ELSEVIER

Journal of Organometallic Chemistry 525 (1996) 151–153

Journal of Organometallic Chemistry

Asymmetric telomerization of buta-1,3-diene with a pair of different telogens

Chhan Siv, Gilbert Peiffer *, Andrée Bendayan

Laboratoire des Organo-Phosphorés associé au CNRS, Université d'Aix-Marseille III, Avenue Escadrille Normandie-Niemen, B.P. 552, 13397 Marseille Cédex 13, France

Received 14 March 1996

Abstract

Telomerization of buta-1,3-diene can be carried out simultaneously with two different telogens. In the example we report, one of them is nucleophilic (isopropanol), whereas the other is electrophilic (paraformaldehyde).

1. Introduction

Telomerization reactions of butadiene and isoprene with various telogens such as water [1], alcohols [2], carboxylic acids [3], amines [4], activated hydrogen compounds [5], carbon dioxide [6], ketones [7], aldehydes [8], nitroalkanes [9], or enamines [10] have been known for a long time. We report here original results concerning the simultaneous action of two different telogens.

It was established that during the telomerization of butadiene with paraformaldehyde in an isopropanol solution, using the triphenylphosphine–palladium acetate system [8] as catalyst, 2,5-divinyl tetrahydropyrane, a cyclic telomer, was formed. Isopropanol seems to act exclusively as a solvent. However, it is well known that alcohols are good telogens [2]. When, in the above mentioned catalyst, triphenylphosphine was replaced by aminophosphinephosphinite (AMPP), we essentially obtained linear telomers (see Table 1), resulting from the simultaneous reaction of isopropanol and formaldehyde as telogens (see Scheme 1). The phosphorus ligands derived from α-amino acids which we used are chiral, and allowed us to achieve both chemoselectivity and enantioselectivity. A good selectivity (65%) was obtained for compound **4** and its enantiomeric excess was 20% when the ligand was L–LeuNOP. In other similar telomerization reactions, enantiomeric excesses were equivalent for compound **1** [11].

The structures of some products obtained from the telomerization of butadiene with isopropanol and paraformaldehyde in the presence of the catalytic system AMPP–palladium acetate are particularly interesting. Whereas compound **2** is a linear telomer of butadiene with formaldehyde, compounds **3**, **4** and **5** exhibit original structures resulting from the telomerization with both isopropanol and formaldehyde. This is explained by the fact that isopropanol acts as a nucleophile and formaldehyde as an electrophile. The structure of compounds **3**, **4** and **5** suggests the production of an unstable intermediate isopropoxymethanol between the isopropanol and formaldehyde in the media [12]. The telomer results from a nucleophilic attack of the isopropoxymethanol formed followed by an electrophilic attack on the formaldehyde [6] (see Scheme 2). The methylenedioxy group, often present in natural products, is stable to many reagents [13]. However, no products could be isolated when a solution of paraformaldehyde in isopropanol was reacted under reflux.

2. Conclusion

This original method presents a considerable advantage; it allows us, in one step, to obtain with yields of

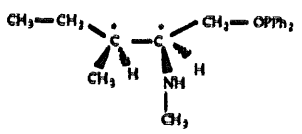
* Corresponding author.

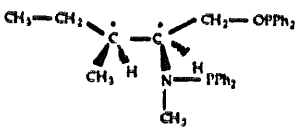
Elsevier Science S.A.
PII S0022-328X(96)06522-9

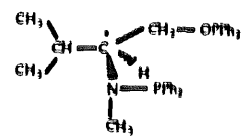
Table 1
Proportions of the different products obtained from the telomerization of butadiene with paraformaldehyde (50 mmol) and isopropanol (10 ml) as a function of ligand nature

