Tetrahedron Vol. 40, No. 17, pp. 3273 to 3276, 1984
Printed in the U.S.A.

0040–4020/84 $3.00 + .00

REACTIONS OF VINYLPHOSPHIRANES WITH METHYLENETRIMETHYLPHOSPHORANE

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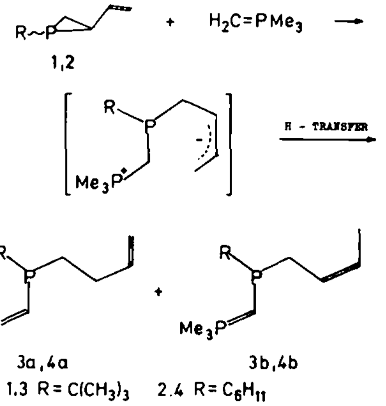
(*Received in Germany* 24 *October* 1983)

Abstract—The reaction of methylenetrimethylphosphorane with isomeric mixtures of *cis* and *trans* 1-t-butyl- or 1-cyclohexyl-2-vinylphosphirane produce new phosphino-substituted phosphorus ylids via ring-opening and proton transfer. The products are fully characterized by NMR.

Although substituted phosphiranes can be prepared relatively easily, the chemistry of these compounds has received little attention[1-3]. This may be due to several features that distinguish phosphiranes from most other phosphanes, for example, quaternation of the P atom leads to decomposition of the molecule and reaction with a wide variety of Lewis acids leads to olefin elimination or to polymerization. MeLi causes cleavage of the 3-membered ring.

Our recent discovery of an easy route to vinylphosphiranes[4] encouraged us to study phosphiranes in more detail, in view of the expected stabilization of the ring system by the vinyl group. The metal-catalyzed rearrangement to substituted phospholenes has already been reported;[5] here we present our results on the reaction of vinylphosphiranes with methylenetrimethylphosphorane.

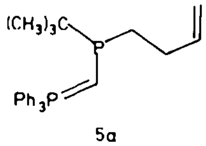


RESULTS AND DISCUSSION

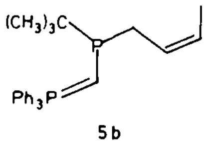
When a solution of methylenetrimethylphosphorane in benzene, toluene or pentane is added to a solution of 1-t-butyl-2-vinylphosphirane (**1**) or 1-cyclohexyl-2-vinylphosphirane (**2**) a slightly exothermic reaction is observed. The 32 MHz-^{31}-P NMR spectra of the isolated products from **1** or **2** show no signals between −170 and −190 ppm characteristic of the starting phosphiranes. In each case, two AB-quartets with a large coupling of *ca* 146 Hz in the region of +2.3 and −24.9 ppm are observed. The mass spectra, which show a strong $(M - C_4H_7)^+$ fragmentation, are consistent with the formation of 1:1 adducts. The initially expected structure—a 5-membered ring containing two P atoms—was rejected after ^{1}H- and ^{13}C-NMR studies, in favour of the two isomeric structures **3a** and **3b** from phosphirane **1** and **4a** and **4b** from compound **2**. The NMR data, which are collected in Tables 1 and 2, are consistent with the assigned structures. The coupling constants ${}^1J_{P\beta C}$ to C_1 and C_2 and also ${}^2J_{P\beta H}$ to the methine proton on C_2 are relatively large, as is characteristic for ylids, while ${}^1J_{P\alpha C}$ to C_2, C_3 and C_7 and ${}^2J_{P\alpha H}$ to the methine proton are relatively small, and fall in the range expected for phosphines. Taken together they are indicative of a phosphino-substituted ylid.[6] Furthermore, while the methine proton on C_2 shows no further proton-proton coupling, the diastereotopic protons on C_3 are coupled to the protons on C_4. This observation establishes that C_5 remains bonded to C_6 and that ring opening has indeed occurred between P and the secondary C of **1** or **2**, respectively.

The compounds **3** and **4** are probably produced by nucleophilic attack of the phosphorane on the P atom accompanied by ring-opening. This zwitterion reacts further by proton transfer from the methylene group (C–2) to either C–4 or C–6 of the butenylic anion to give two isomeric phosphoranes, one bearing a Z-buten-2-yl group, the other a buten-3-yl group on P. Both isomers are formed in roughly equal amounts, i.e., 2:3 for **3a** and **3b** and 3:2 for **4a** and **4b** irrespective of the isomeric ratio or the starting material. Thus the *cis*- and *trans*-phosphiranes must have undergone scrambling at the stage of butenyl anion formation.

