Sequestered Alkyllithiums: Why Phenyllithium Alone is Suitable for Betaine-Ylide Generation

Qian Wang,[a] Dariusz Deredas,[a] Cyril Huynh,[a] and Manfred Schlosser*[a, b]

Abstract: The key step in the *trans*-selective modification of the Wittig reaction is the α-lithiation of the lithium bromide coordinated ylide–aldehyde adduct (the so-called "*P*-betaine"). Only phenyllithium effects this deprotonation rapidly and cleanly. Alkyllithiums (in particular, butyl-, *sec*-butyl-, and *tert*-butyllithium) react only sluggishly and incompletely, being tied up in very stable mixed aggregates with the lithium alkoxide part of the betaines.

Keywords: betaines · deuterium labeling · mixed aggregates · Wittig reactions · ylides

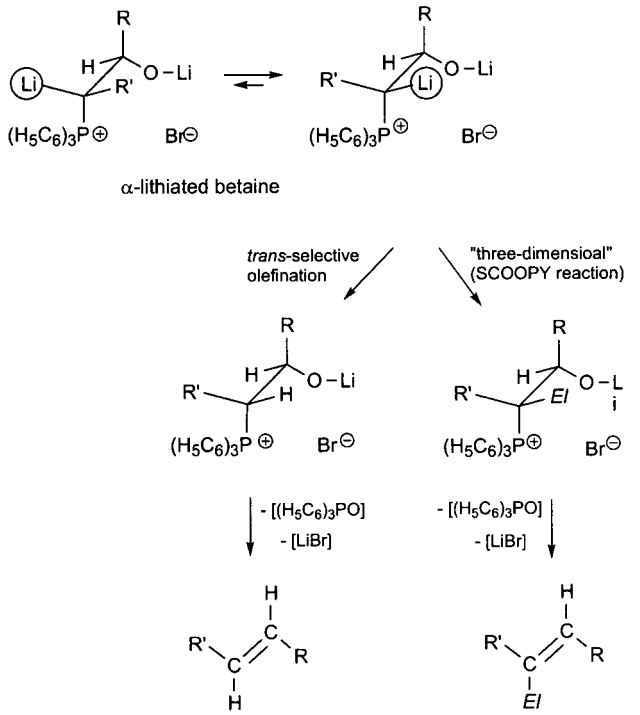
Introduction

"Betaine ylides" (triphenylphosphonio-2-lithiooxyalkanides) are generated by the α-deprotonation of lithium bromide complexed "phosphorus betaines", the zwitterionic adducts of phosphorus ylides and carbonyl compounds. They act as the key intermediates in *trans*-selective[1–3] and "three-dimensional" ("SCOOPY")[3–7] Wittig reactions (see Scheme 1). Stereocontrol is accomplished by the spontaneous pyramidal inversion of the α-lithiated betaine. At equilibrium, the *threo* configuration is strongly favored and typically predominates to the extent of $\geq 99.5\,\%$.[1, 2] In contrast, the *erythro* component is formed preferentially (respectively, $\sim 2{:}1$ and $\geq 10{:}1$ in the presence and absence of soluble lithium salts) if the ylide and aldehyde combine under irreversible conditions.[1, 3, 8, 9]

The crucial epimerization at the α-carbon is just one stage in a multistep one-pot reaction sequence (see Scheme 2). Its success critically depends on a high concentration of a soluble lithium salt, in general lithium bromide. Its role is to suppress the dissociation of the α-lithiated betaine ylide to an α-metal-free betaine ylide.[10] This rules out the unconsidered use of any commercial organolithium reagent and requires ethereal media that are rich in tetrahydrofuran. If these conditions are met, the *trans*-selective modification of the Wittig olefination protocol works with absolute reliability as impressive applications of it to the synthesis of natural products and biomimetics have been amply demonstrated.[11–16]

[a] Prof. Dr. M. Schlosser, Dr. Q. Wang, Dr. D. Deredas, C. Huynh
Institut de Chimie Organique, Université, BCh
1015 Lausanne (Switzerland)
E-mail: manfred.schlosser@epfl.ch

