Pergamon

Tetrahedron 57 (2001) 9873–9875

TETRAHEDRON

Reaction between triphenylphosphine and arylsulfonylglycyl chlorides. Synthesis of *N*-[(*Z*)-2-chloro-2-(1-hydroxy-1,1,1-triphenylphosphoranyl)-ethenyl]-1-arylsulfonamides

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Received 19 June 2001; revised 10 September 2001; accepted 4 October 2001

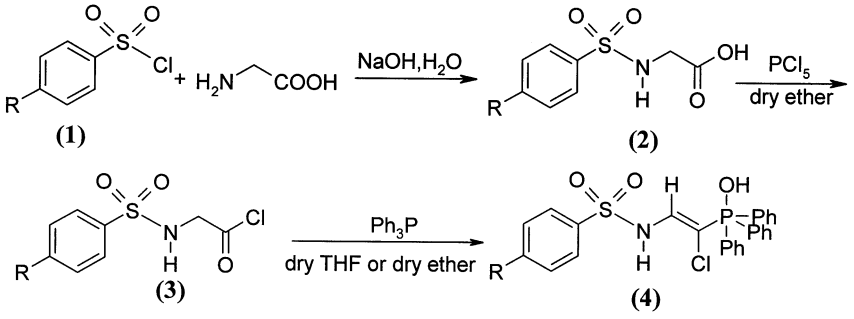
Abstract—Stable hydroxyphosphoranes are obtained in excellent yields from the reaction between triphenylphosphine and arylsulfonylglycyl chlorides in dry tetrahydrofuran or dry diethyl ether. © 2001 Published by Elsevier Science Ltd.

1. Introduction

A number of rearrangements have been observed which involve hydroxyphosphoranes in equilibrium with pentavalent vinyl oxyphosphoranes and vinyl phosphonium hydroxides as elusive transient species.[1–4] In all of the reactions in which this hydroxy-containing pentacoordinated system is postulated, the hydroxyphosphorane cannot be isolated but is believed to occur as an intermediate on the pathway to an observed product. To date, we know of no published report concerning isolation and characterization of such hydroxyphosphoranes. We wish to report a simple one-pot synthesis of fairly stable *N*-[(*Z*)-2-chloro-2-(1-hydroxy-1,1,1-triphenylphosphoranyl)-1-ethenyl]-1-arylsulfonamides **4**. Thus, the reaction of arylsulfonylglycyl chlorides **3** with triphenylphosphine in dry tetrahydrofuran (THF) or dry diethyl ether leads to the corresponding hydroxyphosphoranes **4** in excellent yields (Scheme 1).

2. Results and discussion

The reaction of arylsulfonylglycyl chlorides **3** with triphenylphosphine proceeded spontaneously at room temperature in dry THF or dry diethyl ether, and finished within a few minutes. ^{1}H and ^{13}C NMR spectra of the crude precipitate clearly indicated the formation of *N*-[(*Z*)-2-chloro-2-(1-hydroxy-1,1,1-triphenylphosphoranyl)-ethenyl]-1-arylsulfonamides **4**. Any product other than **4** could not be detected by NMR spectroscopy. The structures of



(1) (2) (3) (4)

(1-4)	R	%Yield of (4)
a	H	94
b	Me	95
c	Et	95
d	i-Pr	95

Scheme 1.

Keywords: arylsulfonylglycyl chlorides; vinyl oxyphosphoranes; hydroxyphosphorane; triphenylphosphine.
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0040–4020/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0040-4020(01)01005-5

compounds **4a–d** were deduced from their elemental analyses and their IR, ^{1}H, ^{13}C and ^{31}P NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at appropriate *m/z* values.

The ^{1}H NMR spectra of compounds **4a–d** in $CDCl_3$ at room temperature (25°C) exhibited a characteristic double doublet ($^{3}J_{HH}$=10.8 Hz, $^{3}J_{HP}$=8.3 Hz) at about δ=5.85–5.95 for the vinylic proton, and a doublet ($^{3}J_{HH}$=10.8 Hz) at about δ=11.5 for the NH group, along with a very broad peak at about δ=9.5–10.5 for the P–OH moiety. Near +50°C the broad P–OH proton signal of compound **4a** becomes sharper. Decreasing the temperature results in the splitting of the broad P–OH resonance into a doublet ($^{2}J_{HP}$=25.7 Hz) with an intensity ratio of 1:1 (coalescence temperature, −28±1°C). At −60°C, a fairly sharp doublet was observed for the P–OH group. From the coalescence of the P–OH proton resonance and using the expression $k = \pi\Delta\nu/\sqrt{2}$, we calculate the first order rate constant (k) for the O–H proton exchange in **4a** to be 55.5 s^{-1} at 245 K. Application of the absolute rate theory with a transmission coefficient of one gave a free-energy of activation $\Delta G^{\neq}$ of 51.4±2 kJ mol^{-1} where all known sources of errors were estimated and included.[5] The experimental data available were not suitable for obtaining meaningful values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, even though the errors in $\Delta G^{\neq}$, were not large.[6]

