minor fractions were tentatively assigned as (II), (III), (IV), butadiene dimers, and norbornadiene dimers by their g.l.p.c. retention times.

The main product has *M* 146 (mass spectrum), in accordance with the codimer structure. Its u.v. spectrum has λ_{max} 230 nm, ϵ 28,000,[2] in cyclohexane, and its i.r. spectrum (liquid film) shows the conjugated 1,3-diene $\nu_{C=C}$ bands at 1650 and 1603 cm^{-1}, the terminal methylene δ =CH$_2$ bands at 1001 and 896 cm^{-1}, and the *cis* δ =CH at 708 cm^{-1}; hence it is a butadienyl derivative. The main peaks of its mass spectrum are, tentative assignments in parentheses; 91 (norbornadienyl cation), 80 (n-hexatriene cation), 79 (n-hexatrienyl cation), 78 (benzene cation), 77 (phenyl cation) and 66 (cyclopentadiene cation), which are explicable as the fragments formed by the retro-Diels–Alder reactions of the norbornene derivative.

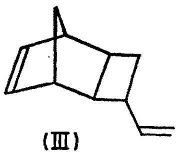
The n.m.r. and the decoupling patterns also agreed with the assigned structure (I).



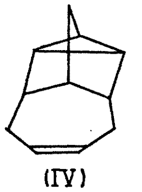
(I)



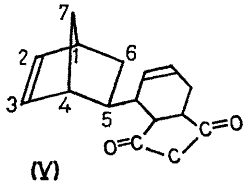
(II)



(III)



(IV)



(V)

The Diels–Alder reaction with maleic anhydride in benzene solution proceeds quite easily at room temperature, over several hours, to give an adduct (V), m.p. 92·6—93·3°, in quantitative yield. Hence a *trans*-configuration about the C(8)–C(9) double bond is indicated.

The apparent triplet pattern (*J* 2—3 Hz) for 2-H and 3-H (τ 4·02 in C_6D_6) of (V) indicates that (I) is an *exo*-substituted norbornene, because 2-H and 3-H would show different chemical shifts if the butadienyl group were *endo*.[3]

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[2] H. Brooker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, 1940, 1453.

[3] P. Laslo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 2709.