PALLADIUM(0) CATALYZED ISOMERIZATION OF ALKYNYLDIETHYL PHOSPHONATE AND ALKYNYLDIPHENYL PHOSPHINE OXIDE

Chunlin Ma^{*1}, Xiyan Lu² and Yongxiang Ma³

¹ Department of Chemistry, Liaocheng Teachers College,
Liaocheng 252059, People's Republic of China

² Shanghai Institute of Organic Chemistry, Academia Sinica

³ Department of Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China

1. Introduction

The isomerization of alkynes to conjugated dienes can represent a useful synthetic approach to these valuable blocks due to the ready accessibility and elaboration of alkynes. Recently there have appeared several reports about the isomerizations of alkynones[1], alkynoic esters[2], alkynoic amides[3] and propargylic alcohols[4] catalyzed by transition metal complexes. We have found that an α -electron-withdrawing carbonyl group is important for this reaction. In order to examine the involvement of an α -electron-withdrawing group, we decided to study the isomerization of acetylenic derivatives with other electron withdrawing group, such as the $P(O)(OR)_2$, $P(O)Ph_2$ groups. We wish to report here the isomerizations of alkynyldiethyl phosphonate and alkynyldiphenyl phosphine oxide catalyzed by palladium.

2. Results and discussion

2. 1. The results of the isomerization were shown in Scheme 1.

Scheme 1.

(i) 1 mmol (1) or (4), 0.05 mmol $Pd_2(dba)_3 \cdot CH_3Cl$, 0.20 mmol $i-Pr_3P$,
1 mmol HOAc, toluene. dba = dibenzylideneacetone.

2. 2. Effect of reaction temperature

The results of these thermal isomerizations are given in Table 1. The thermal isomerization of alkynyldiethyl phosphonates 1a to 1d occurred at 30°C to yield the 1E,3E-alkadienyl(diethyl) phosphonates 2a to 2d; whereas, at 110°C, isomeric 2E,4E-alkadienyl(diethyl) phosphonates 3b to 3d are formed. Compound 1a is transformed into 2a only, even at 110°C, which can be explained by the lower stability of a terminal double bond that would arise if 2a would isomerize, as 2b, 2c, or 2d do. Analogously, the isomerization of alkynyldiphenyl phosphine oxides 4a to 4b yielded only the 1E,3E-alkadienyl(diphenyl) phosphine oxides 5a to 5d, which might be due the donor ability of the phenyl moiety in compounds of type 4.

TABLE 1. Isomerization of (1) and (4) effected by reaction temperature

Compounds	Reaction Temp. (°C)	Reaction Time(h)	Product	Isolated yield (%)
1a	30	58	2a	85
1b	30	64	2b	86
1c	30	67	2c	79
1d	30	69	2d	82
1a	110	24	2a	89
1b	110	30	3b	92
1c	110	27	3c	89
1d	110	34	3d	90
4a	30	64	5a	83
4a	110	25	5a	87
4b	30	72	5b	87
4b	110	30	5b	86
4c	30	70	5c	85
4c	110	30	5c	87
4d	30	68	5d	84
4d	110	28	5d	89

2. 3. Stereochemistry of the isomerization

The stereochemistry of the products can be determined by ^1H NMR and IR spectra. The diene geometry of compounds (2a-2d) was all E, E-form, due to their ^1H NMR and IR spectra were as same as in the literature[5]. For (3b) $(\text{EtO})_2\text{P}(\text{O})-\text{CH}_2-\text{CH}_a=\text{CH}_b-\text{CH}_c=\text{CH}_d-\text{CH}_3$, the coupling constants $J_{a,b}$ and $J_{c,d}$ were both about 15Hz; For (5a-5d) $\text{Ph}_2\text{P}(\text{O})-\text{CH}_f=\text{CH}_g-\text{CH}_h=\text{CH}_i-\text{R}^1$, the $J_{f,g}$ and $J_{h,i}$ were all about 14Hz; in addition, the IR spectra of (3b-3d) and (5a-5d) showed a characteristic band about 960, 985 cm^{-1} respectively, due to the trans-trans alkadienyl moiety. We can conclude from this that the diene of (3b-3d) or (5a-5d) are E,E-type, which shows the high stereospecificity of the isomerization, as shown previously [1c, 1d].

2. 4. Reaction mechanism

The mechanism proposed for the isomerization of the substrate (1) at 30°C and (4) at 30°C or 110°C were similar to that we have explained for the reaction of α,β -ynones [1c, 6], it was an addition and elimination reaction of the [PdH] active species, as outline in Scheme 2.

Scheme 2.

