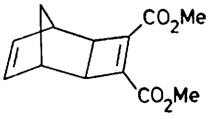
Selective Homo-Diels–Alder Addition of Acetylenic Hydrocarbons to Norbornadiene Catalysed by a Cobalt Complex

By JAMES E. LYONS,* HARRY K. MYERS, and ABRAHAM SCHNEIDER
(*Suntech, Inc., Research and Engineering Division, P.O. Box* 1135, *Marcus Hook, Pennsylvania* 19061)

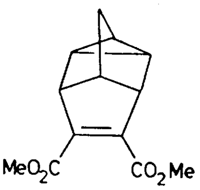
Summary A cobalt complex, formed by reducing [Co(acac)$_3$] (Hacac = acetylacetone) with diethylaluminium chloride in the presence of the bidentate ligand bis(1,2-diphenylphosphino)ethane, is an active catalyst for the selective [2+2+2] cycloaddition of acetylenic hydrocarbons RC≡CH (R = alkyl, H, or aryl) to norbornadiene.

WHEREAS uncatalysed cycloadditions of electron deficient acetylenes to norbornadiene usually produce [2+2+2] cycloaddition products,[1] acetylenes without strongly electron withdrawing groups are quite unreactive.[1] Although several transition metal complexes have been shown to catalyse the reaction of electron deficient acetylenes with norbornadiene,[2–4] simple acetylenic hydrocarbons RC≡CH (R = alkyl, H, or aryl) do not react readily under these conditions. In the case of electron deficient acetylenes metal complexes exert unique control over the products of reaction; however, a predictable pattern of reactivity has not emerged from the limited studies reported to date.

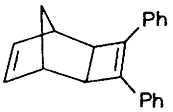
For example, norbornadiene reacts with dimethylacetylenedicarboxylate to give the [2+2] cycloaddition product (I) in the presence of $[RuH_2(PPh_3)_4]$,[2] whereas the [2+2+2] cycloaddition product (II) is obtained in the presence of $[Ni(CO)_2(PPh_3)_2]$.[3,4] Furthermore, $[Ni(CO)_2(PPh_3)_2]$ catalyses the [2+2] cross-addition of diphenylacetylene to norbornadiene to give (III), while acetylene gives low yields of tetracyclo$[4.3.1.1^{8,10}.0^{7,9}]$undeca-2,4-diene (IV) in the presence of this catalyst.



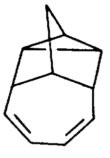
(I)



(II)

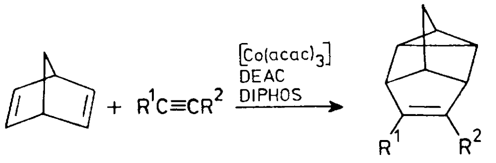


(III)



(IV)

We report that a catalyst system comprised of cobalt(III) acetylacetonate $[Co(acac)_3]$, diethylaluminium chloride (DEAC), and bis(1,2-diphenylphosphino)ethane (DIPHOS) readily promotes [2+2+2] cycloaddition reactions between norbornadiene and acetylenic hydrocarbons $R^1C{\equiv}CR^2$ (R^1 and R^2 = alkyl, H, or aryl) [equation (1)]. This route provides a convenient, direct method for the synthesis of deltacyclene[5] and a variety of alkyl- and aryl-substituted deltacyclenes (Va—e) many of which are not currently available.

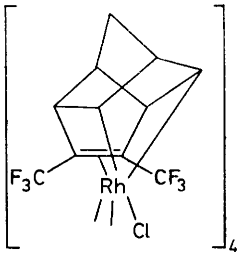


(1)

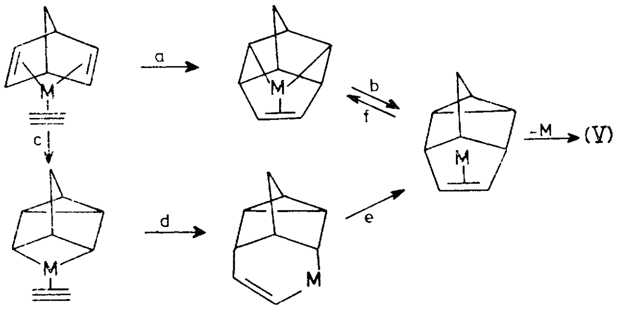
(V)

a; $R^1 = R^2 = H$
b; $R^1 = Ph$, $R^2 = H$
c; $R^1 = Me$, $R^2 = H$
d; $R^1 = Et$, $R^2 = H$
e; $R^1 = R^2 = Ph$

