Catalytic Conversion of Butadiene into Octadienes by Nickel(0) Complexes, Morpholine, and Formaldehyde

By Jean Thivolle-Cazat and Igor Tkatchenko*

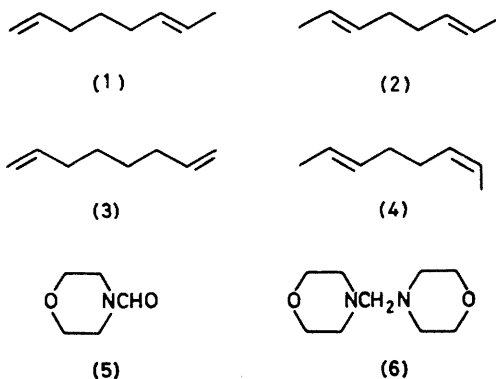(Institut de Recherches sur la Catalyse, 79, Bd du 11 Novembre 1918, 69626 Villeurbanne Cedex, France)

Summary N-Hydroxymethylmorpholine, the product of the reaction of morpholine with formaldehyde, is an efficient H-donor molecule in the hydrodimerisation of butadiene catalysed by nickel(0) complex–phosphine systems; N-formylmorpholine is obtained as a by-product.

Linear dimerisation of butadiene is known to produce octa-1,3,6- and -1,3,7-trienes.[1] The formation of octadienes requires the use of an H donating source such as Grignard reagents,[2] alcohols,[3] or formic acid.[4,5] It has been suggested that reduction occurs either on an η-octatrienediyl–transition metal intermediate, or after the formation of the octatriene.[5]

We report that nickel(0) complexes together with morpholine *and* formaldehyde are able to convert butadiene selectively into a mixture of octadienes. Recently,[6] it was observed that [Ni(cod)$_2$] (cod = cyclo-octa-1,5-diene) with equimolar amounts of phosphines or phosphites catalyses the telomerisation of butadiene with aryl ketones or morpholine; octadienyl-ketones, -alcohols, or -morpholine were obtained, depending on the nature of the P^{III} compound.

Our current interest in formaldehyde chemistry prompted us to study the extension of this reaction to the use of formaldehyde. Reaction of butadiene (400 mmol) with paraformaldehyde (200 mmol) and morpholine (200 mmol) in the presence of the [Ni(cod)$_2$]–PPh$_3$ system (2 mmol), yields exclusively butadiene dimers, and dihydro-dimers and products of the reaction of morpholine with formaldehyde (Table).

The butadiene dimers (C$_8$H$_{12}$ in Table) consist mainly of a mixture of 3-vinylcyclohexene, octa-1,3,6- and 1,3,7-triene, and cyclo-octa-1,5-diene. The predominant products were the dihydro-dimers, the octadienes (1)—(4), however. G.l.c.–mass spectroscopy showed that these consisted of two major and two minor components: *trans*-octa-1,6-diene (1) and *trans,trans*-octa-2,6-diene (2); and octa-1,7-diene (3) and *cis,trans*-octa-2,6-diene (4), respectively. The relative ratio of the octadiene products does not depend markedly on the conditions used (*i.e.* there is a variation from 33:22:8·5:1·5 to 49:40:1·5:3 for the conditions in the Table). The nature of the phosphorus(III) compound affects both the extent of the butadiene conversion and the selectivity. The reaction also occurs in the absence of phosphorus(III) ligands; however, the selectivities for linear dimer formation are then lower.

(1)

(2)

(3)

(4)

(5)

(6)

TABLE. Hydrocondensation of butadiene with [Ni(cod)$_2$] and triphenylphosphine catalyst.[a]

Expt.	Amine	Temp. /°C	Time/ h	Conversion (%)	C$_8$H$_{12}$	Selectivities (%) C$_8$H$_{14}$				Amine derivatives (%)	
						(1)	(2)	(3)	(4)	(5)[b]	(6)[b]
1	Morpholine	35	20	100	17·5	34·5	36	10	2	100	0
2	”	45	3	100	10·5	39	39	10·5	1	100	0
3	”	55	3	61	14	35·5	40	7·5	3	58	42
4	”	45	0·25	50	12·5	49	22	15	1·5	49	51
5	”	45	0·5	81	14	38	36	10	2	74	26
6	”	45	1·5	97	12	38	40	8·5	1·5	87	13
7	c	55	20	50	97	1	2			18	82
8	Piperidine	55	20	43	29	21	49	1		35[d]	65[e]
9	Pyrrolidine	55	20	38	40	22	34	3	1	30[f]	70[g]
10	Et$_2$NH	55	20	5	88	10	2			0·5[h]	99·5[i]

[a] 400 mmol of butadiene unless otherwise stated with [Ni(cod)$_2$] (2 mmol) and PPh$_3$ (2 mmol) without solvent, together with 200 mmol of amine. [b] Unless otherwise stated. [c] 600 mmol of butadiene with [Ni(cod)$_2$] (2 mmol) and PPh$_3$ (2 mmol) + (6) (25 mmol) and D$_2$O (25 mmol). [d] N-Formylpiperidine. [e] Dipiperidin-1-ylmethane. [f] N-Formylpyrrolidine. [g] Dipyrrolidin-1-ylmethane. [h] Et$_2$NCHO. [i] Et$_2$NCH$_2$NEt$_2$.