[PdH] = LmPdH, it represents the active species containing a Pd-H bond. The L represents dba, i-Pr₃P or solvent.

According to B. N. Nokin 1,2-butadienyldiethyl phosphonate exists as an equilibrium mixture of three isomers at 100°C [7]:

The fact that the 2-butynyldiethyl phosphonate is the main one can be due to conjugative ability of 2-butyne with phosphorus was more favorable than 1,2-butadienyl or 1-butyne [7]. Then the reaction mechanism of substrate (1) at 110°C can be explained in Scheme 3.

Scheme 3

The substrate (1) first occurred addition reaction with [PdH], then lost it to form intermediate (6), The (6) was isomerized to (7) at 110°C, the (7) continued to occur isomerization catalyzed by palladium to give (3b-3d). In order to define the intermediate (7), we prepared the 2-hexynyldiethyl phosphonate (8), which can be isomerized to form 2E,4E-hexadienyldiethyl phosphonate (3b) catalyzed by the palladium complex at 110°C. as shown in Scheme 4.

To summarize, alkynyldiethyl phosphonates or alkynyldiphenyl phosphine oxides isomerize in high yield and highly stereoselectively. The 2E,4E-alkadienyl(diethyl) phosphonates 3b, 3c, and 3d can be used as synthons in organic synthesis[8].

3. Experimental section

All reactions were carried out under a prepurified argon atmosphere. Toluene was distilled from sodium and benzophenone under nitrogen atmosphere. ^1H -NMR were recorded on a Varian XL-200 or Bruker MSL-300 spectrometer. Chemical shifts were reported as values in parts per million with Me_4Si as an internal standard. ^{31}P -NMR spectra were recorded on a JEOL-FX-90Q FT NMR spectrometer and referenced to H_3PO_4 (85%) contained in a coaxial tube and measured under conditions of complete ^1H decoupling. Infrared spectra were taken as liquid film or KBr disc with Shimadzu IR-440 instrument. Mass spectral data were obtained with electron ionization on a Finnigan 4021 spectrometer.

3.1. Material;

Alkynyldiethyl phosphonate (1) and alkynyldiphenyl phosphine oxide (4) were prepared according the reported methods[9], all their ^1H -NMR, IR and MS spectra were determined.

Preparation of 2-hexynyldiethyl phosphonate (8) referenced to literature[10]. Oil liquid, yield 94%. IR(neat): 2900, 2200, 1390, 1250, 1020 cm^{-1} . ^1H -NMR (CDCl_3 /200 MHz): 4.2(m, 4H), 2.70(d, J 21Hz, 2H), 2.2(m, 2H), 1.5(m, 2H), 1.3(t, J 6 Hz, 6H), 1.0(t, J 7 Hz, 3H)ppm. MS: m/e 218(M^+ , 100), 190(90), 134(50), 109(62), 81(70), 43(38). Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_3\text{P}$: C, 55.04; H, 8.78; Found: C, 55.16; H, 8.92.

3.2. General procedure for the isomerization of (1), (4) and (8) catalyzed by palladium complex $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$.

Under argon, a mixture of (1), (4) or (8) (1mmol), HOAc(1mmol), $i\text{-Pr}_3\text{P}$ (0.2 mmol), $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$ (0.05 mmol) and toluene (5 ml) was heated at 30°C or 110°C, as monitored by TLC. After cooling and removal of solvent, the residue chromatographed on a silica gel column (eluting with acetone and petroleum ether) to give (2), (3), (5).

3.2.1. 1E,3E-pentadienyldiethyl phosphonate (2a)[10]

Pale yellow oil. IR(neat): 2950, 1640, 1590, 1250, 1030, 970 cm^{-1} . ^1H -NMR (CDCl_3 /200 MHz): 7.07(ddd, J 10, 17, 21 Hz, 1H), 6.10(m, 2H), 5.60(dd, J 17, 19.5 Hz, 1H), 4.10(m, 4H), 1.85(d, J 5.4Hz, 3H), 1.20(t, J 7 Hz, 6H) ppm. ^{31}P -NMR (CDCl_3 /90 MHz): 19.85 ppm. MS: m/e 204(M^+ , 19), 163(61), 135(100), 81(59), 43(71).

3.2.2. 1E,3E-hexadienyldiethyl phosphonate (2b)[11]

Pale yellow oil. IR(neat): 3000, 1645, 1600, 1250, 1040, 975 cm^{-1} . ^1H -NMR (CDCl_3 /200 MHz): 7.10(ddd, J 10, 16.8, 20 Hz, 1H), 6.12(m, 2H), 5.56(dd, J 17, 20 Hz, 1H), 4.10(m, 4H), 2.20(m, 2H), 1.30(t, J 7 Hz, 6H), 1.0(t, J 7 Hz, 3H) ppm. ^{31}P -NMR (CDCl_3 /90 MHz): 19.94 ppm. MS: m/e 218 (M^+ , 64), 189(43), 176(45), 148(100), 147(77), 120(47), 79

(46).

