45. A Facile Conversion of Tertiary Amines into [2-(Dialkylamino)vinyl]triphenylphosphonium Salts

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Dedicated to *Günther Ohloff*

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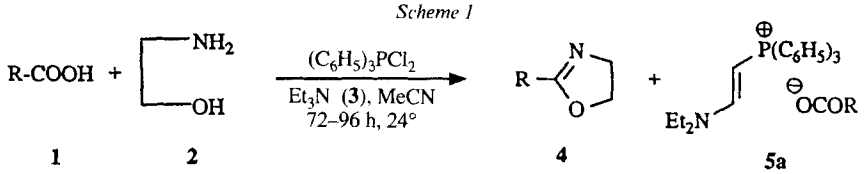
Halogenation of Et_3N, $(i\text{-}Pr)_2EtN$, and *N*-ethylmorpholine or of enamines with dichlorotriphenylphosphorane gives in up to 75% yield the corresponding [2-(dialkylamino)vinyl]triphenylphosphonium chlorides, which can be readily converted into the corresponding stable crystalline tetraphenylborates (*Schemes 2* and *3*).

1. Introduction. – [(Dialkylamino)vinyl]triphenylphosphonium salts such as [2-(diethylamino)vinyl]triphenylphosphonium salt **5** were hitherto prepared by condensation of alkyl- or benzyltriphenylphosphonium salts with aminals [1] or amide acetals [2], by reaction of triphenylphosphonium ylides with tetramethylformamidinium chlorides [3], by reaction of vinylenebis(triphenylphosphonium) salts with primary amines [4], as well as by addition of secondary amines to ethynyl- [5] or propargyltriphenylphosphonium salts [6] [7].

During studies on the conversion of carboxylic acids **1** with 2-aminoethanol (**2**) into the corresponding dihydro-1,3-oxazoles **4** employing dichlorotriphenylphosphorane and Et_3N (**3**) at room temperature in MeCN/pyridine, we isolated, after chromatography (silica gel, AcOEt/MeOH), besides the desired **4** the corresponding [2-(diethylamino)-vinyl]triphenylphosphonium salts **5a** as minor side products [8] (*Scheme 1*)[1]).

Scheme 1

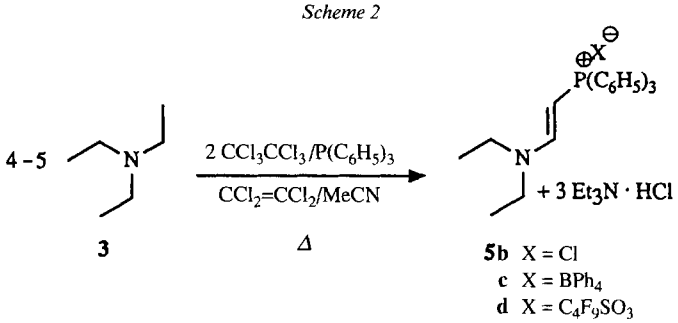


1 **2** **4** **5a**

2. Preparation of [2-(Dialkylamino)vinyl]triphenylphosphonium Salts. – Since the [2-(diethylamino)vinyl]triphenylphosphonium salt **5a** could only have derived from Et_3N (**3**) and dichlorotriphenylphosphorane (Ph_3PCl_2), we reacted 4–5 equiv. of **3** with Ph_3PCl_2 generated *in situ* from Ph_3P/hexachloroethane [9], for 5 days at 24° or 8 h at 85° in abs.

[1]) The formation of [(dialkylamino)vinyl]triphenylphosphonium salts from tertiary amines was discussed in several lectures, *e.g.* in May 1989 at *Firmenich SA* in Geneva, Switzerland, and in February 1990 in Erlangen, Germany.

Scheme 2



MeCN (*Scheme 2*). After filtration of the precipitated $Et_3N \cdot HCl$, the dark filtrate gave, after chromatography (silica gel) and crystallization, *ca.* 30–40% of [2-(diethylamino)vinyl]triphenylphosphonium chloride (**5b**) as well as several side products such as (cyanomethyl)triphenylphosphonium chloride [10] derived from MeCN. To avoid these side reactions of Ph_3PCl_2 with MeCN, we subsequently conducted these chlorinations of **3** in boiling tetrachloroethylene ($CCl_2=CCl_2$), which was generated anyhow in the reaction between Ph_3P and hexachloroethane (CCl_3CCl_3) [9]. In the less polar solvent $CCl_2=CCl_2$, the polar salts such as **5b** were precipitated and thus apparently protected against further chlorination (65% yield of **5b** after 16 h heating).