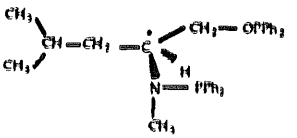
Ligand [14]	IleOP	IleNOP	ValNOP	LeuNOP	AlaNOP	PheNOP
Butadiene weight (g)	4.5	4.5	6	6	6	6
Telomer weight (g)	2	2	3	1.5	2.5	2.5
1 (%)	13	74	18	11	16	21
(E/Z ratio)	(3/1)	(5/1)	(3/1)	(5/1)	(4/1)	(6/1)
%ee of E	(3)	(4)	(1)	(10)	(4)	(9)
%ee of Z	(36)	(1)	(7)	(8)	(3)	(19)
2 (%)	12	0	17	14	11	12
(%ee)	(3)		(10)	(11)	(12)	(20)
3 (%)	9	13	8	10	7	7
4 (%)	66	13	52	54	54	48
(%ee)	(0)	(3)	(1)	(20)	(8)	(4)
5 (%)	0	0	5	11	12	12
(%ee)			(13)	(21)	(7)	(8)

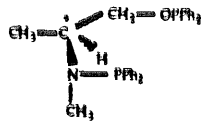
Enantiomeric excesses have been determined by capillary gas chromatography with CHIRASIL-DEX CB 25 m × 0.32 mm column. The absolute configuration of the major enantiomer remains unknown.

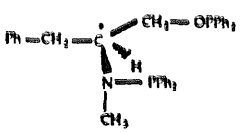

(2S,3S) IleOP


(2S,3S) IleNOP

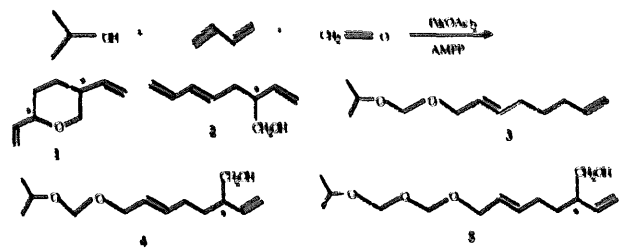

(S) ValNOP


(S) LeuNOP


(S) AlaNOP


(S) PheNOP

about 60% (*ee* 20%) a synthon consisting of eight carbons. It possesses two different functional groups, an alcohol and an ether.



Scheme 1. Telomerization of butadiene with isopropanol and paraformaldehyde.

3. Experimental part

22.5 mg (0.1 mmol) of palladium acetate and 0.15 mmol of ligand diphos (or 0.3 mmol of monophos) were dissolved in 10 ml of isopropanol under nitrogen in a flask. 1.5 g (50 mmol) of paraformaldehyde was then added to this yellow–orange solution. After cooling this mixture by constant stirring in an ice bath, we added 5.24 g (97 mmol) of butadiene. The stirring was continued at room temperature for 24 h. After evaporating the solvent the residue was analyzed by GC and the different compounds were purified by liquid chromatography on silica gel with a mixture of hexane/ethyl acetate (8:2) as eluting solvents. The identification was done by NMR spectroscopy.

3.1. 2,5-Divinyl tetrahydropyran (1)

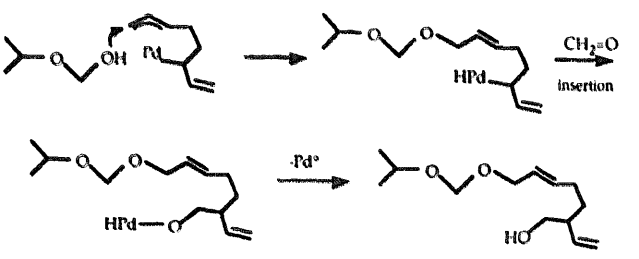
^{1}H NMR (solvent $CDCl_3$), δ (ppm): 1.40–2.00 (m, 4H); 2.20–2.40 (m, 1H); 3.20 (t, J = 11 Hz, 1H); 3.65–4.05 (m, 2H); 5.00–5.30 (m, 4H); 5.55–5.95 (m, 2H). ^{13}C NMR (solvent $CDCl_3$), δ (ppm): 29.2 (CH_2); 31.0 (CH_2); 39.9 (CH); 72.0 (CH_2O); 77.8 (CHO); 114.7 (CH_2); 138.8 (CH); 138.9 (CH).