The reaction of methylenetriphenylphosphorane with t-butylvinylphosphirane gives the analogous ylids **5a** and **5b**, which have been characterized by ^{31}P- and ^{1}H-NMR. However, the reaction with the aryl-substituted ylid is still incomplete after stirring for 8 days at 20°. The highly strained hexamethylsilirane (hexamethylsilacyclopropane) is reported to react readily in a similar manner with methylenetrimethylphosphorane to give the Si substituted phosphorane $Me_2CHCMe_2SiMe_2CH = PMe_3$,[8]



5a



5b

Table 1. ^{1}H-NMR-data of 3–4; 400 MHz; T = 300 K. All chemical shifts vs TMS as internal standard; solvent [D$_6$] benzene

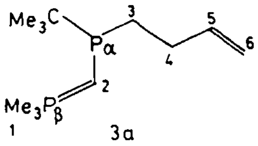
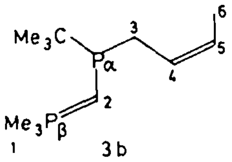
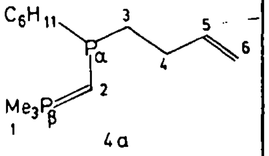
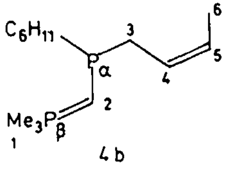
No	 3a 42% δ	 3b 58% δ	 4a 67% δ	 4b 33% δ
1	0.94 $^3J_{P_\alpha}=0.5$; $^2J_{P_\beta}=12.5$	0.95 $J_{P_\alpha}=0.5$; $J_{P_\beta}=12.3$	0.96 $J_{P_\alpha}=0.4$; $J_{P_\beta}=12.4$	0.97 $J_{P_\alpha}=0.4$; $J_{P_\beta}=12.4$
2	0.08 $^2J_{P_\alpha}=3.7$; $^2J_{P_\beta}=15.3$	0.18 $J_{P_\alpha}=3.5$; $J_{P_\beta}=14.6$	0.14 $J_{P_\alpha}=4.1$; $J_{P_\beta}=15.3$	0.28 $J_{P_\alpha}=3.7$; $J_{P_\beta}=14.9$
3	1.45 $J_{P_\alpha}=7.5$; $J_{P_\beta}=1.0$ 1.65 $J_{P_\alpha}=6.1$; $J_{P_\beta}=2.9$	2.41 2.29	1.56 $J_{P_\alpha}=4.8$; $J_{P_\beta}=0.5$ 1.69 $J_{P_\alpha}=6.7$; $J_{P_\beta}=2.0$	not assigned
4	2.45 2.32	5.79 $J_{P_\alpha}=5.5$; $^3J_{4,5}=10.6$	not assigned	5.88 $J_{P_\alpha}=5.2$; $J_{4,5}=10.5$
5	6.12	5.57 $J_{P_\alpha}=3.5$	6.15	5.63 $J_{P_\alpha}=3.0$
6	5.16 trans 5.00 cis $J_{P_\alpha}=1.0$	1.72 $J_{P_\alpha}=2.7$	5.19 trans 5.04 cis $J_{P_\alpha}=0.8$	1.76 $J_{P_\alpha}=3.2$
7	1.16 $J_{P_\alpha}=11.4$	1.20 $J_{P_\alpha}=11.5$	Cyclohexylprotons not assigned	

Table 2. ^{13}C and ^{31}P-NMR data of 3–4

^{13}C a)	3a					3b					4a					4b				
Carbon No	δ_C	Mult	$J_{P_\alpha C}$	$J_{P_\beta C}$	J_{CH}	δ_C	Mult	$J_{P_\alpha C}$	$J_{P_\beta C}$	J_{CH}	δ_C	Mult	$J_{P_\alpha C}$	$J_{P_\beta C}$	J_{CH}	δ_C	Mult	$J_{P_\alpha C}$	$J_{P_\beta C}$	J_{CH}
1	17.93	q	59.7	7.0	128	17.89	q	59.5	7.3	128	17.92	q	59.6	7.0	129	17.89	q	59.5	7.1	129
2	5.75	d	117.4	17.4	150	6.11	d	116.0	18.0	150	5.95	d	117.2	16.0	150	6.15	d	116.1	17.3	150
3	27.42	t	10.9	14.0	c)	27.78	t	8.9	16.9	c)	30.33	t	11.5/10.5 d)		126	30.34	t	9.6	24.0	126
4	32.10	t	0.9	17.7	127	130.65	d	0.6	8.9	152	31.46	t	0.7	15.0	127	129.60	d	-	5.5	153
5	41.80	d	-	13.2	151	121.95	d	-	9.3	153	41.78	d	-	21.1	151	122.14	d	-	7.8	153
6	13.06	t	-	-	153 157	13.41	q	-	0.9	125	13.12	t	-	-	153 156	13.51	q	-	0.9	125
7	28.56	s	7.7	7.7	-	29.18	s	9.8	9.8	-	40.36	d	8.6/6.8 d)		126	39.61	d	8.2/10.1 d)		127
8	27.64	q	-	14.2	125	27.64	q	-	14.2	125	31.03	t	-	16.7	126	34.14	t	-	17.7	126
8'											29.31	t	-	8.0	128	29.31	t	-	8.0	128
9,9'											28.07	t	-	10.6	126	28.04	t	-	9.7	126
10'											27.57	t	-	-	128	27.59	t	-	-	128
^{31}P b)																				
P_α	-9.5					-6.1					-24.9					-21.4				
P_β	+2.3					+2.0					+1.9					+1.6				
$^2J_{PP}$	145.9					146.5					145.9					147.1				

a) 75.6 MHz, 313 K. Chemical Shifts relative to internal TMS. Solvent $[D_6]$-Benzene

b) 32.2 MHz, 311 K. Chemical Shifts relative to external 85% aqueous phosphoric acid. Solvent $[D_6]$-Benzene

c) Partially observed, J_{CH} not determined accurately d) $J_{P_\alpha C}$ and $J_{P_\beta C}$ have not been assigned demonstrating the stereochemical analogy between small ring compounds of P and Si. On the other hand, we found that the substituted vinylphosphiranes **1** and **2** did not react with water, methanol, CCl_4, and diazomethane—unlike the siliranes, which give ring-opening reactions with all of these reagents.

