Journal of Organometallic Chemistry, 296 (1985) C11—C15
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

A NEW PALLADIUM-CATALYZED SYNTHESIS OF 1,2,3,4,4*a*,8*b*-HEXAHYDRO-1,4-METHANOBIPHENYLENES AND 2-PHENYLBICYCLO[2.2.1]HEPT-2-ENES*

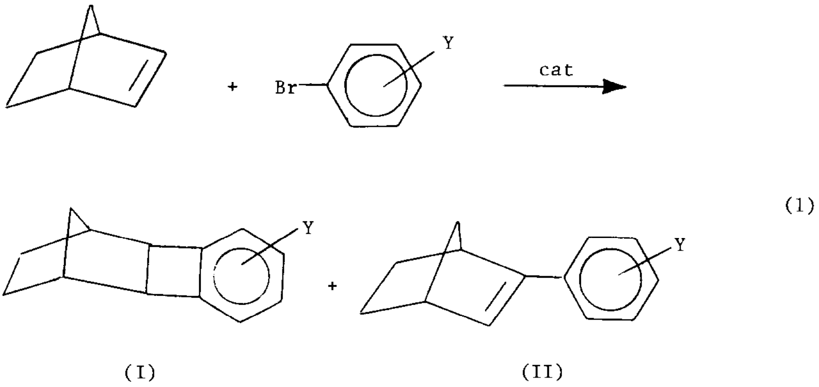
MARTA CATELLANI, GIAN PAOLO CHIUSOLI and STEFANO RICOTTI
Istituto di Chimica Organica, Universitá, via D'Azeglio 85, 43100 Parma (Italy)

(Received March 21st, 1985)

Summary

Aromatic bromides react with bicyclo[2.2.1]hept-2-ene in the presence of palladium(0) complexes and alkali phenoxides to give hexahydromethanobiphenylenes and phenylbicycloheptenes, probably via palladacyclic intermediates. Use of hindered phenoxides leads to selective cyclobutene ring closure.

We report a new palladium-catalyzed synthesis of 1,2,3,4,4*a*,8*b*-hexahydro-1,4-methanobiphenylenes (I) and 2-phenylbicyclo[2.2.1]hept-2-enes (II) from aryl bromides and bicyclohept-2-ene, according to eq. 1:



---

*Dedicated to Professor Lamberto Malatesta in recognition of his important contribution to organometallic chemistry.

0022-328X/85/$03.30

TABLE 1

REACTIONS OF PHENYL BROMIDES WITH BICYCLO[2.2.1]HEPT-2-ENE AND POTASSIUM PHENOXIDE (1:1.2:1.2 mol) IN THE PRESENCE OF $Pd(PPh_3)_4$ (0.1 mol) IN ANISOLE (2 ml) AT 105°C FOR 24 h

Y	Yield of I+II[a]	$\frac{I}{I+II}$ (%)	$\frac{II}{I+II}$ (%)
H	71	41	59
o-OMe	85	92 (5-OMe)	8
m-OMe	81	10 (6-OMe/5-OMe, 3/1)	90
p-OMe	50	60 (6-OMe)	40
p-F	75	60 (6-F)	40
p-CN	75	40(6-CN)	60
o-NO_2	40 [b]	100 (5-NO_2)	0
m-NO_2[c]	55	100 (6-NO_2/5-NO_2, 10/1)	0
p-NO_2	60	33 (6-NO_2)	67

[a] By-products, resulting from further insertion of bicycloheptene, were also formed. [b] 1-Nitro-2-phenoxybenzene (27%) was also formed. [c] 0.2 Mol of $Pd(PPh_3)_4$ and 48 h were required for complete conversion.

TABLE 2

^{1}H NMR [a] SPECTRAL DATA (δ in ppm, *J* in Hz)

Compound	H(1)	H(2*exo*), H(3*exo*)	H(2*endo*), H(3*endo*)	H(4)	H(4a)	H(5)	H(6)
I (Y = 5-OMe)	2.31(m)	1.70—1.55	1.26—1.11	2.25(m)	3.14(d) *J* 3.8	—	6.59(d) *J* 7.1
I (Y = 6-OMe)	2.24(brs)	1.66—1.50	1.24—1.10	2.24(brs)	3.10(brs)	6.60(dd) *J* 2.2, 0.6	—
I (Y = 6-CN)	2.32(brs)	1.69—1.56	1.28—1.13	2.32(brs)	3.24(brs)	7.27(brs)	—
I (Y = 5-NO_2)	2.34(m)	1.78—1.55	1.37—1.20	2.59(m)	3.56(d) *J* 3.8	—	7.92(d) *J* 8.0
I (Y = 6-NO_2)	2.35(brs)	1.72—1.51	1.32—1.10	2.35(brs)	3.25(brs)	7.85(dd) *J* 2.0, 0.7	—