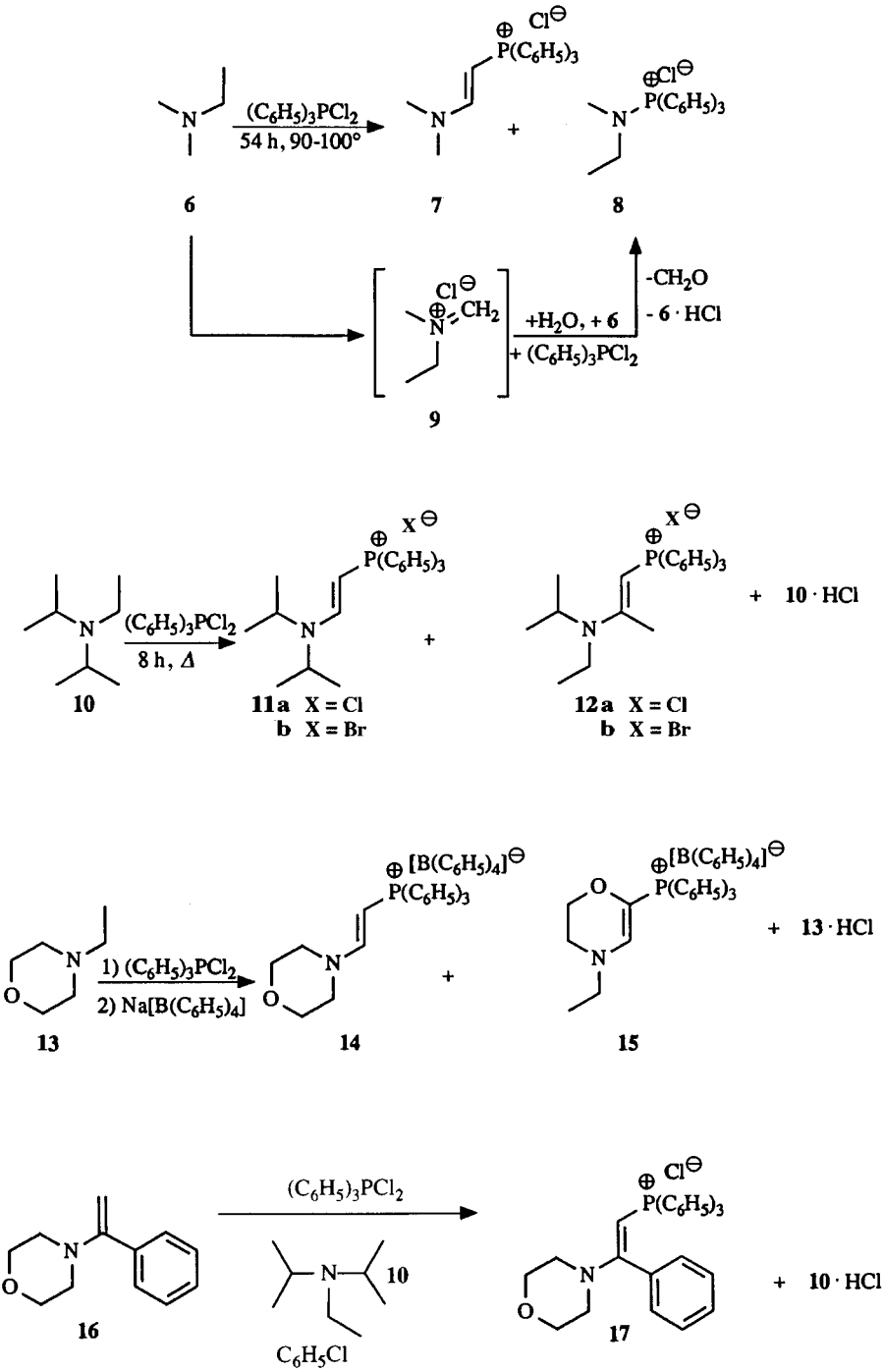
Since Et_3N (**3**) reacted with CCl_3CCl_3 on heating in $CCl_2=CCl_2$ or other solvents to give dark solutions as well as a precipitate of $Et_3N \cdot HCl$, we heated CCl_3CCl_3 with Ph_3P in $CCl_2=CCl_2$ before adding **3**, but without any improvement in the yield of **5b**. The 'soft' Ph_3P reacted apparently with CCl_3CCl_3 in preference to the 'hard' Et_3N (**3**). Also the replacement of $CCl_2=CCl_2$ (b.p. 121°) by chlorobenzene (b.p. 132°) and distillative removal of $CCl_2=CCl_2$ (formed in the reaction of Ph_3P with CCl_3CCl_3) before adding **3** and subsequent heating did not raise the yield of **5b**.

