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NICKEL CHLORIDE CATALYZED REARRANGEMENT OF ALLYLIC PHOSPHITES

XIYAN LU* and JINGYANG ZHU

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032 (China)

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Summary

Allylic phosphites can be rearranged to the corresponding allylic phosphonates under the catalysis of nickel chloride. Dienes and dialkyl phosphonates are formed by an elimination reaction when there is a hydrogen atom at the β-position of the carbon–metal bond in the allylic intermediate. The mechanisms of these reactions are discussed.

Introduction

The thermal rearrangement of allylic phosphites to the corresponding allylic phosphonates is well known, the Arbuzov rearrangement, in organophosphorus chemistry [1,2], but it generally requires high temperatures and yields are low. We have reported the rearrangement of allylic phosphites to the corresponding allylic phosphonates under the catalysis of a nickel(0) complex, $Ni(cod)_2$ (cod = cyclooctadiene) and found that $Ni(cod)_2$ is an effective catalyst for these transformations [3].

On the other hand, Balthazor reported that nickel(II) chloride can be reduced directly by trialkyl phosphites on heating to form the nickel(0)-phosphite complex [4]. We now report that the nickel(0)-phosphite complex can also catalyze the rearrangement of allylic phosphites to the corresponding allylic phosphonates. In other words allylic phosphites can be rearranged to the corresponding allylic phosphonates under the catalysis of anhydrous nickel chloride.

Results and discussion

Allylic phosphites can be rearranged to the corresponding allylic phosphonates when anhydrous nickel chloride is used as the catalyst. The reaction behavior is similar to that when $Ni(cod)_2$ is used as catalyst [3] and the reaction can be carried out without solvent, at lower temperature, in shorter time and with a higher yield

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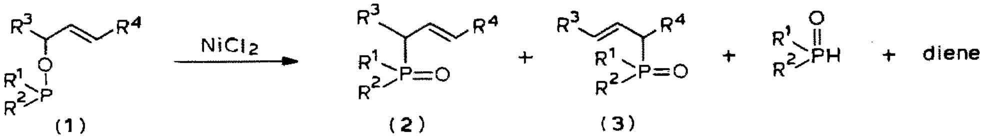
than in the corresponding thermal reaction. The results are shown in Table 1 and the reaction scheme is as follows:



The mechanism of the rearrangement may be similar to that of the $Ni(cod)_2$ catalyzed rearrangement [3]. First, the allylic phosphites oxidatively add to the zerovalent nickel complex formed in situ from the reaction of nickel chloride and the allylic phosphites, and the allyl–oxygen bond is split to give the π-allyl nickel complex. At present, it is not clear whether the π-allyl complex is neutral with an Ni–P bond (**5**) or cationic, with the anion $O{=}P(OEt)_2$ outside the coordination sphere (**4**) [5]. The phosphite anion formed, which is an ambident nucleophile [6,7], couples with one of the soft π-allyl carbon atoms by its softer phosphorus atom to form the rearranged products, allylic phosphonates. The almost identical composition mixture of products **2** and **3** is obtained from compound **1d** and **1e**, which strongly indicates that the reaction proceeds with the π-allyl nickel complex as the intermediate as shown in the following scheme:

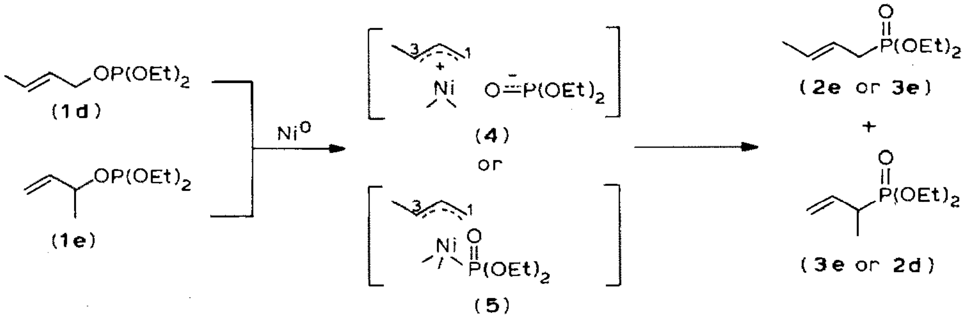
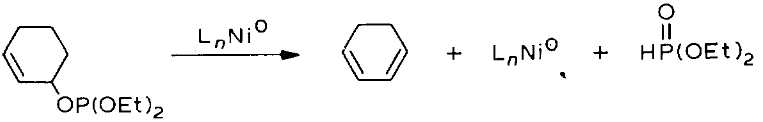