The ^{1}H-decoupled ^{13}C NMR spectra of **4a–d** showed two characteristic doublets at about δ=119 ($^{1}J_{CP}$=133 Hz) and δ=123 ($^{2}J_{CP}$=42–43 Hz) for the P–*C*=C and P–C=*C* moieties, respectively. The ^{13}C NMR spectra are in agreement with the hydroxyphosphorane structure. Partial assignments of these resonances are given in Section 3. The ^{1}H-decoupled ^{31}P NMR spectra of **4a–d** exhibited a sharp signal at about δ=18.7.

We have not established a mechanism for the formation of *N*-[(*Z*)-2-chloro-2-(1-hydroxy-1,1,1-triphenylphosphoranyl)-ethenyl]-1-arylsulfonamides (**4**) in an experimental manner, but a reasonable possibility is indicated in Scheme 2. The first step of this mechanism involves the nucleophilic attack of the phosphine to the carbonyl group of the acid chloride and formation of the tetrahedral intermediate **5**, which can be in equilibrium with the cyclic oxyphosphorane **6**. Such an addition product may isomerize under the reaction conditions employed to produce the hydroxyphosphorane **4** (see Scheme 2).

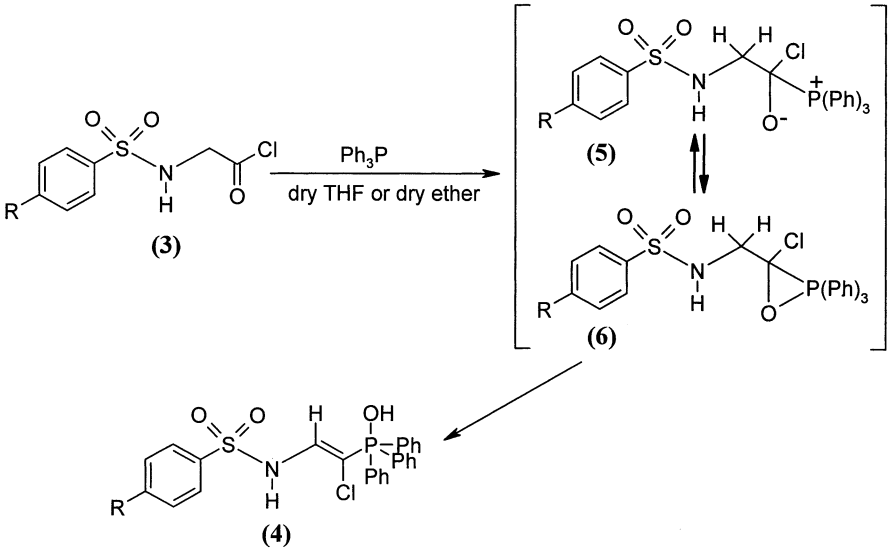
In conclusion, we have found that the reaction of arylsulfonylglycyl chlorides with triphenylphosphine in dry THF or dry diethyl ether at room temperature leads to a simple synthesis of the highly functionalized hydroxyphosphoranes **4a–d** in excellent yields. The present method carries the advantage that not only is the reaction performed under neutral conditions, but the substances can be mixed without any activation or modification. Dynamic ^{1}H NMR spectroscopy was employed to study proton-exchange reaction of the P–OH group in **4a**.

3. Experimental

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded as KBr discs on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 500.1, 125.7 and 202.5 MHz, respectively, on a BRUKER DRX 500-AVANCE FT-NMR instrument with $CDCl_3$ as solvent. Compounds **2** and **3** were prepared according to the published procedures.[7–9] The reagents and solvents used in this work were obtained from Fluka (Buchs, Switzerland) and used without further purification.

3.1. General procedure

The arylsulfonylglycyl chloride (2 mmol) and triphenylphosphine (2 mmol, 0.525 g) were dissolved in 5 mL anhydrous tetrahydrofurun (anhydrous diethyl ether for **4c** and **4d**) after 10 min stirring at room temperature, the product was then filtered off, washed with anhydrous THF and dried in vacuum.



Scheme 2.

