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Preliminary communication

PALLADIUM-CATALYZED C—C BOND FORMATION INVOLVING AROMATIC C—H ACTIVATION. X-RAY STRUCTURE OF 5-NITRO-8-(2-[2.2.1]BICYCLOHEPTYL)-1,2,3,4,4*a*,8*b*-HEXAHYDRO-1,4-METHANOBIPHENYLENE

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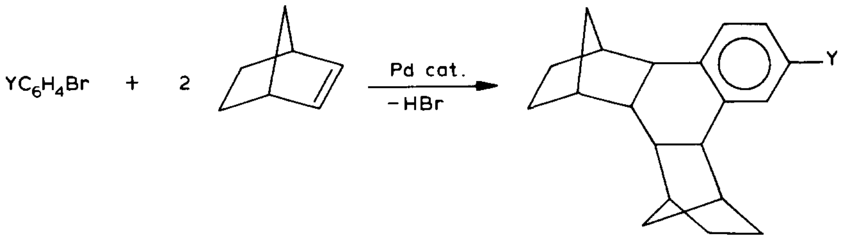
Summary

A new C—C bond formation reaction involving activation of two aromatic C—H bonds is reported. The X-ray structure of the title methanobiphenylene derivative is described.

In a previous paper we reported a new catalytic reaction involving insertion of a double bond into an aromatic C—Pd bond followed by a second double bond insertion and ring closure on the aromatic ring (eq. 1, Y = H) [1]:

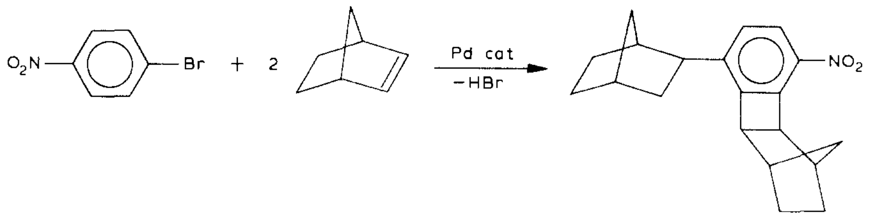


(1)

(I)

To ascertain whether an electrophilic attack was responsible for the aromatic C—H activation we have now studied the behaviour of several aromatic bromides containing various substituents in the *para* position.

The presence of the *p*-OMe group led to the predominant formation of I, whereas electron withdrawing groups such as *p*-Br and *p*-NO_2 caused formation of new products, with mass and NMR spectra rather similar to those of I. One of these compounds, (II), from the reaction of *p*-nitrobromobenzene with two molecules of norbornene (eq. 2) was isolated in a suitable form for X-ray investigation. Its structure is shown in Fig. 1.



(2)

(II)

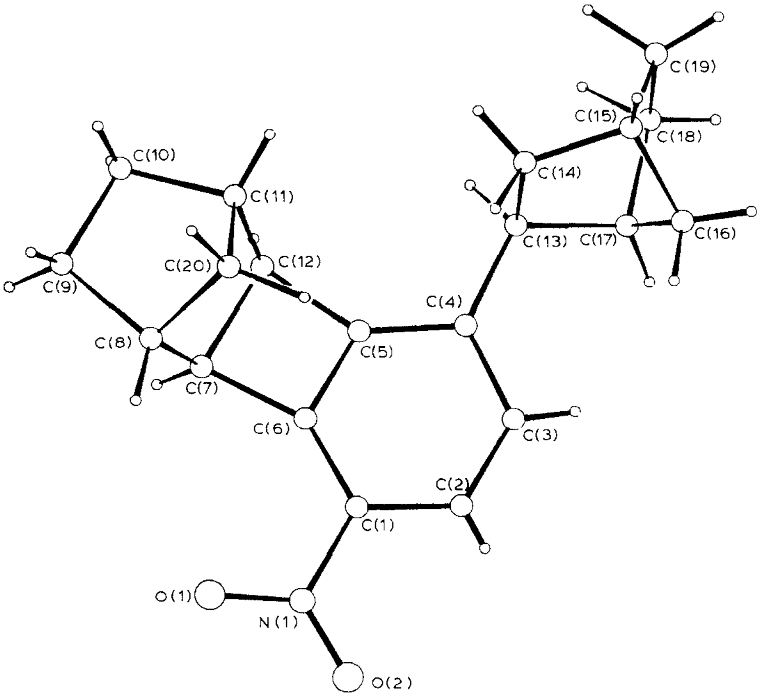


Fig. 1. Structure of compound II.

The crystals of II* are triclinic, space group $P\bar{1}$, a 10.328(3), b 9.028(3), c 9.876(2) Å; α 105.09(3), β 97.32(4), γ 107.72(3)°, M_r = 309.4, Z = 2, V 825.3(5) Å^3, D_c 1.25 g cm^{-3}, $F(000)$ = 332, μ 5.94 cm^{-1}.

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*Atomic coordinates and thermal parameters for this compound are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England. Any request should be accompanied by a full literature citation for this communication. List of observed and calculated structure factors is available from one of the authors (G.B.) on request.

The intensities of 1368 independent reflections with $I \geqslant 2\sigma(I)$ were measured at room temperature on a Siemens AED single crystal diffractometer using the Cu-K_α radiation (λ 1.5418 Å) up to θ 70°. The data were obtained with two different crystals since the first decomposed during the half-data collection. The two data sets were subsequently merged. The structure was solved by direct methods with SHELX* and refined by least-squares to a final R value of 0.077.

Anisotropic thermal parameters were used for O, N and C atoms and isotropic ones for H. Bond distances and angles are normal. The nitro group is slightly bent (7.3(2)°) with respect to the aromatic ring, which lies almost in the same plane as the fused cyclobutene ring (dihedral angle 2.9(3)°).

The formation of II suggests that arynes may be intermediates in this reaction (eq. 2). Further research is in progress to clarify this point and to ascertain whether a common cyclopalladated intermediate is involved in the reactions leading to I and II.

Experimental

A mixture of $Pd(PPh)_4$ (140 mg, 0.12 mmol) potassium acetate (118 mg, 1.2 mmol), norbornene (226 mg, 2.4 mmol), and *p*-nitrobromobenzene (241 mg, 1.2 mmol) in anisole (3 ml) was heated under nitrogen at 105°C for 48 h. After conventional work-up the products were separated by chromatography on a SiO_2 column, using n-hexane and n-hexane/ethyl acetate (99.5/0.5) as eluents. Yield of II, 85 mg (23%). Crystallization from ethanol gave yellow crystals, m.p. 114–115°C. Compound I ($Y = NO_2$) was also isolated, 41 mg (11%).

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Reference

1 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 239 (1982) C35.

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*G.M. Sheldrick, SHELX (1976) Computer Program for Crystal Structure Determination, University of Cambridge.