3.2. 6-Hydroxymethyl octa-1,3,7-triene (2)

^{1}H NMR (solvent $CDCl_3$), δ (ppm): 2.15–2.25 (m, 2H); 2.25–2.40 (m, 1H); 3.47 (dd, J_1 = 7 Hz, J_2 = 10.5 Hz, 1H); 3.60 (dd, J_1 = 5 Hz, J_2 = 10.5 Hz, 1H); 4.95–5.20 (m, 4H); 5.55–5.75 (m, 2H); 6.00–6.15 (m, 1H); 6.2–6.4 (m, 1H). ^{13}C NMR (solvent $CDCl_3$), δ (ppm): 33.9 (CH_2); 46.5 (CH); 64.9 (CH_2O); 115.4 (CH_2); 117.6 (CH_2); 131.9 (CH); 132.6 (CH); 136.8 (CH); 139.0 (CH).

3.3. 12-Methyl 9,11-dioxatrideca-1,6-diene (3)

^{1}H NMR (solvent $CDCl_3$), δ (ppm): 1.15 (d, J = 6 Hz, 6H); 1.5 (quint., J = 6 Hz, 2H); 2.05 (q, J = 6 Hz, 4H); 3.9 (sept., J = 6 Hz, 1H); 4.0 (d, J = 6 Hz, 2H); 4.7 (s, 2H); 5.0 (m, 2H); 5.7 (m, 3H). ^{13}C NMR (solvent $CDCl_3$), δ (ppm): 22.32 (CH_3); 28.03 (CH_2); 31.49 (CH_2); 33.00 (CH_2); 67.67 (CH_2O); 68.77 (CHO); 92.08 (OCH_2O); 114.39 (CH_2); 126.03 (CH); 134.34 (CH); 138.46 (CH).



Scheme 2. Mechanism suggested for the formation of compound 4.

3.4. 3-Hydroxymethyl 12-methyl 9,11-dioxatrideca-1,6-diene (4)

^{1}H NMR (solvent $CDCl_3$), δ (ppm): 1.13 (d, J = 6.2 Hz, 6H); 1.2–1.5 (m, 2H); 1.65 (s, 1H); 1.9–2.1 (m, 2H); 2.1–2.3 (m, 1H); 3.41 (dd, J_1 = 8 Hz, J_2 = 10.6 Hz, 1H); 3.54 (dd, J_1 = 5.2 Hz, J_2 = 10.6 Hz, 1H); 3.86 (sept., J = 6.2 Hz, 1H); 4.0 (d, J = 6 Hz, 2H); 4.7 (s, 2H); 5.0–5.2 (m, 2H); 5.4–5.8 (m, 3H). ^{13}C NMR (solvent $CDCl_3$), δ (ppm): 22.6 (CH_3); 29.7 (CH_2); 30.1 (CH_2); 46.5 (CH); 65.6 (CH_2O); 67.9 (CH_2O); 69.1 (CHO); 92.4 (OCH_2O); 117.7 (CH_2); 126.5 (CH); 134.2 (CH); 139.6 (CH).

3.5. 3-Hydroxymethyl 14-methyl 9,11,13-trioxapentadeca-1,6-diene (5)

^{1}H NMR (solvent $CDCl_3$), δ (ppm): 1.15 (d, J = 6.2 Hz, 6H); 1.2–1.5 (m, 2H); 1.6 (s, 2H); 1.9–2.1 (m, 2H); 2.1–2.3 (m, 1H); 3.38 (dd, J_1 = 7.8 Hz, J_2 = 10.6 Hz, 1H); 3.55 (dd, J_1 = 5.3 Hz, J_2 = 10.6 Hz, 1H); 3.88 (sept., J = 6.2 Hz, 1H); 4.0 (d, J = 6 Hz, 2H); 4.75 (s, 2H); 4.78 (s, 2H); 5.0–5.2 (m, 2H); 5.4–5.8 (m, 3H). ^{13}C NMR (solvent $CDCl_3$), δ (ppm): 22.5 (CH_3); 29.7 (CH_2); 30.1 (CH_2); 46.5 (CH); 65.6 (CH_2O); 66.6 (CH_2O); 69.7 (CHO); 90.1 (OCH_2O); 91.0 (OCH_2O); 117.6 (CH_2); 126.3 (CH); 134.3 (CH); 139.6 (CH).