3.1.1. *N*-[(*Z*)-2-Chloro-2-(1-hydroxy-1,1,1-triphenylphosphoranyl)-1-ethenyl]-1-benzenesulfonamide (4a). White powder, 0.93 g, yield 94%, mp 145–150°C (dec.). IR (KBr) (ν_{max}, cm^{-1}): 2970 (N–H), 2830 and 2380 (PO–H), 1336 and 1156 (SO_2), 927 (P–O). ^1H NMR (500 MHz, $CDCl_3$): δ_H=5.87 (1H, dd, $^3J_{HH}$=10.8 Hz, $^3J_{HP}$=8.3 Hz, P–C=CH), 7.5–7.8 (20H, m, $4C_6H_5$), 9.5 (1H, br, O–H), 11.57 (1H, d, $^3J_{HH}$=10.8 Hz, N–H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C=117.41 (d, $^1J_{CP}$=90.4 Hz, C_{ipso} of P–Ph), 119.05 (d, $^1J_{CP}$=132.63 Hz, P–*C*=CH), 122.72 (d, $^2J_{CP}$=43 Hz, P–C=*C*H), 126.40 (C_{meta} of Ph–SO_2), 128.69 (C_{ortho} of Ph–SO_2), 129.7 (d, $^3J_{CP}$= 12.6 Hz, C_{meta} of P–Ph), 132.5 (C_{para} of Ph–SO_2), 133.70 (d, $^2J_{CP}$=10.37 Hz, C_{ortho} of P–Ph), 134.80 (d, $^4J_{CP}$=2.5 Hz, C_{para} of P–Ph), 139.66 (C–SO_2). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P=18.76 (P–OH). MS, *m/z* (%): 495 (M^+, 1), 479 (1), 419 (2), 277 (83), 141 (54), 77 (100), 51 (50). Anal. Calcd for $C_{26}H_{23}NO_3PSCl$ (495.958): C, 62.96; H, 4.67; N, 2.82%. Found: C, 62.9; H, 4.7; N, 2.9%.

3.1.2. *N*-[(*Z*)-2-Chloro-2-(1-hydroxy-1,1,1-triphenylphosphoranyl)-1-ethenyl]-4-methyl-1-benzenesulfonamide (4b). White powder, 0.97 g, yield 95%, mp 130–133°C (dec.). IR (KBr) (ν_{max}, cm^{-1}): 2965 (N–H), 2850 (PO–H), 1633 (C=C), 1342 and 1158 (SO_2), 936 (P–O). ^1H NMR (500 MHz, $CDCl_3$): δ_H=2.38 (3H, s, CH_3), 5.85 (1H, dd, $^3J_{HH}$=10.8 Hz, $^3J_{HP}$=8.3 Hz, P–C=CH), 7.25 (2H, d, $^3J_{HH}$=8.10 Hz, 2CH of Ar–SO_2), 7.69 (2H, d, $^3J_{HH}$=8.16, 2CH of Ar–SO_2), 7.6–7.8 (15H, m, Ph_3P), 9.5 (1H, br, O–H), 11.52 (1H, d, $^3J_{HH}$=10.8 Hz, N–H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C=21.13 (CH_3), 117.42 (d, $^1J_{CP}$= 90.4 Hz, C_{ipso} of Ph–P), 118.88 (d, $^1J_{CP}$=132.4 Hz, P–C=CH), 122.84 (d, $^2J_{CP}$=42.4 Hz, P–C=CH), 126.41 (2CH of Ar–SO_2), 129.27 (2CH of Ar–SO_2), 129.69 (d, $^3J_{CP}$=12.6 Hz, C_{meta} of Ph_3P), 133.7 (d, $^2J_{CP}$=10.8 Hz, C_{ortho} of P–Ph_3), 134.80 (d, $^4J_{CP}$=2.6 Hz, C_{para} of Ph_3P), 136.73 (C–SO_2), 143.35 (C–CH_3). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P=18.75 (P–OH). MS, *m/z* (%): 509 (M^+, 1), 445 (3), 369 (2), 262 (100), 183 (82), 108 (52), 77 (16), 51 (42). Anal. Calcd for $C_{27}H_{25}NO_3PSCl$ (509.98): C, 63.58; H, 4.94; N, 2.74%. Found: C, 63.6; H, 5.0; N, 2.8%.