Compound	H(1)	H(3)	H(4)	H(5*exo*), H(6*exo*)	H(5*endo*), H(6*endo*)	H(7*syn*)
II (Y = 3'-OMe)	3.29(brs)	6.28(d) *J* 3.2	2.98(m)	1.81—1.69	1.18—1.08	1.53(d further split) *J* 8.2, 2.0
II (Y = 4'-F)	3.27(brs)	6.21(d) *J* 3.2	2.98(m)	1.86—1.68	1.17—1.07	1.52(d further split) *J* 8.0, 2.0
II (Y = 4'-CN)	3.30(brs)	6.47(d) *J* 3.3	3.06(brs)	1.91—1.73	1.20—1.07	1.56(d further split) *J* 8.5, 2.0
II (Y = 4'-NO_2)	3.34(brs)	6.55(d) *J* 3.2	3.07(brs)	1.95—1.74	1.20—1.09	1.57(d further split) *J* 8.0, 2.0

[a] Recorded on Bruker CXP-200 spectrometer in $CDCl_3$, with TMS as internal standard.

The reaction occurs at temperatures between 80 and 120°C in the presence of a palladium(0) complex such as $Pd(PPh_3)_4$ and of an alkali phenoxide. Compound I is the *exo* isomer.

Table 1 lists some results obtained with potassium phenoxide.

Bases weaker than phenoxides, such as potassium acetate, mainly led to further insertion of bicycloheptene, as previously described [1]. With stronger bases such as potassium t-butoxide or sodium methoxide different reaction paths were observed[2], and so it is evident that the phenoxides play a special role in this synthesis.

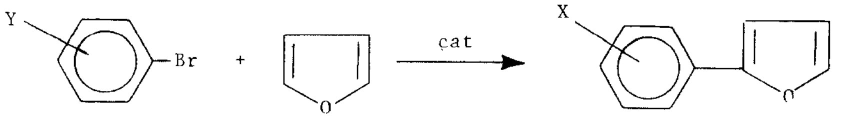
The reaction can be made selective towards formation of I by using hindered phenoxides. Bromobenzene reacts with bicycloheptene at 105°C in the presence of the sodium salt of di-t-butyl-*p*-cresol to give 81% of I.

The same feature was observed with other bromobenzenes.

Although it is too early to suggest a detailed mechanism of the reaction we can rule out an aryne intermediate on the basis of the failure to trap it with furan [3]. The reaction gave 2-phenylfurans, instead, according to eq. 2.

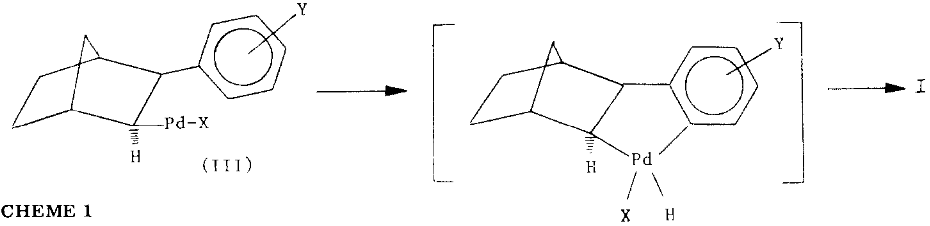
H(7)	H(8)	H(8b)	H(methano *syn*)	H(methano *anti*)	Other
7.12(ddd) *J* 8.4, 7.1, 0.4	6.66(d) *J* 8.4	3.29(d) *J* 3.8	1.0(brs)	1.0(brs)	OCH_3 3.87
6.75(dd) *J* 7.9, 2.2	6.90(dd) *J* 7.9, 0.6	3.10(brs)	0.85(d further split) *J* 10.0, 1.9	0.96(brd) *J* 10.0	OCH_3 3.75
7.50(dd) *J* 7.6, 1.2	7.08(dd) *J* 7.6, 0.8	3.24(brs)	0.80(brd) *J* 10.0	1.02(brd) *J* 10.0	
7.40—7.32	7.32—7.25	3.30(d) *J* 3.8	0.79(d further split) *J* 10.5, 1.6	1.05(d further split) *J* 10.5, 1.2	
8.14(dd) *J* 8.0, 2.0	7.12(dd) *J* 8.0, 0.7	3.25(brs)	0.79(d quintets) *J* 10.5, 2.1	1.03(d quintets) *J* 10.5, 1.4	

