Tetrahedron Letters, Vol.32, No.23, pp 2619-2620, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

Synthesis and Oxidation of 1,2 λ^5-Azaphosphinines

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Key words : 1,5 λ^5-azaphosphinines ; non sensitized oxidation ; phosphine oxides ; isomerization.

Abstract : *1,2 λ^5-azaphosphinines are prepared from 1-t.butyl 1,2-dihydro 1,2 λ^3-azaphosphinines by methylation on phosphorus atom, thermolysis of the resulting phosphonium salts and treatment with potassium carbonate. The 1,2 λ^5-azaphosphinines, oxidized on exposure to air give phosphine oxides.*

The synthesis of λ^3-azaphosphinines has received recent attention [1,2], but there are few reports on the λ^5-azaphosphinines : 4,4-diphenyl 1,4 λ^5-azaphosphinines [3], 3,3-diethoxy 1,3 λ^5-azaphosphinines [4], and 2,2-dialkoxy 1,2 λ^5-azaphosphinines [5] have been prepared. Recently, the synthesis of the 1,2-dihydro 1,2 λ^3-azaphosphinines has been reported [6]. We describe here the preparation of new 1,2 λ^5-azaphosphinines from 1-tert.butyl 1,2-dihydro 1,2 λ^3-azaphosphinines.

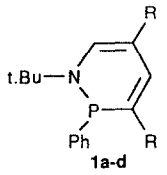
Alkylation of **1** with MeI in toluene gave the phosphonium salts **2** (60 - 70 %). The thermolysis of **2** at 210-230°C for 15-20 min. yielded isobutene and phosphonium salts **3** (95 %). The formation of isobutene from **1** has been previously reported [2]. Treatment of a solution of salts **3** in ether-acetonitrile with dry K_2CO_3 at room temperature produced 1,2 λ^5-azaphosphinines **4** (table).

1,2 λ^5-Azaphosphinines were oxidized and hydrolyzed slowly on exposure to air to give formamide, identified by ^1H NMR, and phosphine oxides. Azaphosphinines **4a** and **4b** afforded **5aZ** and **5bZ**. Azaphosphinine **4c** gave a mixture of phosphine oxides **5cZ**, **6c** and **7c** (product ratios 76:12:12) ; **4d** gave a mixture of **5dZ**, **6d** and **7d** (product ratios 48:22:30). Compounds **5**, **6** and **7** were separated by chromatography on silica gel. A slow isomerization of **5Z** into **5E** was observed in solution at room temperature. The isomerization of **5c** and **5d** in basic media (BaO) gave quantitatively **6c** and **6d**.

Table : Synthesis and NMR data [a] of 1,2 λ^5-azaphosphinines **4** and phosphine oxides **5**.

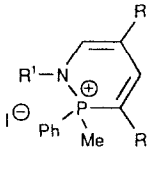
		4, δ (J Hz)				**5Z**, δ (J Hz)		**5E**, δ (J Hz)	
	Yield(%)[b]	^{31}P	H_4(JPH)	H_6(JPH)	C_3(JPC)	^{31}P	H_3(JPH)	^{31}P	H_3(JPH)
a	97	21.8	7.07(46)	6.76(28.6)	91.8(75)	31.8	6.68(33.6)	33.1	7.07(20)
b	86	21.7	7.06(46)	6.80(29.6)	97.9(73)	30.7	6.60(33.6)	33.7	7.01(21)
c	80	22.1	7.08(47)	6.79(29.0)	95.7(73)	32.5	6.61(36.0)	33.2	6.99(21)
d	83	22.0	7.05(45)	6.78(28.8)	96.1(75)	32.5	6.61(35.7)	33.2	7.00(20)

[a] Spectra recorded on Bruker AC 300, in $CDCl_3$. [b] Isolated yield based on the amount of **3**.

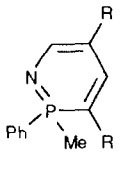


1a-d

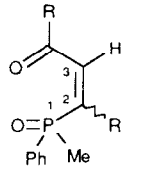
a : R = Me ; **b** : R = Et ; **c** : R = Pr ; **d** : R = Bu.



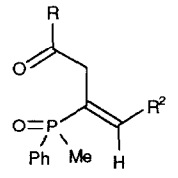
2a-d R^1 = t.Bu
3a-d R^1 = H



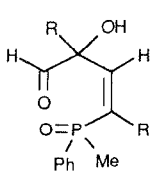
4a-d



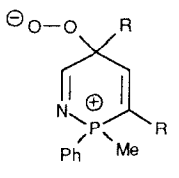
5a-d



6c R = Pr, R^2 = Et
6d R = Bu, R^2 = Pr



7c,d



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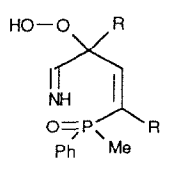

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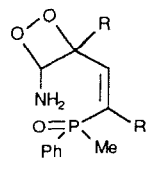

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Structures of **5**, **6**, **7** were determined by IR, ^{1}H NMR, ^{13}C NMR and MS spectral analyses [7]. The structures Z and E were assigned by ^{1}H NMR : the coupling constants between phosphorus and H-3 were 33-36 Hz in the Z isomer and 20-21 Hz in the E isomer [8]. The suggested reaction mechanism involves the formation of **8** as in the oxidation of alkylidenphosphoranes [9,11] and the oxidation of enamines [10]. Hydrolysis of **8** can lead to **9**, precursor of **7** and **10**, which is the precursor of **5** and $HCONH_2$ [10].

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7. Selected spectral data ^{1}H NMR, $CDCl_3$, δ, J_{PH} (Hz) : **6c** δ 1.74 (3H, d, J = 12.8) ; 3.27 (2H, d, J = 15.2) ; 6.47 (1H, dt, J = 20). HRMS found 278.1435. $C_{16}H_{23}O_2P$ requires 278.1436. **6d** δ : 1.76 (3H, d, J = 13.6) ; 3.31 (2H, d, J = 14.4) ; 6.48 (1H, dt, J = 20.8). HRMS found 306.1750. $C_{18}H_{27}O_2P$ requires 306.1749. **7c** IR 1722, 3150 cm^{-1}. δ 1.88 (3H, d, J = 12.8) ; 6.50 (1H, d, J = 36.8) ; 9.71 (1H, s). HRMS found 279.1513. $C_{16}H_{24}O_2P$ (M^+-CHO) requires 279.1514. **7d** IR 1720, 3150 cm^{-1}. δ 1.90 (3H, d, J = 13.6) ; 6.50 (1H, d, J = 36.8) ; 9.69(1H, s). HRMS found 307.1847 ; $C_{18}H_{28}O_2P$ (M^+-CHO) requires 307.1826.
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(Received in France 4 February 1991)