Ruthenium-catalysed [2+2] Cross-addition of Norbornene Derivatives and Dimethyl Acetylenedicarboxylate. A Novel Route to the *exo*-Tricyclo[4.2.1.$0^{2,5}$]nonene System

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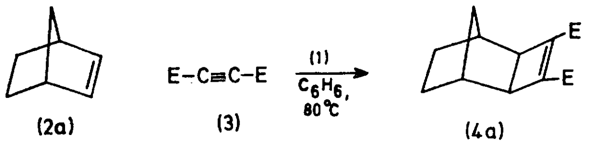
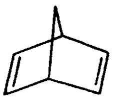
Summary $[H_2Ru(PPh_3)_4]$ catalyses the [2+2] cross-addition of norbornene derivatives and dimethyl acetylenedicarboxylate to give *exo*-tricyclo[4.2.1.$0^{2,5}$]nonenes.

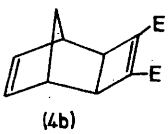
TRANSITION metal-catalysed [2+2] cross-additions of norbornadiene and acetylenes[1] or olefins[2] have been reported, but there have been no reports on the efficient [2+2] cross-addition of norbornenes and acetylenes.† We report the first example of transition metal-catalysed [2+2] cross-addition of norbornenes and dimethyl acetylenedicarboxylate.

$[H_2Ru(PPh_3)_4]^3$ (**1**) (0·1—0·2 mmol), benzene (10 ml), the norbornene derivatives (**2a**—**d**, and **4b**) (10 mmol), and dimethyl acetylenedicarboxylate (**3**) (10 mmol) were heated to 80—100 °C for 6—48 h in an ampoule which had been flushed with argon. After evaporation of the solvent *in vacuo*, the [2+2] cross-addition products (**4a**—**d**, and **5**)‡ were isolated in moderate yields (Table) by distillation under reduced pressure or recrystallization from methanol. By-products such as 1 : 2 adducts of (**2**) and (**3**), cyclohexadiene derivatives,[4] or homodimers of the olefins[5] were not detected. A 1 : 2 mixture of furan (**6**) and (**3**) also gave (**4e**).[6] The *exo*-structure of the adducts (**4a**—**d**, and **5**) is confirmed by the n.m.r. spectra showing that the protons of the cyclobutene rings do not couple with the protons at the bridge-heads.[7]

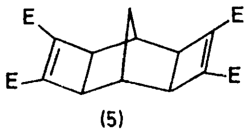


(2a) **(3)** **(4a)**

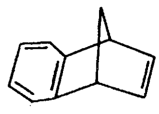

(2b)

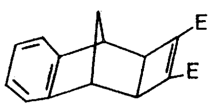


(4b)

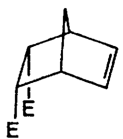


(5)

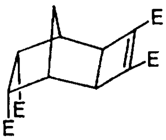

(2c)



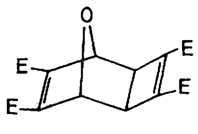
(4c)



(2d)



(4d)



(4e)

E = CO_2Me

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† The reaction has been achieved only by photo-addition with very low yield (<5%) (R. L. Cargill and M. R. Willcott, *J. Org. Chem.*, 1966, **31**, 3938; M. Hara, Y. Odaira, and S. Tsutsumi, *Tetrahedron*, 1966, **22**, 95).

‡ All formulated products gave satisfactory elemental analyses and spectral data.

TABLE. [2+2] Cross-addition of norbornenes with (**3**).

Norbornene derivatives	$[H_2Ru(PPh_3)_4]$ /mmol	Reaction temp./°C	Reaction time/h	Product	Yield[a]/%
(**2a**)	0·20	80	24	(**4a**)[b]	52
(**2b**)	0·20	80	48	(**4b**)[c]	50
				(**5**)[e]	2
(**4b**)	0·20	80	20	(**5**)	21
(**2c**)	0·10	100	20	(**4c**)[e]	57
(**2d**)	0·10	100	6	(**4d**)[e]	39
(**6** + **3**) (10 mmol)	0·10	100	6	(**4e**)[d]	13

[a] Based on the amount of the norbornenes. [b] See W. Eberbach, *Chem. Ber.*, 1974, **107**, 3287. [c] See ref. 7. [d] See ref. 6. [e] To our knowledge (**4c**,**d**) and (**5**) have not been reported: (**4c**), m.p. 94—95 °C, ν (KBr) 1728 and 1713 (C=O) and 1628 (C=C) cm^{-1}; δ (CCl_4) 7·1 (4H, m, ArH), 3·80 (6H, s, OMe), 3·23 (2H, s, bridgehead H), 2·68 (2H, s, *endo*-H), and 1·77 (2H, m, bridge H); *m/e* 284, 283, 252, 251, 225, 224, 193, 166, and 165; (**4d**), m.p. 105—106 °C, ν (KBr) 1737 and 1699 (C=O) and 1626 (C=C) cm^{-1}; δ ($CDCl_3$) 3·78 (6H, s, OMe), 3·67 (6H, s, OMe), 3·38 (2H, s, *endo*-H), 3·15 (2H, m, *exo*-H), 2·67 (2H, m, bridgehead H), and 1·44 (2H, AB q, bridge H); *m/e* 352, 321, 320, 293, 277, 261, 260, 232, 201, 176, and 116; (**5**), m.p. 142—143 °C, ν (KBr) 1738 and 1715 (C=O) and 1628 (C=C) cm^{-1}; δ (CCl_4) 3·72 (12H, s, OMe), 2·70 (4H, s, *endo*-H), 2·35 (2H, s br, bridgehead H), and 1·37 (2H, s br, bridge H); *m/e* 376, 345, 344, 312, 284, 256, and 252.

This new cycloaddition may be rationalized by assuming that a zero-valent ruthenium–olefin or -acetylene complex is formed by the reaction of (**1**) with (**2**) or (**3**)[8] and the successive formation of metallocyclopentene complex[9] followed by reductive elimination.

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