H(7*anti*)	Other
1.24(brd) *J* 8.2	OCH_3 3.80, aromatic 7.21, 7.00, 6.94, 6.74
1.24(brd) *J* 8.0	aromatic 7.42—7.28, 7.05—6.91 (AA′,BB′ system)
1.29(brd) *J* 8.5	aromatic 7.68—7.42 (AA′, BB′ system)
1.30(brd) *J* 8.0	aromatic 8.23—8.08 7.56—7.41 (AA′,BB′ system)



(2)

We thus are left with the possibility of a palladacycle intermediate as shown in Scheme 1 (X = Cl, Br, OPh):



SCHEME 1

In helping with this suggestion, complex III (Y = H, X = Cl) [4] was found to give I when heated at 105°C with two molecules of triphenylphosphine and one molecule of potassium phenoxide.

The nature of the substituent effects is not yet clear. Thus, while the presence of the *m*-nitro group leads to formation of I and that of the *m*-methoxy group mainly to II, in accord with the respective opposed electron-withdrawing and electron-releasing substituent effects to the aromatic ring positions (*para* and *ortho*) for palladacycle and cyclobutene ring formation, the presence of the *o*-methoxy group again leads to I. These effects and that of the *para* substituents, which also lead to mixtures of I and II, reveal a complex situation requiring further study.

The closest analogy to the behaviour of the proposed palladacycle is provided by Group VIII metallacyclopentanes, which can decompose to cyclobutane and or 1-butene depending on reaction conditions [5—7, 12].

Formation of II is rather puzzling in view of the difficulty of achieving the type of *syn* elimination which is required by the *exo*-substituted bicycloheptane system [8]. Base-catalyzed *exo*→*endo* isomerization of the bicycloheptyl—palladium bond could possibly provide the correct arrangement for elimination. This feature is also under further investigation.

General procedure

A mixture of the aromatic bromide (2.0 mmol), bicycloheptene (2.4 mmol) and potassium phenoxide (2.4 mmol) in dry anisole (4 ml) containing $Pd(PPh_3)_4$ (0.2 mmol) is kept at 105°C for 24 h under nitrogen. The products are separated by chromatography and flash chromatography on a SiO_2 column, with hexane or hexane/THF as eluent.

For the reaction with furan an analogous procedure is followed, but a large excess (10—15 fold) of furan is used.

Compounds I (Y = H [9], Y = 6-F [1]) and II (Y = H [10], Y = 2'-OMe, 4'-OMe [11]) have been reported.

The ^1H NMR data for new compounds are shown in Table 2. ^{13}C NMR and mass spectra are in agreement with the assigned structures. The mass spectrum of compounds I is characterized by a base peak derived from loss of a fragment of mass 41, whereas the loss of a fragment of mass 28 is a common feature for compounds II.

Acknowledgement. We thank the Italian Ministero Pubblica Istruzione and National Research Council for financial support.

References

1 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 239 (1982) C35; G. Bocelli, M. Catellani, G.P. Chiusoli, and S. Larocca, ibid., 265 (1984) C9; 279 (1985) 225.
2 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 286 (1985) C13.
3 R.W. Hoffmann, Dehydrobenzene and Cycloalkynes, Academic Press, New York 1967, p. 208.
4 H. Horino, M. Arai, and N. Inoue, Tetrahedron Lett., (1974) 647.
5 R.H. Grubbs and A. Miyashita, J. Am. Chem. Soc., 100 (1978) 7416, 7418, and ref. therein.
6 J.X. McDermott, J.F. White, and G.M. Whitesides, J. Am. Chem. Soc., 98 (1976) 6521.
7 R.J. McKinney, D.L. Thorn, R. Hoffmann, and A. Stockis, J. Am. Chem. Soc., 103 (1981) 2595.
8 J. Sicher, Angew. Chem. Int. Ed. Engl., 11 (1972) 200.
9 H.E. Simmons, J. Am. Chem. Soc., 83 (1961) 1657.
10 D.C. Kleinfelter and P. von R. Schleyer, J. Org. Chem., 26 (1961) 3741.
11 L.A. Kheifits and A.E. Gol'dovski, Zh. Org. Khim., 5 (1969) 1798.
12 P. Diversi, G. Ingrosso, A. Lucherini, and S. Murtas, J. Chem. Soc. Dalton Trans., (1980) 1633.