Table 1 shows that the yield is higher for the allylic esters with a terminal double bond (compounds **1a**–**1c**). The reaction is slower and the yield lower when there is a methyl substituent on the end of the double bond (compound **1e**) and the rearrangement reaction does not occur for the cinnamic derivatives (compound **1g**). This may be due to the steric effect of the substituent group which makes the coordination of the olefin to nickel difficult. Only **3f** is obtained from compound **1f**, probably because of a conjugation effect between the phenyl group and the double bond in the product, which makes the compound more stable. The rearrangement of compound **1b** indicates that the allylic ester of phosphonous acid can also be rearranged to the corresponding allylic phosphinate under this condition.

As reported in the $Ni(cod)_2$ catalyzed reaction [3], a considerable amount of dialkylphosphonate is formed as well as the rearrangement products from compound **1d** and **1e**. After careful study of the reaction mixture, we found that butadiene is formed simultaneously with the dialkyl phosphonate. No rearrangement occurs with 2-cyclohexenyl diethyl phosphite (**1h**) but only 1,3-cyclohexadiene and diethyl phosphonate are isolated as the products. The allylic phosphite (**1h**) reacts with the nickel(0) catalyst giving the π-allyl nickel complex which has been proposed above, followed by elimination of diethyl phosphonate and nickel(0) to give 1,3-cyclohexadiene.



(1h)

Diethyl phosphonate and isomers of hexadiene are obtained from compound **1i** because there are two possibilities for the β-hydrogen abstraction reaction.

This is a convenient preparative method for the dienes based on the elimination of dialkyl phosphonates from easily available allylic phosphites using only nickel chloride as the catalyst.

It is clear that the nickel chloride catalyzed rearrangement and elimination are competitive reactions. Simple allyl phosphites undergo a rearrangement reaction only to form the corresponding allyl phosphonates (**1a**–**1c**), but dienes and dialkyl phosphonate are formed by the elimination reaction when there is an easily abstracted β-hydrogen atom in the allylic group (**1h**, **1i**). Both rearrangement and elimination reactions can occur for compounds having a methyl group at the β-position of the carbon metal bond (**1d**, **1e**).

Experimental

All reactions were carried out, using the Schlenk technique, under prepurified nitrogen. All solvents and starting materials were distilled under nitrogen before use. Starting materials and products were characterized by boiling point, IR, ^{1}H NMR, MS and compared with the literature data. ^{1}H NMR spectra were recorded on an EM-360 spectrometer. Infrared spectra were taken as liquid film using a SPECORP 75 or Perkin–Elmer 683 IR spectrometer. Mass spectra were obtained on a Finnigan 4021 GC/MS/DC instrument. GLC was performed on a 2 m column (10% OV-101 supported on 102 silanized white support, 60–80 mesh) at 120°C.