It appears that a low-valent cobalt complex acts as the catalyst in this reaction involving intermediates with discrete metal–carbon σ-bonds.[6] The observation of the tetrameric metallocycle (VI), formed from the reaction of hexafluorobut-2-yne and chloro(norbornadiene)rhodium(I) dimer,[7] suggests the mechanism shown in the Scheme (pathway a and b) for metal-catalysed [2+2+2] cross-additions of this type. Alternatively, the metal centre may add to norbornadiene (Scheme, pathway c) followed by insertion of acetylene (pathway d) and ring closure (pathway e). In certain instances[7] a metallocycle might then be formed by further reaction of the co-ordinated metal with the three-membered ring (Scheme, pathway f).[6]



(VI)



Scheme

In a typical reaction, the acetylenic hydrocarbon was added to a solution of norbornadiene (10 mmol) and benzene (11 mmol) containing 2×10^{-2} mmol of $[Co(acac)_3]$ and 3×10^{-2} mmol of DIPHOS. 1 ml of a 1 M solution of DEAC was then added, the mixture was stirred under argon at the temperatures given in the Table for the designated times, and then quenched with propan-2-ol, and analysed by g.l.c.

Table. [2+2+2] Cross-additions of norbornadiene with acetylenes catalysed by $[Co(acac)_3]$–DIPHOS–DEAC.

Acetylenic hydrocarbon	Temp./°C	Time/min	Norbornadiene converted/%	Product	Selectivity/%
HC≡CH	45	90	49	(Va)[a]	90
PhC≡CH	35	120	20	(Vb)[b]	86
MeC≡CH	62	61	95	(Vc)[b]	16
EtC≡CH	62	30	50	(Vd)[b]	25
PhC≡CPh	58	330	61	(Ve)[a]	41

[a] Structures were determined by comparison of physical properties, and i.r., n.m.r., and mass spectra with those of authentic samples (refs. 4 and 5). [b] The [2+2+2] co-dimers were obtained in ⩾99% purity (capillary g.l.c.) and their structures were deduced from a combination of i.r., n.m.r., and mass spectra.

In all cases the by-products of the reaction were mixtures of BINOR-S[3] (*endo-cis-endo*-heptacyclo[$5.3.1.1^{2,6}.1^{4,12}.1^{9,11}.0^{3,5}.0^{8,10}$]tetradecane) and hexacyclic norbornadiene homodimers[3] from which the desired co-dimers were easily separable. Thus, 100 mmol of norbornadiene was converted (48%) into deltacyclene (Va) with 89% selectivity and was obtained in >99% purity by distillation (44 °C at 0·19 mmHg) directly from the reaction mixture.

The authors thank Mr. R. W. Warren for his help with structure elucidation and the Air Force Wright Aeronautical Laboratories, U.S. Air Force Systems Command and the Research and Technology Group, U.S. Naval Air Systems Command, for financial support.

(*Received*, 20*th March* 1978; *Com*. 296.)

---

[1] T. Sasaki, S. Eguchi, M. Sugimoto, and F. Hiki, *J. Org. Chem.*, 1972, **37**, 2317.

[2] T. Mitsudo, K. Kokuryo, and Y. Takegami, *J.C.S. Chem. Comm.*, 1976, 722.

[3] G. N. Schrauzer, *Adv. Catalysis*, 1968, **18**, 375.

[4] G. N. Schrauzer and P. Glockner, *Chem. Ber.*, 1964, **97**, 2451.

[5] G. L. Cannell, *Tetrahedron Letters*, 1966, 5967.

[6] J. Halpern, *Org. Synth. Metal Carbonyls*, 1977, **2**, 705.

[7] L. A. Evans, R. D. W. Kemmit, B. Y. Kimura, and D. R. Russell, *J.C.S. Chem. Comm.*, **1972**, **509**.