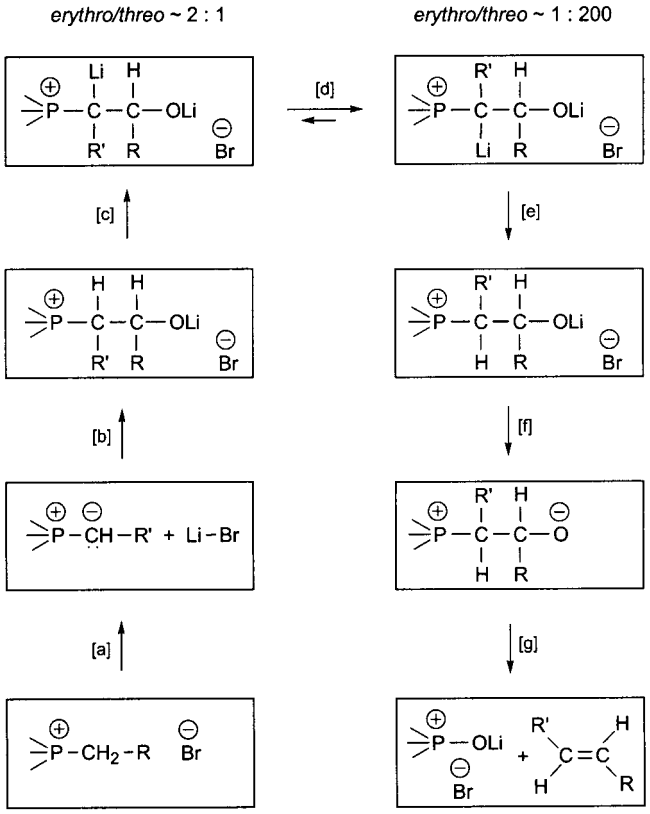
[b] Prof. Dr. M. Schlosser
Institut de Chimie Moléculaire et Biologique
Ecole Polytechnique Fédérale, BCh
1015 Lausanne (Switzerland)



Scheme 1. Betaine-ylides as the key intermediates in *trans*-selective and "three-dimensional" olefination reactions.

At first sight, the exact nature of the organometallic reagent would not be expected to matter. Any alkyl- or aryllithium should be basic enough to enable the complete deprotonation of the phosphorus betaine, the acidity of which can be assumed to approximate that of ordinary alkyltriphenylphosphonium salts ($pK_a \sim 20$[17–19]). The consecutive treatment of (ω-hydroxyalkyl)triphenylphosphonium bromide with lithium bromide containing butyllithium, an aldehyde and butyllithium again has indeed been reported to give rise, after

0947-6539/03/0902-0570 $ 20.00+.50/0 *Chem. Eur. J.* **2003**, *9*, No. 2



Scheme 2. The multistep, if one-pot protocol for *trans*-selective olefin formation. a) Lithium bromide containing phenyllithium (or any other organolithium) in THF and diethyl ether. b) Aldehyde R–CH=O. c) Lithium bromide containing phenyllithium in diethyl ether. d) Either 1 min at 25 °C or 30 min at −75 °C. e) Hydrogen chloride (1.0 equiv) in diethyl ether at −75 °C. f) Potassium *tert*-butoxide. g) Some 15 min at −25 °C.

neutralization and decomplexation, to the highly *trans*-selective ($Z/E \leq 3{:}97$) formation of alken-1-ols.[2] However, as we have recognized meanwhile, only phenyllithium ensures maximum stereoselectivities throughout.

The results are clear-cut. Straight-chain and monobranched aliphatic aldehydes (heptanal, isobutyraldehyde) as well as α,β-unsaturated aldehydes (methacroleine, benzaldehyde) give olefins with excellent ($Z/E < 1{:}200$), acceptable ($Z/E \sim 50$), and poor (Z/E 16:1 – 1:1) *trans* selectivity depending on what reagent was employed to generate the betaine ylide, phenyllithium, methyllithium, or one of the butyllithiums (butyllithium, *sec*-butyllithium, or *tert*-butyllithium), respectively (see Table 1). The doubly α-branched pivaldehyde favors *cis* olefination under all circumstances, however (Table 1). Pivaldehyde is known to produce exceptionally high *erythro*/*threo* ratios, and, consequently, in the absence of an efficient epimerization mechanism, high *cis*/*trans* ratios when allowed to react with any kind of ylide.[20–22]

Abstract in German: *Der Schlüsselschritt bei der transselektiven Variante der Wittig-Reaktion ist die α-Deprotonierung des mit Lithiumbromid koordinierten Ylid/Aldehyd-Addukts (des sogenannten "P-Betains"). Nur Phenyllithium vermag diese Umsetzung rasch und sauber zu bewerkstelligen. Aliphatische Organolithium-Verbindungen (insbesondere, Butyl-, sec-Butyl- und tert-Butyllithium) reagieren nur schleppend und unvollständig, weil ihnen Fesseln angelegt sind durch den Lithiumalkoholat-Teil der Betaine, womit sie sehr stark gebundene Mischaggregate bilden.*