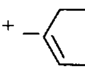
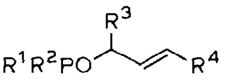
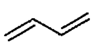
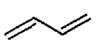
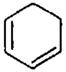
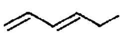
Allylic phosphites were prepared according to the literature [1,10,11]. The unknown allylic phosphites **1f** and **1h** were prepared by the reaction of diethyl phosphorochloridite and the corresponding allylic alcohols in the presence of triethylamine [1]. Data for the new compounds: **1f**; b.p. 75–76.5°C/1×10^{-4} Torr; Found: C, 61.08; H, 7.48; P, 12.29. $C_{13}H_{19}O_3P$ calcd.: C, 61.41; H, 7.53; P, 12.18%. ν_{max} (film): 1025s (P–O–C), 1640m (C=C) cm^{-1}; δ(H) 7.13–7.70 (m, 5H), 5.03–6.30 (m, 4H), 3.50–3.98 (m, 4H), 1.13 (t, 6H, J(H–H) 7 Hz); m/z: 254 (M^+), 117 ($M^+ - OP(OC_2H_5)_2$); **1h**: b.p. 78–79°C/0.2 Torr. Found: C, 54.83; H, 8.85; P, 13.93; $C_{10}H_{19}O_3P$ calcd.: C, 55.03; H, 8.78; P, 14.20%). ν_{max} (film): 1025s (P–O–C), 1650m (C=C) cm^{-1}; δ(H) 5.57–5.91 (m, 2H), 4.25–4.65 (m, 1H), 3.51–3.98 (m, 4H), 1.71–1.91 (m, 6H), 1.21 (t, 6H, J(H–H) 7 Hz); m/z: 218 (M^+), 139 ($HP(OH)(OC_2H_5)_2$), 138 (M^+ − ), 111 ($HP(OH)_2OC_2H_5$), 81 ($M^+ - OP(OC_2H_5)_2$).

TABLE 1

NICKEL-CATALYZED REARRANGEMENT OF PHOSPHITES 
$R^1R^2PO{-}CH(R^3){-}CH{=}CH{-}R^4$ TO PHOSPHONATES[a]

Phosphite	R¹	R²	R³	R⁴	T (°C)	t (h)	Yield[b] (%)				Thermal reaction	
							Rearrangement		Elimination		(°C/h)	Yield (%)
							2	3	dialkyl phosphonate	diene		
1a			H	H	80	10	68		0	0	130/10	0[c]
1b	Ph		H	H	90	4	82		0	0	100/4	10[d]
1c	OEt	OEt	H	H	80	8	85		0	0	180/4–6	25.1 [1]
1d	OEt	OEt	Me	H	100	20	44 (48)	(52)	29[d]	 [e]	180/4–6	36.8 [1]
1e	OEt	OEt	H	Me	105	20	49 (57)	(43)	21[d]	 [e]	200/4–6	15.4 [1]
1f	OEt	OEt	Ph	H	100	24	42 (0)	(100)	0	0	100/24	0[c]
1g	OEt	OEt	H	Ph	120	12	0		0	0		
1h	OEt	OEt	$-CH_2CH_2CH_2-$		120	16	0		60	 53	120/16	0[c]
1i	OEt	OEt	Et	Me	85	35	0		73	 (28)  (72) 69	85/24	0[c]

[a] 5 mol% $NiCl_2$ was used without solvent. [b] Isolated yield (the figures without parentheses indicate the total yield, the figures in parentheses show the percentage composition of **2** and **3** which were determined by NMR). [c] Starting material was recovered. [d] Determined by ^1H NMR. [e] Characterized by GLC.

General procedure for the nickel chloride catalyzed reaction of allylic phosphites

Allylic phosphite (2 mmol) was added with a syringe to anhydrous nickel chloride (0.1 mmol) under nitrogen. The solution immediately turned deep violet. The reaction mixture was heated, stirred and monitored with gas chromatography or TLC (silica gel/petroleum ether/ethyl acetate 2/1) until the disappearance of the starting material. At the end of the reaction, the color of the reaction mixture changed to yellow and the mixture was distilled to collect the diene in the cooling trap (dry ice). The residue was separated by column chromatography using silica gel and petroleum ether/ethyl acetate (16/1–3/1) as the eluent. On removing the solvent, the residue was distilled and the dialkyl phosphonate and the rearrangement product were isolated. The product was characterized by IR, ^{1}H NMR and MS. The reaction conditions and the distribution of products were shown in Table 1.

Acknowledgement

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