Since the crude crystalline **5b** seemed to be hygroscopic and difficult to purify and characterize, we converted it with $NaBPh_4$ in CH_2Cl_2 or MeCN into the corresponding tetraphenylborate **5c**, which was obtained in *ca.* 60–70% overall yield. The corresponding crystalline nonaflate **5d** was prepared analogously from **5b** with $C_4F_9SO_3K$ in MeCN.

Reaction of excess $Me_2(Et)N$ (**6**; b.p. 34–36°) with Ph_3PCl_2 in $CCl_2=CCl_2$ at 90–110° gave, besides minute amounts of the desired [2-(dimethylamino)vinyl]triphenylphosphonium chloride (**7**), the crystalline (*N*-methylethylamino)triphenylphosphonium chloride (**8**) as the major product (*Scheme 3*). The latter is probably derived from the intermediate iminium salt **9** which is hydrolyzed to formaldehyde and *N*-methylethylamine hydrochloride. Subsequent reaction of *N*-methylethylamine hydrochloride with Ph_3PCl_2 in the presence of excess **6** affords **8** [11].

Reaction of excess $(i\text{-}Pr)_2EtN$ (*Hünig*'s base; **10**) with Ph_3PCl_2 for 20 h in boiling $CCl_2=CCl_2$ afforded *ca.* 30% of the corresponding [2-(*N*,*N*-diisopropylamino)vinyl]-triphenylphosphonium chloride (**11a**) as well as *ca.* 30% of ([*N*-ethylisopropylamino)-propenyl]triphenylphosphonium chloride (**12a**), whose structure was assigned on the basis of its ^1H-NMR spectrum. The analogous reaction of **10** with 1,2-dibromo-1,1,2,2-tetrachloroethane and Ph_3P gave a *ca.* 1:1 mixture (by NMR) of the corresponding bromides **11b** and **12b** in *ca.* 50% yield. Excess *N*-ethylmorpholine (**13**) and Ph_3PCl_2 furnished, after subsequent reaction with $NaBPh_4$, *ca.* 20% of **14** as well as *ca.* 20% of **15**.