3. 2. 3. 1E,3E-heptadienyldiethyl phosphonate (2c)

Pale yellow oil. IR (neat): 2930, 1620, 1570, 1210, 1020, 965 cm^{-1} . $^1\text{H-NMR}$ ($\text{CDCl}_3/200$ MHz): 7.08(ddd, J 10, 17, 21 Hz, 1H), 6.15(m, 2H), 5.60(dd, J 17, 20 Hz, 1H), 4.10(m, 4H), 2.10(m, 2H), 1.35(m, 3H), 0.95(t, J 7 Hz, 3H) ppm. $^{31}\text{P-NMR}$ ($\text{CDCl}_3/90$ MHz): 20.0 ppm. MS: m/e 233($\text{M}^+ + 1$, 100), 232(M^+ , 12), 189(30), 177(27), 79(24). Anal. Calcd for $\text{C}_{11}\text{H}_{21}\text{O}_3\text{P}$: C, 56.89; H, 9.11; Found: C, 56.93; H, 8.98.

3. 2. 4. 1E,3E-octadienyldiethyl Phosphonate (2d)

Pale yellow oil. IR (neat): 2950, 1640, 1600, 1250, 1040, 960 cm^{-1} . $^1\text{H-NMR}$ ($\text{C}_6\text{D}_6/200$ MHz): 7.30(ddd, J 10, 17, 21 Hz, 1H), 5.80(dd, J 17, 20 Hz, 1H), 5.6(m, 2H), 4.0(m, 4H), 1.5(m, 2H), 1.05(m, 13H) ppm. $^{31}\text{P-NMR}$ ($\text{CDCl}_3/90$ MHz): 19.83 ppm. MS: m/e 246(M^+ , 29), 189(100), 176(54), 120(64), 65(55). Anal. Calcd for $\text{C}_{12}\text{H}_{23}\text{O}_3\text{P}$: C, 58.52; H, 9.41; Found: C, 58.97; H, 9.62.

3. 2. 5. 2E,4E-hexadienyldiethyl phosphonate (3b)[12]

Colorless liquid. IR (neat): 2950, 1640, 1595, 1250, 1050, 965 cm^{-1} . $^1\text{H-NMR}$ ($\text{CDCl}_3/300$ MHz): 6.20(m, 1H), 6.05(ddd, J 2.5, 7, 15 Hz, 1H), 5.70(m, 1H), 5.50(dd, J 7, 14.5 Hz, 1H), 4.10(m, 4H), 2.70(dd, J 8, 23 Hz, 2H), 1.80(d, J 7 Hz, 3H), 1.30(t, J 7.5 Hz, 6H) ppm. $^{31}\text{P-NMR}$ ($\text{CDCl}_3/90$ MHz): 27.39 ppm. MS: m/e 218(M^+ , 100), 190(18), 162(21), 109(24), 80(79).

3. 2. 6. 2E,4E-heptadienyldiethyl phosphonate (3c)

Colorless oil. IR (neat): 2950, 1640, 1595, 1250, 1030, 960 cm^{-1} . $^1\text{H-NMR}$ ($\text{CDCl}_3/200$ MHz): 6.10(m, 2H), 5.60(m, 2H), 4.10(m, 4H), 2.65(dd, J 7.5, 24 Hz, 2H), 1.8(m, 2H), 1.25(t, J 7 Hz, 6H), 0.95(t, J 7.5 Hz, 3H) ppm. $^{31}\text{P-NMR}$ ($\text{CDCl}_3/90$ MHz): 27.48 ppm. MS: m/e 232(M^+ , 100), 204(16), 175(12), 94(100), 79(82). Anal. Calcd for $\text{C}_{11}\text{H}_{21}\text{O}_3\text{P}$: C, 56.89; H, 9.11; Found: C, 56.48; H, 9.34.

3. 2. 7. 2E,4E-octadienyldiethyl phosphonate (3d)[12]

Colorless oil. IR (neat): 2951, 1642, 1595, 1249, 1040, 960 cm^{-1} . $^1\text{H-NMR}$ ($\text{CDCl}_3/200$ MHz): 6.10(m, 2H), 5.40(m, 2H), 4.0(m, 4H), 2.60(dd, J 8, 22 Hz, 2H), 1.80(m, 2H), 1.20(m, 8H), 0.95(t, J 7.5 Hz, 3H) ppm. $^{31}\text{P-NMR}$ ($\text{CDCl}_3/90$ MHz): 27.41 ppm. MS: m/e 246(M^+ , 100), 217(30), 189(21), 108(57), 79(98), 59(52).