EXPERIMENTAL

Reaction of **1** *with methylenetrimethylphosphorane.* 1-t-Butyl-2-vinylphosphirane (**1**), 0.45 g (3.2 mmol) was dissolved in 15 ml of pentane under argon. This soln was cooled to 0° and 0.29 g (3.2 mmol) of methylenetrimethylphosphorane in 5 ml of pentane was then added dropwise. The mixture was noted to turn yellow, which faded after stirring overnight. After 16 hr, the solvent was removed, leaving a slightly yellow oil. Bulb-to-bulb distillation at 93–95°/0.001 mm Hg gave 0.6 g (85%) of (t-butylbuten-3-ylphosphinometylene)-trimethylphosphorane **3a** and its buten-2-yl isomer **3b**. ^1H- and ^{13}C-NMR: see Tables 1 and 2, IR (20 μ) (cm^{-1}): ν(P=C) 1155, ν(C=C) 1635; MS (70 eV) *m/e* (rel. intensity): 232 (5%), 177 (70%), 175 (80%), 121 (100%), 77 (60%), 76 (55%). (Found: C, 62.08; H, 11.16; P, 26.65. Calc for: $C_{12}H_{26}P_2$ (232.34) C, 62.03; H, 11.28; P, 26.68%).

Reaction of **2** *with methylenetrimethylphosphorane.* 1-Cyclohexyl-2-vinylphosphirane, 0.86 g (5.1 mmol) and 0.46 g (5.1 mmol) of methylenetrimethylphosphorane gave after distillation at 98° – 100°/0.001 mm Hg 1.2 g (90%) of **4a** and its buten-2-yl isomer **4b**. IR (20 μ) (cm^{-1}): ν(P=C) 1155, ν(C=C) 1635; MS (70 eV) *m/e* (rel. intensity): 258 (5%), 203 (30%), 175 (40%), 121 (100%), 76 (30%). Found: C, 64.98; H, 10.85; P, 24.05. Calc for $C_{14}H_{28}P_2$ (258.37): C, 65.07; H, 10.92; P, 24.00%).

Reaction of **1** *with methylenetriphenylphosphorane.* 1-t-Butyl-2-vinylphosphirane, 0.20 g (1.4 mmol), and 0.39 g (1.4 mmol) of methylenetriphenylphosphorane in 20 ml of pentane yielded after 6 d at room temp, ~0.5 g of **5a** and its buten-2-yl isomer **5b** as an orange, viscous oil. Compounds **5a** and **5b** were found to decompose on distillation. The ^{31}P-NMR spectra of the crude products showed unreacted **1** to be present; $\delta_P = -170.6$ ppm. ^{31}P-NMR (C_6D_6): – 9.4 and 21.5 ppm, $^2J_{pp}$: 131.8 Hz (**5a**); – 6.5 and 21.0 ppm, $^2J_{pp}$: 133.3 Hz (**5b**), **5a**: **5b** = 8:5, ^1H-NMR (C_6D_6) 1.0, 2*s* (2H, P=CH), 1.13, 1.14, 2d (18H, $C(CH_3)_3$, J_p = 11 Hz), ~ 1.7, m (CH_3,CH_2), ~ 2.3, m (CH_2), 5.0, m (4H, =CH_2), 5.55, m (4H, HC=CH), 6.05, m (2H, CH=), 7.1, 7.72, m (30H, C_6H_5); IR (neat) (cm^{-1}): ν(P=C) 1155, ν(C=C) 1635, ν($CH=CH_2$) 910, 995; MS (70 eV) *m/e* (rel. intensity): 418 (3%), 361 (100%), 307 (50%), 262 (20%), 183 (50%), 108 (20%). $C_{27}H_{32}P_2$ (418.55)

Reaction of **1** *with diazomethane.* A soln of 1.75 mmol of **1** in 20 ml of pentane was added dropwise to 1.75 mmol of diazomethane dissolved in 5 ml of pentane. Very little N_2 evolution was observed. After stirring overnight the pentane was removed yielding a residue of essentially pure unreacted **1**, which was readily determined by ^{31}P- and ^1H-NMR.

Reaction of **1** *with water, methanol or* CCl_4, Solns of **1** in d_4-MeOH, MeOH/D_2O, or CCl_4/C_6D_6 were heated in sealed NMR tubes to 50°. No reaction was observed.

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