Scheme 3

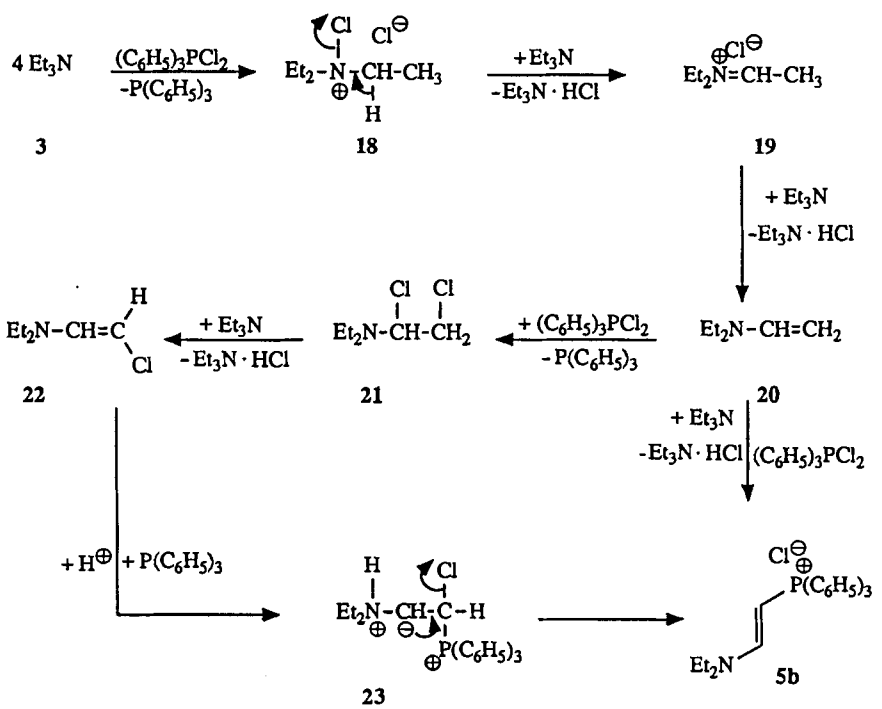

(C6H5)3PCl2
54 h, 90-100°
6
7
8
9
+H2O, + 6
+ (C6H5)3PCl2
-CH2O
- 6 · HCl
(C6H5)3PCl2
8 h, Δ
10
11a X = Cl
b X = Br
12a X = Cl
b X = Br
+ 10 · HCl
1) (C6H5)3PCl2
2) Na[B(C6H5)4]
13
14
15
+ 13 · HCl
16
(C6H5)3PCl2
10
C6H5Cl
17
+ 10 · HCl

Since the chlorination/dehydrochlorination sequence of tertiary amines should eventually pass through an enamine intermediate, we reacted 1-(morpholino)-1-phenylethylene (**16**) with Ph_3PCl_2 in chlorobenzene for 1 h at 130° in the presence of $(i\text{-}Pr)_2EtN$ (**10**) and obtained the anticipated **17** in 75% yield. The analogous reaction of 1-(morpholino)cyclohexene did not give any of the desired corresponding [2-(morpholino)-cyclohex-1-enyl]triphenylphosphonium chloride, since chlorination of such cyclic enamines leads, after aqueous workup, to the corresponding α-chloroketones [12]. It can be anticipated, however, that 1-(morpholino)cyclohexene will react with $[Ph_3P{-}O{-}PPh_3](CF_3SO_3)_2$ [13] in the presence of **10** to give the desired [2-(morpholino)-cyclohex-1-enyl]triphenylphosphonium triflate.

The ready reaction of enamines with dichlorotriphenylphosphorane or dibromotriphenylphosphorane offers thus another simple access to [2-(dialkylamino)vinyl]-triphenylphosphonium salts.

3. Mechanism. – The conversion of Et_3N (**3**) into phosphonium chloride **5b** can be rationalized as fellows (*Scheme 4*). In the chlorination-dehydrochlorination of **3**[2]), *N*-chloro compound **18** leads, probably *via* iminium salt **19** (see also the postulated iminium salt **9**), to the enamine intermediate **20**. Enamine **20** can then be chlorinated-dehydrochlo-

Scheme 4



[2]) There are relatively few examples of chlorinations of tertiary amines in the literature [14]. For a review on amines as hydride-ion donors in reactions with unsaturated electrophilic compounds, see [14j].

rinated to **21** and **22**. The HCl-catalyzed addition of Ph_3P to **22** might then give intermediate **23**, which eliminates HCl to phosphonium chloride **5b**. Alternatively, enamine **20** can react directly with Ph_3PCl_2 to give **5b** as exemplified by the reaction of **16** to **17**.

Mechanistically, however, we cannot exclude that Et_3N (**3**) as well as **6**, **10**, **13**, and **16** are chlorinated *via* the corresponding radical cations as discussed for the reaction of **3** or **10** with hexachloroacetone to give (*E*)-1,1,1-trichloro-4-(diethylamino)but-3-en-2-one or (*E*)-1,1,1-trichloro-4-(diisopropylamino)but-3-en-2-one, respectively, in high yields [15].

Analogous reactions of further tertiary amines with Ph_3PCl_2 and Ph_3PBr_2 as well as synthetic applications of [2-(dialkylamino)vinyl]triphenylphosphonium salts, which have thus become simply accessible, are being investigated and will be reported later.

In summary, tertiary amines are readily chlorinated by Ph_3PCl_2, which is a general intermediate in the Ph_3P/CCl_4 cascade [16], to the corresponding [2-(dialkylamino)-vinyl]triphenylphosphonium chlorides. Thus, on generating Ph_3PCl_2 in the presence of tertiary amines, the potential formation of [2-(dialkylamino)vinyl]triphenylphosphonium chlorides has to be reckoned with.

Experimental Part

General. IR Spectra: in cm^{-1}. ^{1}H-NMR Spectra: δ in ppm rel. to TMS (= 0 ppm), J in Hz.