Two high-boiling products were isolated by liquid chromatography. N-Formylmorpholine (5) was characterised by i.r. [ν(CO) 1670 cm^{-1}] and n.m.r. [δ 3·55 (8H) and 8·05 (1H)] comparison with an authentic sample prepared from morpholine and formic acid.[7] Dimorpholinomethane (6) was characterised by n.m.r. [δ 2·65 (8H, t, J 5 Hz), 3·1 (2H), and 3·80 (8H, t, J 5 Hz)] comparison with an authentic sample prepared from morpholine and formaldehyde.[8]

Blank experiments showed that all three components: the Ni complex, morpholine, and formaldehyde, are necessary for the conversion of butadiene into octadienes. The reaction is suppressed when carefully dried (6) is used as the amine component. However, addition of an equivalent amount of D$_2$O favours the formation of octadienes (Table, expt. 7); g.l.c.–mass spectroscopy shows the incorporation of approximately one deuterium atom per octadiene (m/e 111).

We interpret this as indicating that the hydrogen transfer reaction proceeds through the intermediacy of the amino-alcohol (7) which is obtained either by the direct reaction of morpholine with formaldehyde or by the protonolysis of (6) (Scheme 1).

Interestingly, the combination diethylamine–formaldehyde–[Ni(cod)$_2$]–PPh$_3$ does not catalyse the formation of octadienes (Table, expt. 10). However, cyclic amine–formaldehyde mixtures favour the production of octadienes although the yields are decreased (Table, expts. 8 and 9).

This hydrogen transfer system is active for the reduction of octa-1,3,6-triene to octadienes, but under the catalytic conditions used the rate of reduction is low. Furthermore, the product selectivities do not depend drastically on the conversion of butadiene (Table). Thus, one can assume that the hydrodimerisation of butadiene occurs directly within the co-ordination sphere of the nickel and not through the intermediate formation of the octatrienes.

SCHEME 2

SCHEME 1

Since aliphatic and aromatic alcohols are known to promote the linear dimerisation of butadiene to octa-1,3,6- and -1,3,7-trienes,[9] the amino-alcohol (7) must have some particular characteristics which facilitate the hydrogen transfer reaction.†

Although the location of the deuterium label in the products of expt. 7 has not yet been ascertained, we suggest that the octadienes result from the reaction of an η-octadienediyl-nickel intermediate [e.g. (8)] with the nucleophilic co-reagent. Protonolysis of the nickel–allyl σ-bond would occur first with the formation of a species such as (9) (Scheme 2).

† It should be pointed out that the reported [Ni(cod)$_2$]–alcohol systems have only slight catalytic activity.

‡ An intramolecular hydrogen bond may stabilize (7) sufficiently for it to react with a catalytic intermediate.

The positioning of a nitrogen atom γ to nickel could facilitate the hydride transfer into the allylic unit and the elimination of (5) from the nickel co-ordination sphere. This could explain why the direct reaction of aldehydes with nickel–allyl complexes is not catalytic.[10]

[1] J. Tsuji, *Accounts Chem. Res.*, 1973, **6**, 8; P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1975.
[2] U.S.P. 3,359,337 (appl. 11th June 1965).
[3] N. Yamazaki and T. Ohta, *Polym. J.*, 1973, **4**, 616.
[4] S. Gardner and D. Wright, *Tetrahedron Letters*, 1972, 163.
[5] P. Roffia, G. Gregorio, F. Conti, G. F. Pregaglia, and R. Ugo, *J. Organometallic Chem.*, 1973, **55**, 405.
[6] H. Bandmann, P. Heimbach, and A. Roloff, *J. Chem. Research*, 1977, (S) 261; (M) 3056.
[7] S. Komori, M. Okohara, and E. Shinsugi, *Technol. Repts. Osaka Univ.*, 1958, **8**, 497.
[8] J. Burkus, *J. Org. Chem.*, 1961, **26**, 779.
[9] J. Ohta, K. Ebina, and Y. Yamazaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 1321.
[10] J. Thivolle-Cazat and I. Tkatchenko, *Tetrahedron Letters*, 1979, 345.