3.1.3. *N*-[(*Z*)-2-Chloro-2-(1-hydroxy-1,1,1-triphenylphosphoranyl)-1-ethenyl]-4-ethyl-1-benzenesulfonamide (4c). White powder, 0.99 g, yield 95%, mp 117–119°C (dec.). IR (KBr) (ν_{max}, cm^{-1}): 2960 (N–H), 2848 (PO–H), 1632 (C=C), 1334 and 1153 (SO_2), 929 (P–O). ^1H NMR (500 MHz, $CDCl_3$): δ_H=1.23 (3H, t, $^3J_{HH}$=7.6 Hz), 2.68 (2H, q, $^3J_{HH}$=7.6 Hz), 5.88 (1H, dd, $^3J_{HH}$=10.8 Hz, $^3J_{HP}$=8.3 Hz, P–C=CH), 7.26 (2H, d, $^3J_{HH}$=8.26 Hz, 2CH of Ar–SO_2), 7.73 (2H, d, $^3J_{HH}$=8.31, 2CH of Ar–SO_2), 7.6–7.8 (15H, m, PPh_3), 10.5 (1H, br, O–H), 11.52 (1H, d, $^3J_{HH}$=10.8 Hz, N–H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C=14.64 (CH_3), 28.36 (CH_2), 117.46 (d, $^1J_{CP}$=90.4 Hz, C_{ipso} of PPh_3), 118.66 (d, $^1J_{CP}$=132.4 Hz, P–*C*=CH), 122.93 (d, $^2J_{CP}$=42.7 Hz, P–C=*C*H), 126.49 (2CH of Ar–SO_2), 128.13 (2CH of Ar–SO_2), 129.67 (d, $^3J_{CP}$=12.75 Hz, C_{meta} of Ph_3P), 133.70 (d, $^2J_{CP}$=10.1 Hz, C_{ortho} of Ph_3P), 134.77 (d, $^4J_{CP}$=2.9 Hz, C_{para} of Ph_3P), 136.91 (C–SO_2), 149.43 (*C*–Et). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P=18.75 (P–OH). MS, *m/z* (%): 523 (M^+, 1), 451 (42), 386 (44), 322 (23), 279 (56), 277 (55), 169 (83), 105 (100), 77 (79). Anal. Calcd for $C_{28}H_{27}NO_3PSCl$ (524.01): C, 64.17; H, 5.19; N, 2.67%. Found: C, 64.2; H, 5.2; N, 2.7%.

3.1.4. *N*-[(*Z*)-2-Chloro-2-(1-hydroxy-1,1,1-triphenylphosphoranyl)-1-ethenyl]-4-isopropyl-1-benzenesulfonamide (4d). White Powder, 1.023 g, yield 95%, mp 107–109°C (dec.). IR (KBr) (ν_{max}, cm^{-1}): 2960 (N–H), 2855 (PO–H), 1630 (C=C), 1336 and 1156 (SO_2), 923 (P–O). ^1H NMR (500 MHz, $CDCl_3$): δ_H=1.26 (6H, d, $^3J_{HH}$=6.9 Hz, $2CH_3$), 2.96 (1H, sept, $^3J_{HH}$=6.9 Hz, CH), 5.95 (1H, dd, $^3J_{HH}$=10.8 Hz, $^3J_{HP}$=8.3 Hz, P–C=CH), 7.25 (2H, d, $^3J_{HH}$=8.5 Hz, 2CH of Ar–SO_2), 7.77 (2H, d, $^3J_{HH}$=8.23 Hz, 2CH of Ar–SO_2), 7.48–7.8 (15H, m, PPh_3), 10.2 (1H, br, O–H), 11.55 (1H, d, $^3J_{HH}$=10.8 Hz, N–H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C=23.17 ($2CH_3$), 33.73 (CH), 117.65 (d, $^1J_{CP}$=90.5 Hz, C_{ipso} of PPh_3), 118.16 (d, $^1J_{CP}$=133.2 Hz, P–*C*=CH), 123.23 (d, $^2J_{CP}$=42.7 Hz, P–C=*C*H), 126.52 (2CH of Ar–SO_2), 126.8 (2CH of Ar–SO_2), 129.65 (d, $^3J_{cp}$=13 Hz, C_{meta} of Ph_3P), 133.76 (d, $^2J_{CP}$ 10.4 Hz, C_{ortho} of Ph_3P), 134.5 (d, $^4J_{CP}$ 3 Hz, C_{para} of Ph_3P), 137.05 (*C*–SO_2), 153.922 (*C*–Pr^i). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P=18.74 (P–OH). MS, *m/z* (%): 537 (M^+, 1), 479 (13), 279 (100), 277 (51), 167 (58), 91 (88), 77 (50). Anal. Calcd for $C_{29}H_{29}NO_3PSCl$ (538.03): C, 64.73; H, 5.43; N, 2.60%. Found: C, 64.6; H, 5.4; N, 2.6%.

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