[2-(Diethylamino)vinyl]triphenylphosphonium Chloride (**5b**), *Tetraphenylborate* (**5c**), *and Perfluorobutanesulfonate* (**5d**). To a soln. of abs. redistilled Et_3N (**3**; 101.2 g, 1 mol) and Ph_3P (52.46 g, 0.2 mol) in redest. $CCl_2{=}CCl_2$ (350 ml), CCl_3CCl_3 (96.5 g, 0.4 mol) was added under N_2 and the mixture heated under reflux (→turbid mixture and dark brown oily precipitate). After 10.5 h reflux, the mixture was taken up in ice-cold sat. $NaHCO_3$ soln. (300 ml) and CH_2Cl_2 (250 ml). After reextraction of the aq. phase with CH_2Cl_2 (3 × 150 ml) the combined org. phase was dried (Na_2SO_4) and concentrated (→brown oily precipitate). The $CCl_2{=}CCl_2$ soln. was decanted and the residual oil washed with $CCl_2{=}CCl_2$ (2 × 50 ml). The combined $CCl_2{=}CCl_2$ phase gave, on evaporation, 16 g of yellowish crystalline Ph_3PO. The crude, in $CCl_2{=}CCl_2$ insoluble brownish salt **5b** (77.4 g) crystallized partly after removal of the last traces of $CCl_2{=}CCl_2$ *in vacuo*. TLC (silica gel, CH_2Cl_2/MeOH 9:1): R_f 0.45; traces of polar impurities. *Ca.* 0.4 g of crude **5b** were recrystallized from acetone (115 ml) and AcOEt (2 ml) overnight: *ca.* 0.27 g of pure **5b**. M.p. 174.5°. IR ($CHCl_3$): 2980, 2930, 1605, 1438, 1333, 1110, 891, 690, 660. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*t*, *J* = 7, 3H); 1.35 (*t*, *J* = 7, 3H); 3.28 (*q*, *J* = 7, 2H); 3.57 (*q*, *J* = 7, 2H); 4.62 (*t*, *J* = 14.8, 1H); 6.46 (*t*, *J* = 14.8, 1H); 7.4–7.85 (*m*, 15H). Anal. calc. for $C_{24}H_{27}ClNP$ (395.9): C 72.80, H 6.87, Cl 8.95, N 3.54, P 7.83; found: C 72.75, H 6.83, Cl 9.30, N 3.43, P 7.67.

The crude **5b** (77.0 g) was dissolved in abs. MeCN (250 ml) and $NaBPh_4$ (68.44, 0.2 mol) added (→temp. rise to 30–35° and precipitate). After 1 h stirring, the MeCN was evaporated and the residue taken up in CH_2Cl_2 (400 ml) and H_2O (200 ml). After extraction of the CH_2Cl_2 phase with H_2O (200 ml), the combined H_2O phase was reextracted with CH_2Cl_2 (100 ml), and the combined CH_2Cl_2 extract dried (Na_2SO_4) and evaporated: 112 g of dark-brown crystalline crude **5c**. Crude **5c** in CH_2Cl_2 (250 ml) was filtered over silica gel (300 g). The first fraction (500 ml) was discarded, the next one (1.5 l) yielded 96 g of slightly brownish **5c**. Recrystallization from AcOEt (*ca.* 1.5–2 l) in several crops gave 89.4 g (65.76%) of pure **5c**. M.p. 180.2°. TLC (silica gel, CH_2Cl_2): R_f 0.25. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.95 (*t*, *J* = 7, 3H); 1.13 (*t*, *J* = 7, 3H); 2.9 (*q*, *J* = 7, 2H); 3.15 (*q*, *J* = 7, 2H); 4.02 (*t*, *J* = 14.8, 1H); 6.75 (*t*, *J* = 14.8, 1H); 6.8 (*m*, 4H); 6.95 (*m*, 8H, BPh_4); 7.4–7.65 (*m*, 23H). Anal. calc. for $C_{48}H_{47}BNP$ (679.71): C 84.82, H 6.97, N 2.06, P 4.56; found: C 85.25, H 6.83, N 2.22, P 4.71.