3. 2. 8. 1E,3E-pentadienyldiphenyl phosphine oxide (5a)[13]

White crystal, m. p. 155–156 $^{\circ}\text{C}$ (literature [13]). m. p. 154–155 $^{\circ}\text{C}$. IR (KBr): 2950, 1645, 1590, 1170, 1120, 985 cm^{-1} . $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}/200$ MHz): 7.75(m, 4H), 7.5(s, 6H), 7.1(ddd, J 10, 17, 18.5 Hz, 1H), 6.45(m, 2H), 6.20(dt, J 7, 14 Hz, 1H), 1.8(d, J 7 Hz, 3H)

ppm. ^{31}P -NMR $\{(\text{CD}_3)_2\text{CO}/200\text{MHz}\}$ 20.83 ppm. MS: m/e 268(M^+ , 100), 253(83), 202(59), 183(64), 144(52), 115(11), 129(44), 77(40).

3. 2. 9. 1E,3E-hexadienyldiphenyl phosphine oxide (5b)

White crystal, m. p. 119-121°C. IR(KBr). 2900, 1620, 1560, 1420, 1160, 1100, 988 cm^{-1} .

^1H -NMR $\{(\text{CD}_3)_2\text{CO}/200\text{ MHz}\}$: 7.75(m, 4H), 7.5(s, 6H), 7.10(ddd, J 10, 16.5, 18.5 Hz, 1H), 6.50(m, 2H), 6.20(dt, J 7, 13.5 Hz, 1H), 2.2(m, 2H), 1.0(t, J 7 Hz, 3H) ppm. ^{31}P -NMR $\{(\text{CD}_3)_2\text{CO}/90\text{ MHz}\}$: 20.92 ppm. MS: m/e 282(M^+ , 64), 267(12), 253(100), 201(63), 183(48), 158(26), 129(28), 77(19). Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{OP}$: C, 76.58; H, 6.78; Found: C, 76.50; H, 6.47.

3. 2. 10. 1E,3E-heptadienyldiphenyl phosphine oxide (5c)

White crystal, m. p. 91-93°C. IR(KBr). 2950, 2850, 1620, 1560, 1420, 1100, 985 cm^{-1} .

^1H -NMR $\{(\text{CD}_3)_2\text{CO}/200\text{ MHz}\}$: 7.75(m, 4H), 7.5(s, 6H), 7.10(ddd, J 9.5, 16.7, 18.6 Hz, 1H), 6.5(m, 2H), 6.19(dt, J 7, 14.3 Hz, 1H), 2.08(m, 2H), 1.30(m, 2H), 0.95(t, J 7 Hz, 3H) ppm. ^{31}P -NMR $\{(\text{CD}_3)_2\text{CO}/90\text{MHz}\}$: 21.07 ppm. MS: m/e 297($\text{M}^+ + 1$, 100), 253(35), 201(31), 183(6), 115(5), 77(12). Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{OP}$: C, 77.01; H, 7.14; Found: C, 76.80; H, 6.86.

3. 2. 11. 1E,3E-octadienyldiphenyl phosphine oxide (5d)

White crystal, m. p. 73-75°C. IR(KBr). 2952, 2851, 1620, 1565, 1420, 1165, 985 cm^{-1} .

^1H -NMR $\{(\text{CD}_3)_2\text{CO}/200\text{ MHz}\}$: 7.76(m, 4H), 7.52(s, 6H), 7.11(ddd, J 10, 16.5, 18.5 Hz, 1H), 6.48(m, 2H), 6.20(dt, J 7, 14 Hz, 1H), 2.10(m, 2H), 1.30(m, 4H), 0.95(t, J 7 Hz) ppm. ^{31}P -NMR $\{(\text{CD}_3)_2\text{CO}/90\text{ MHz}\}$: 20.87 ppm. MS: m/e 311($\text{M}^+ + 1$, 95), 281(100), 253(8), 231(96), 201(23), 177(7), 77(11). Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{OP}$: C, 77.40; H, 7.47; Found: C, 77.86; H, 7.52.

Acknowledgements

This work was finished at Shanghai Institute of Organic Chemistry, Academia Sinica. Financial support from the National Natural Science Foundation of China and Academia Sinica is gratefully acknowledged.

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Received: June 12, 1995 - Accepted: June 23, 1995 - Received in revised camera-ready format: July 13, 1995