Table 1. *trans*-Selective Wittig reactions involving betaine-ylides prepared from ylides $(H_5C_6)_3P^{\oplus}-{}^{\ominus}CH-R'$ and aldehydes R–CH=O: Z/E ratios and, in parentheses, yields of olefins.[a]

R	R′	LiC_6H_5	$LiCH_3$	LiC_4H_9	LIS[b]	LIT[c]
$H_{13}C_6$	C_4H_9	< 0.5:99.5 (88%)[d]	3:97 (87%)	50:50 (92%)	33:67 (86%)	17:83 (84%)
H_5C_6	C_3H_7	< 0.5:99.5 (88%)[d]	1.5:98.5 (92%)	12:88 (77%)	6:94 (63%)	23:77 (60%)
$H_2C{=}C{-}CH_3$[e]	$(CH_2)_2C_6H_5$	< 0.5:99.5 (58%)[d]	2:98 (59%)	16:84 (57%)	12:88 (45%)	36:64 (42%)
$(H_3C)_2CH$	C_5H_{11}	< 0.5:99.5 (66%)[f]	2:98 (59%)	16:84 (57%)	–	13:87 (62%)
$(H_3C)_3C$	C_5H_{11}	94:6 (59%)	98:2 (63%)	97:3 (56%)	–	76:24 (42%)

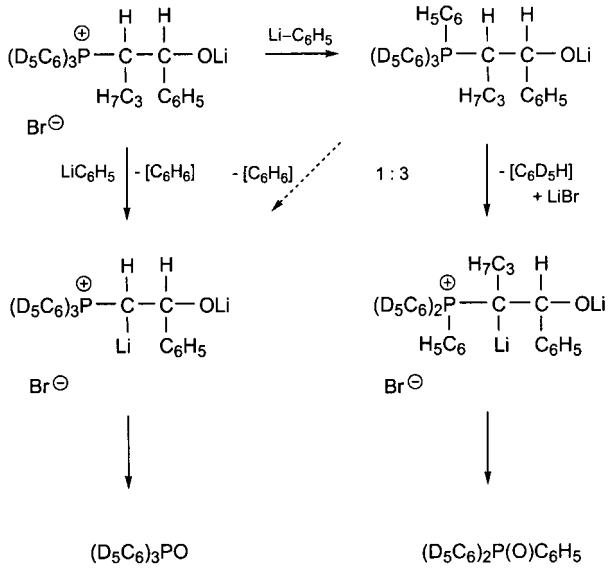
[a] Standard working procedure: see Experimental Section. At the decisive stage of betaine ylide formation, the tetrahydrofuran/diethyl ether ratio approached 1:1. [b] LIS = $LiCH(CH_3)C_2H_5$ (*sec*-butyllithium). [c] LIT = $LiC(CH_3)_3$ (*tert*-butyllithium). [d] The same limit of stereoselectivity and virtually the same yields were attained when the reaction was performed in an approximate 7:1:2 (*v*/*v*/*v*) mixture of tetrahydrofuran, diethyl ether, and cyclohexane, respectively. [e] 2-Methyl-2-propenal (methacroleine). [f] A Z/E ratio of 3:97 and a yield of 65% were found when the reaction was performed in an approximate 7:1:2 (*v*/*v*/*v*) mixture of tetrahydrofuran, diethyl ether, and cyclohexane, respectively.

At first sight one might feel tempted to rationalize the reagent effect on the *E* stereoselectivity by side reactions reflecting structural individuality of the organometallics involved. In particular, the highly reactive family of butyllithiums (butyllithium, *sec*-butyllithium, and *tert*-butyllithium) may promote substitution of a "stationary"[1, 3, 23] P-substituent rather than α-deprotonation. Following well-established precedents, this group displacement at phosphorus may occur by addition of the organolithium to the betaine and subsequent elimination of benzene,[24–27] or, alternatively, by phenyl/alkyl exchange at the level of an ylide,[28–29] including a betaine ylide. The resulting *P*-alkyl derivative, if a betaine, would be reluctant to undergo the required α-deprotonation, or, if a betaine ylide, would no longer discriminate so strictly against the *erythro* configuration. To account for the fairly good performance of methyllithium in the framework of this hypothesis, one would merely have to assume a more pronounced decrease in nucleophilicity than in basicity with this reagent. Phenyllithium would clearly avoid such complications as it could not cause any structural alteration if involved in group displacement at phosphorus.