To a stirred soln. of **5b** (*ca.* 3.95 g, 10 mmol) in MeCN (20 ml) at 22°, $C_4F_9SO_3K$ (3.38 g, 10 mmol) was added, which passed into soln. After 6 h (→sticky precipitate), the mixture was evaporated and the residue (6.9 g) taken up in CH_2Cl_2 (100 ml) and H_2O (20 ml). After reextraction of the aq. phase with CH_2Cl_2, the combined org. phase was dried (Na_2SO_4) and evaporated: 6.5 g (98.6%) of **5d**, which crystallized on standing. M.p. 67°. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.12 (*t*, *J* = 7, 3H); 1.3 (*t*, *J* = 7, 3H); 3.24 (*q*, *J* = 7, 2H); 3.50 (*q*, *J* = 7, 2H); 4.95 (*t*, *J* = 14, 1H); 6.44 (*t*, *J* = 14, 1H); 7.7 (*m*, 15H). Anal. calc. for $C_{28}H_{27}F_9NO_3PS$ (630.6): C 50.99, H 4.13, N 2.12, P 4.69; found: C 50.78, H 4.34, N 1.96, P 4.64.

[2-(Dimethylamino)vinyl]triphenylphosphonium Chloride (7) *and* (N-*Methylethylamino)triphenylphosphonium Chloride* (**8**). A soln. of $Me_2(Et)N$ (**6**; 17.55 g, 240 mmol; b.p. 36–38°), Ph_3P (11.54 g, 44 mmol), and CCl_3CCl_3 (18.94 g, 80 mmol) in $CCl_2{=}CCl_2$ (120 ml) was heated under reflux for 54 h at 120° bath temp. under Ar (→gradual temp. rise to 90° and viscous precipitate). After cooling to 24°, the crude mixture was diluted with CH_2Cl_2 (150 ml) and poured on ice-cold sat. $NaHCO_3$ soln. (300 ml). After 30 min stirring at +5°, the aq. phase was extracted with CH_2Cl_2 (4 × 100 ml) and the org. phase dried (Na_2SO_4) and evaporated: 18 g of crude product. Chromatography (silica gel (150 g)) gave with CH_2Cl_2 (3.5 l) Ph_3PO and some Ph_3P. Elution with CH_2Cl_2 i-PrOH 95:5→85:15 (5.5 l) afforded 5.3 g of crude **8** which crystallized from AcOEt/MeOH *ca.* 20:1: 3.2 g (40.8%) of pure **8**. M.p. 128.1°. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.21 (*t*, *J* = 7, 3H); 3.04 (*d*, *J* = 10, 3H); 3.36 (*dq*, *J* = 7, 10, 2H); 7.80 (*m*, 15H). Anal. calc. for $C_{21}H_{33}ClNP \cdot H_2O$ (373.87): C 67.46, H 6.74, N 3.75; found: C 67.25, H 6.80, N 3.74.

The mother liquor gave the following ^{1}H-NMR (300 MHz, $CDCl_3$; assigned to 7): 3.15 (weak signals, *J* = 10, MeN groups); 4.56, 6.55 (*t*, *J* = 14, vinyl-H's).

[2-(Diisopropylamino)vinyl]triphenylphosphonium Chloride (**11a**) *and [2-(*N-*Ethylisopropylamino)prop-1-enyl]triphenylphosphonium Chloride* (**12a**). A soln. of Ph_3P (20.98 g, 80 mmol) and CCl_3CCl_3 (18.94 g, 80 mmol) in chlorobenzene (150 ml) was heated for 1 h to 90° and then to *ca.* 140°, whereupon *ca.* 30 ml of distillate containing $CCl_2{=}CCl_2$ were removed. After cooling to *ca.* 40°, $(i\text{-}Pr)_2EtN$ (**10**; 20.98 g, 160 mmol) was added and the mixture refluxed for 20 h at 145° (oil-bath temp.). The cooled mixture was diluted with chlorobenzene (50 ml) and extracted with sat. aq. $NaHCO_3$ soln. (300 ml). The separated chlorobenzene phase was reextracted with sat. $NaHCO_3$ soln. (3 × 100 ml). The chlorobenzene phase contained only Ph_3P and Ph_3PO (by TLC (CH_2Cl_2/MeOH 9:1)). The combined $NaHCO_3$ soln. was extracted with CH_2Cl_2 (4 × 150 ml), the CH_2Cl_2 extract dried (Na_2SO_4) and evaporated to give 12.6 of dark brown oil. The oil was dissolved in CH_2Cl_2/MeOH 9:1 (60 ml) and filtered over silica gel (150 g). On elution with CH_2Cl_2/MeOH 9:1, the first 1500 ml gave 9.7 g (55.87%) of light yellow crystalline **11a**/**12a** *ca.* 1:1, which nearly separated on TLC (silica gel, upper phase of BuOH/AcOH/H_2O 4:1:5, R_f 0.75–0.80). Repeated recrystallization from acetone/AcOEt 1:1 gave pure **11a**. M.p. 197–200°. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.98 (*d*, *J* = 7, 6H); 1.33 (*d*, *J* = 7, 6H); 3.62 (*m*, *J* = 7, 1H); 4.43 (*m*, *J* = 7, 1H); 4.94 (*t*, *J* = 15, 1H); 6.37 (*t*, *J* = 15 and 17, 1H); 7.6–7.85 (*m*, 15H). Anal. calc. for $C_{26}H_{31}ClNP$ (433.97): C 73.65, H 7.37, Cl 8.36, N 3.30, P 7.31; found: C 73.58, H 7.5, Cl 8.17, N 3.39, P 7.29.

