Tetrahedron Letters No.1, pp. 15-17, 1968. Pergamon Press Ltd. Printed in Great Britain.

STEREOSPECIFIC SELECTIVE HYDROGENATION OF 1,2-DIENE PHOSPHONIC ESTERS

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(Received in UK 15 July 1967)

Abstraction of hydrogen chloride from 2-chloroalkane phosphonic esters[1] and some other reactions[2,3] result in the formation of 1-alkene phosphonic esters with trans arrangement of phosphonic groups and bulky substituents. The cis compounds are much less available.[4,5]

The purpose of this paper is to show the catalytic hydrogenation of 1,2-diene phosphonic esters to be useful as a general route to cis-1-alkene phosphonates. This hydrogenation carried out in alcohol solution at ordinary pressure and temperature with 5% Pd/$CaCO_3$ as a catalyst is highly selective and stereospecific. Physical properties of four cis-olefinic esters prepared in this way are given in Table 1.

TABLE 1

Physical Properties of cis-1-Alkene Phosphonates

$RCH{=}CR'P(O)(OC_2H_5)_2$

R	R'	b.p.,°C/mm Hg	d_4^{20}	n_D^{20}
CH_3	H	142/13	1.0381	1.4359
C_2H_5	H	69.5/1	1.0132	1.4400
iso-C_3H_7	H	55-57/0.5	0.9900	1.4392
CH_3	CH_3	84-85/7	1.0210	1.4381

Geometrical structure of these compounds is determined unequivocally by n.m.r. spectra. The assignment is based on the ranges of cis and trans spin coupling constants which are believed to be following (in c.p.s.):

J_{HH} cis 8-12, J_{HH} trans 14-18, J_{HP} cis 10-30,[4,6] J_{HP} trans 30-50.[4,6]

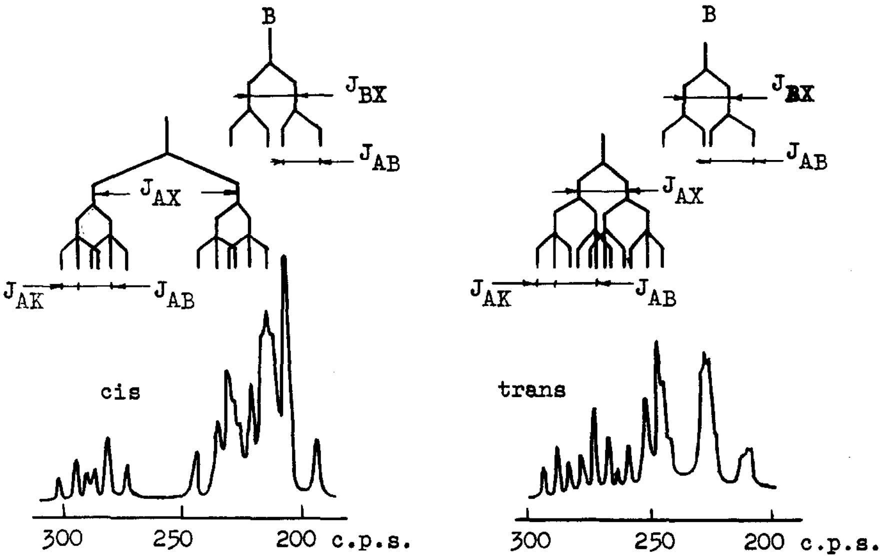

FIG.1. 40 Mc n.m.r. spectra of ethylenic protons of the diethyl 1-butene phosphonates $CH_3\overset{K}{CH_2}\overset{A}{CH}=\overset{B}{CH}\overset{X}{P}(O)(OC_2H_5)_2$

Left: prepared by catalytic hydrogenation of diethyl 1,2-butadiene phosphonate (this work); right: prepared accordingly ref.[1]

Fig. 1 shows ethylenic proton spectra of diethyl cis- and trans-1-butene phosphonates and their interpretation. Partial spectral parameters of these and other compounds investigated are given in Table 2.

These cis compounds are surprisingly stable; diethyl cis-1-butene- and cis-3-methyl-1-butene-phosphonates do not change their structures when heated for 4 hours at 250-280°C. This stability is apparently due to poor conjugation between a double bond and an adjacent phosphonic group.

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TABLE 2

Parameters of n.m.r. Spectra of Diethyl cis- and trans-1-Alkene Phosphonates $RCH{=}CR'P(O)(OC_2H_5)_2$

R	R'		Chemical Shifts, p.p.m. from TMS		Spin Coupling Constants, c.p.s.		
			A	B	AB	AX	BX
CH_3	H	cis	6.89	5.78	12.6	57.3	18.4
		trans	6.95	6.00	17.4	23.0	21.5
C_2H_5	H	cis	6.35	5.40	12.0	52.3	17.6
		trans	6.74	5.72	17.2	22.0	21.3
iso-C_3H_7	H	cis	6.42	5.47	11.7	54.2	21.0
CH_3	CH_3	cis	6.27	-	-	43.2	-

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