References

[1] J.P. Bianchini, E.M. Gaydou, B. Waegell, A. Eisenbeis and W. Keim, *J. Mol. Catal.*, *30* (1985) 197–212.

[2] D. Commereuc and Y. Chauvin, *Bull. Soc. Chim. France*, *3–4* (1974) 652–656; M. Hidai, H. Mizuta, H. Yagi, Y. Nagai, K. Hata and Y. Uchida, *J. Organomet. Chem.*, *232* (1982) 89–98.

[3] D. Rose and H. Lepper, *J. Organomet. Chem.*, *49* (1973) 473–476; M. Green, G. Scholes, F. Gordon and A. Stone, *J. Chem. Soc., Dalton Trans.*, (1978) 309–314.

[4] W. Keim and M. Roper, *J. Org. Chem.*, *46* (1981) 3702–3707; J. Tsuji and M. Takahashi, *J. Mol. Catal.*, *10* (1981) 107–114; T. Antonsson, A. Langlet and C. Moberg, *J. Organomet. Chem.*, *363* (1989) 237–241; W. Keim, M. Roper and M. Schieren, *J. Mol. Catal.*, *20* (1983) 139–151.

[5] G. Hata, K. Takahashi and A. Miyake, *Chem. Ind.*, (1969) 1836; K. Takahashi, A. Miyake and G. Hata, *Chem. Ind.*, (1971) 488; G. Hata, K. Takahashi and A. Miyake, *J. Org. Chem.*, *36* (1971) 2116–2123; S. Watanabe, K. Suga and T. Fujita, *Can. J. Chem.*, *51* (1973) 848–849; R. Baker and R.J. Popplestone, *Tetrahedron Lett.*, *38* (1978) 3575–3578.

[6] P. Braunstein, D. Matt and D. Nobel, *J. Am. Chem. Soc.*, *110* (1988) 3207–3212.

[7] K. Ohno, T. Mitsuyasu and J. Tsuji, *Tetrahedron*, *28* (1972) 3705–3720; R. Bortolin, G. Gatti and A. Musco, *J. Mol. Catal.*, *14* (1982) 95–103.

[8] P. Haynes, *Tetrahedron Lett.*, *42* (1970) 3687–3690; K. Ohno, T. Mitsuyasu and J. Tsuji, *Tetrahedron Lett.*, *1* (1971) 67–70; W. Keim, W. Meltzow, A. Koehnes and T. Roethel, *J. Chem. Soc., Chem. Commun.*, (1989) 1151–1152.

[9] T. Mitsuyasu, M. Hara and J. Tsuji, *J. Chem. Soc., Chem. Commun.*, (1971) 345; T. Mitsuyasu and J. Tsuji, *Tetrahedron*, *30* (1974) 831–834.

[10] J. Tsuji, *Bull. Chem. Soc. Jpn.*, *46* (1973) 1896.

[11] W. Keim, A. Koehnes, T. Roethel and D. Anders, *J. Organomet. Chem.*, *382* (1990) 295–301.

[12] R.O.C. Norman, *Principles of Organic Synthesis*, Science Paperbacks, 1970, p. 113.

[13] T.W. Greens, *Protective Groups in Organic Synthesis*, Wiley, New York, 1981, pp. 150–151.

[14] A. Karim, A. Mortreux, F. Petit, G. Buono, G. Peiffer and C. Siv, *J. Organomet. Chem.*, *317* (1986) 93–104.