The mixture **11a**/**12a** (3.2 g) was dissolved in CH_2Cl_2/EtOH 96:4 (30 ml) and chromatographed (silica gel (20 g), CH_2Cl_2/EtOH 96:4). After a forrun of 7.5 l, the subsequent 2 l eluted pure **11a** (0.54 g), the subsequent 2.5 l **11a**/**12a** (1:1 (1.2 g)), and the final 7 l nearly homogeneous crystalline **12a** (1.06 g), which gave, on recrystallization from acetone/AcOEt 1:3, the anal. sample. **12a**: M.p. 238°. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.2–1.4 (*m*, 9H); 1.93 (*s*, 3H); 3.48 (*q*, *J* = 7, 2H); 3.82 (*d*, *J* = 14, 1H); 4.27 (*m*, *J* = 7, 1H); 7.5–7.8 (*m*, 15H). Anal. calc. for $C_{26}H_{31}ClNP \cdot 3H_2O$ (478.03): C 65.33, H 7.8, Cl 7.42, N 2.93, P 6.48; found: C 65.46, H 7.74, Cl 7.55, N 2.98, P 6.03.

In the same manner, the bromides **11b** and **12b** (1:1) were prepared using $CBrCl_2CBrCl_2$ instead of CCl_3CCl_3. Yield 50%.

[2-(Morpholin-4-yl)vinyl]triphenylphosphonium Tetraphenylborate (**14**) *and (2,3-Didehydro-4-ethylmorpholin-2-yl)triphenylphosphonium Tetraphenylborate* (**15**). A mixture of *N*-ethylmorpholine (**13**; 28.79 g, 0.25 mol), Ph_3P (13.11 g, 0.05 mol), CCl_3CCl_3 (23.67 g, 0.1 mol) was heated in abs. $CCl_2{=}CCl_2$ (120 ml) at 120° (bath temp. 140°) under stirring for 13 h (→dark mixture). After cooling and decanting of the $CCl_2{=}CCl_2$ soln., the residual solidified oil was washed twice with additional $CCl_2{=}CCl_2$ (25 ml) and then dissolved in CH_2Cl_2 (300 ml) and extracted with ice-cold aq. $NaHCO_3$ soln. (250 ml). After reextracting the aq. phase, which had been saturated with NaCl, with CH_2Cl_2 (2 × 100 ml), the combined CH_2Cl_2 phase was dried (Na_2SO_4) and evaporated: 15.47 (75.5%) of the crude oily mixture of the chlorides corresponding to **14** and **15**. This mixture in abs. MeCN (150 ml) was treated with $NaBPh_4$ (17.1 g, 0.05 mol) at 21°, whereupon the soln. warmed up to 29°. After 3 h, the MeCN was evaporated and the residue taken up in CH_2Cl_2 (200 ml) and H_2O (200 ml). After separation and reextraction of the aq. phase, the combined org. phase was dried (Na_2SO_4) and evaporated. The crude brown residue (28.5 g) was filtered in CH_2Cl_2 (2 l) over silica gel (100 g): 13 g (38%) of **14**/**15**. A sample (2 g) of **14**/**15** was chromatographed in CH_2Cl_2 silica gel (100 g). Elution with CH_2Cl_2 (900 ml) afforded first homogeneous **15** (0.83 g) which was recrystallized from CH_2Cl_2/MeOH to give 0.48 g of pure **15**. M.p. 169.7. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.91 (*t*, *J* = 7, 3H); 2.76 (*q*, *J* = 7, 2H); 3.04 (*t*, *J* = 3, 2H, NCH_2CH_2O); 3.8 (*t*, *J* = 3, 2H, NCH_2CH_2O); 5.88 (*d*, *J* = 5, 1 vinyl-H); 6.77–6.98 (*m*, 16H, BPh_4); 7.3–7.52, 7.6–7-7 (*m*, PPh_3, BPh_4). Anal. calc. for $C_{48}H_{45}BNOP$ (693.69): C 83.11, H 6.54, N 2.02, P 4.46; found: C 83.19, H 6.75, N 2.45, P 4.72.