Despite its prima facie plausibility, the possibility of P-substituent displacement had to be ruled out for two reasons. For one thing, we were unable to detect even trace amounts of alkyldiphenylphosphine oxides in the crude reaction mixtures when the *trans*-selective olefination protocol had been performed with a butyllithium variety. Moreover, we have consecutively treated butyltriphenylphosphonium bromide, which was perdeuterated at all aromatic positions, with unlabeled phenyllithium/lithium bromide, benzaldehyde, phenyllithium/lithium bromide (again), hydro-

  0947-6539/03/0902-0571 $ 20.00+.50/0

gen chloride, and potassium *tert*-butoxide. The phosphonium salt had been prepared by quaternization of perdeuterated triphenylphosphonium, which was made from hexadeuterobenzene by metalation with the LIC-KOR superbase.[30–32] The triphenylphosphine oxide isolated was found to consist of the [$^2H_{15}$] and [$^2H_{10}$] isomers in a ratio of 99:1. In other words, virtually all of the betaine ylide had been formed by direct deprotonation rather than through a transient phosphorane (Scheme 3).

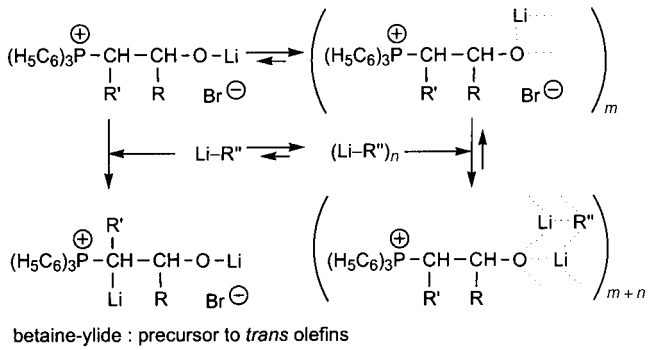


Scheme 3. Phenyllithium acting towards a betaine/lithium bromide adduct almost exclusively as a base and only marginally as a nucleophile.

Evidently, the next step was to monitor the reaction between betaines and butyllithiums. This was done in two ways. On the one hand, we probed for unconsumed organometallic reagent (e.g., butyllithium) by trapping it with benzaldehyde and identifying the adduct (i.e., 1-phenylpentan-1-ol). On the other hand, we quantified the amount of isotope incorporation after successive addition of the alkyllithium (for 1 h at $-75\,^{\circ}C$), deuterium chloride, and potassium *tert*-butoxide to the betaine/lithium bromide adduct.

For example, consecutive treatment of butyltriphenylphosphonium bromide in the presence of excess lithium bromide, with phenyllithium, benzaldehyde, phenyllithium (again), deuterium chloride, and potassium *tert*-butoxide afforded pure (*E*)-2-[^{2}H]1-phenyl-1-pentene (88%). When only the first time (ylide generation) phenyllithium, but the second time (betaine ylide generation) *tert*-butyllithium was employed as the base, the olefin (60%) was obtained as a 1:3 (*Z*/*E*) mixture which could be easily separated by column chromatography. The *cis* isomer was found to contain no deuterium at all, whereas the *trans* isomer was labeled to the extent of 40%.

A consistent picture emerges from these findings. Both deuteration and *trans* selectivity depend on betaine ylide generation as a prerequisite. The α-deprotonation of the betaine precursor can be cleanly achieved with phenyllithium, which shows little propensity to aggregate,[33] but also, if less perfectly, with methyllithium, which exists as an exceptionally tight tetramer.[33] The homoaggregates of primary, secondary, and tertiary alkyllithiums being less optimally constructed,[33] heteroaggregation evidently offers better binding interactions in such a situation. Lithium alcoholates are known to bind to organolithiums under mixed aggregate formation.[34–38] Accordingly, all members of the butyllithium family combine strongly with betaine/lithium bromides, which represent a special class of oligomeric alcoholates. The resulting mixed superclusters, tied together by multiple electron-deficient bonds, are so stable that the sequestered alkyllithium component loses some of its inherent reactivity, being no longer able to bring about complete betaine ylide formation (Scheme 4).



Scheme 4. Betaine/lithium bromide adducts sequestering alkyllithium by heteroaggregate formation.