Further elution with CH_2Cl_2 (200 ml) afforded **14**/**15** (0.21 g) and with CH_2Cl_2 (1 l) pure **14** (0.85 g) which was recrystallized from CH_2Cl_2/MeOH: 0.57 g of pure **14**. M.p. 212.9°. ^{1}H-NMR (300 MHz, (D_6)DMSO): 3.15 (*t*, *J* = 3, 2H, NCH_2CH_2O); 3.43 (*t*, *J* = 3, 2H, NCH_2CH_2O); 5.0 (*t*, *J* = 4.8, 1H, NCH=CHP); 6.72 (*t*, *J* = 4.8, 1H,

NCH=CHP); 6.73–6.78 (*m*); 6.9 (*m*, BPh_4); 7.2 (*m*); 7.6–7.82 (*m*). Anal. calc. for $C_{48}H_{45}BNOP$ (693.69)·$2H_2O$: C 79.01, H 6.77, N 1.92, P 4.24; found: C 78.97, H 6.37, N 2.42, P 4.59.

[(E)-2-(Morpholin-4-yl)-2-phenylvinyl]triphenylphosphonium Chloride (**17**). A soln. of Ph_3P (7.868 g, 30 mmol) and CCl_3CCl_3 (7.10 g, 30 mmol), in chlorobenzene (100 ml) was refluxed for 30 min. Then *ca.* 30 ml of soln. were distilled off to remove the $CCl_2{=}CCl_2$ formed. The slightly yellowish soln. of Ph_3PCl_2 was cooled to +2° ($i\text{-}Pr)_2EtN$ (**10**; 3.88 g, 30 mmol) and 1-(morpholin-4-yl)-1-phenylethylene [17] (**16**; 5.67 g, 30 mmol) were added, and the mixture was refluxed under Ar for 45 min. The cooled soln. was diluted with chlorobenzene (40 ml) and CH_2Cl_2 (200 ml) and stirred with ice-cold sat. aq. $NaHCO_3$ soln. (150 ml). The yellow aq. phase was reextracted with CH_2Cl_2 (4 × 150 ml) and the combined org. phase dried (Na_2SO_4) and concentrated to 50 ml, whereupon a yellow crystalline precipitate formed, which was filtered after 1 h at 21° and washed with chlorobenzene (30–40 ml): 10.98 g (75.3%) of **17** as faintly yellowish crystal. M.p. 255.2° (dec.). On evaporation of the mother liquor, the residue (2.6 g) contained *ca.* 30–40% additional **17** (by TLC (CH_2Cl_2/MeOH 9:1)). ^{1}H-NMR (300 MHz, $CDCl_3$): 3.5–3.8 (br., 4H, NCH_2CH_2O); 3.8–4.2 (br. 4H, NCH_2CH_2O); 5.15 (*d*, *J* = 12, 1 vinyl-H); 6.75 (*dd*, *J* = 1, 8, $2H_o$); 6.92 (*t*, *J* = 8, $2H_m$); 7.15 (*t*, *J* = 8, $1H_p$); 7.48–7.68 (*m*, 15H, PPh_3); NOE experiments: morpholino *cis* to vinyl-H; Ph *cis* to Ph_3P^+. Anal. calc. for $C_{30}H_{29}ClNOP$ (486.00): C 74.14, H 6.01, Cl 7.29, N 2.88, P 6.37; found: C 73.94, H 5.88, Cl 7.29, N 2.90, P 6.30.

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