Salt-free phenyllithium is commercially available in a 3:7 (*v*/*v*) diethyl ether/cyclohexane solvent mixture at a moderate price (€125 per mol). It may be employed as a reagent for *trans*-selective Wittig reactions if, after the evaporation of the original solvents, the residue is taken up in tetrahydrofuran and sufficient amounts of anhydrous lithium bromide are added. It is more convenient to use "homemade" material, which can be easily prepared from bromobenzene in tetrahydrofuran[39, 40] or diethyl ether,[41–43] the precious by-product lithium bromide remaining in solution in either solvent.

Experimental Section

For working habits and abbreviations, see recent publications (e.g., ref. [44]) which have emanated from this laboratory. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded of samples dissolved in deuterochloroform at 400, 101, and 162 MHz, respectively, chemical shifts being given relative to the internal standard tetramethylsilane (^{1}H and ^{13}C) or the external standard 85% aqueous phosphoric acid (^{31}P).

***trans*-Selective Wittig reactions**: At $-75\,^{\circ}C$, a 0.70 M solution of phenyllithium (28 mmol) containing one molar equivalent of lithium bromide (28 mmol) in ethyl ether (40 mL) was added to the alkyltriphenylphosphonium bromide (25 mmol) in tetrahydrofuran (80 mL). After 30 min of vigorous stirring at $25\,^{\circ}C$, the reaction mixture was cooled to $-75\,^{\circ}C$ to be treated with the aldehyde (25 mmol) and, a few minutes later, when complete decolorization had occurred, again with the phenyllithium/lithium bromide complex (28 mmol) in diethyl ether (40 mL). A clear solution was obtained that rapidly turned cherry-red when stored each time 30 min at $-75\,^{\circ}C$, $25\,^{\circ}C$, and again $-75\,^{\circ}C$. Hydrogen chloride (28 mmol) in diethyl ether (10 mL) decolorized it instantaneously. After addition of potassium *tert*-butoxide (3.4 g, 30 mmol), the reaction mixture was stirred 1 h at $25\,^{\circ}C$ before being poured into water (59 mL) and extracted with

0947-6539/03/0902-0572 $ 20.00+.50/0 *Chem. Eur. J.* **2003**, *9*, No. 2

diethyl ether (3 × 25 mL). The combined organic layers were washed with brine (2 × 15 mL), dried, and evaporated. The semisolid residue was triturated with pentanes (3 × 25 mL). The extracts were filtered and distilled. The olefinic product was identified and its *Z*/*E* ratio determined by comparison of the gas chromatographic retention times with those of authentic samples: 5-dodecene[45] (b.p. 70–71 °C/10 Torr; n_D^{20} 1.42998; 50 m, MSV, 30 m, DB-210, 40 °C), 1-phenyl-1-pentene[46] (b.p. 111–113 °C/10 Torr; n_D^{20}1.5287; 3 m, 5% C-20M, 160 °C; 3 m, 5% SE-30, 170 °C), 2-methyl-6-phenyl-1,3-hexadiene[47] (b.p. 75–78 °C/0.5 Torr; n_D^{20} 1.5404; 30 m, DB-1, 80 °C; 30 m, DB-FFAP, 80 °C), 2-methyl-3-nonene[48] (b.p. 55–57 °C/17 Torr; n_D^{20} 1.4217; 30 m, DB-1, 30 °C; 50 m, MSV, 40 °C), and 2,2-dimethyl-3-nonene[49] (b.p. 65–67 °C/20 Torr; n_D^{20} 1.4281; 30 m, DB 1701, 30 °C; 30 m, DB-FFAP, 30 °C).

To prepare solutions of alkyllithiums containing one molar equivalent of lithium bromide, the original solvents (pentanes, hexanes, or cyclohexanes) were stripped off from the commercial reagents (0.70 mol). The residue was then dissolved in the precooled (−75 °C) solution of lithium bromide (61 g, 0.70 mol) in diethyl ether (1.0 L).

To determine the water content (in general some 5%) of commercial lithium bromide, a sample was dissolved in anhydrous tetrahydrofuran and titrated with butyllithium in the spatula tip of triphenylmethane as an indicator until the cherry red color (of triphenylmethyllithium) persisted.

The protocol had to be modified when the "homemade" lithium bromide containing ethereal phenyllithium (see above) was replaced by the commercial product (1.8 M in a 3:7 mixture of diethyl ether and cyclohexane, twice 15 mL). The missing lithium bromide (4.8 g, 55 mmol) was dissolved in tetrahydrofuran (15 mL) and was added from the beginning to phosphonium salt (suspended in 60 mL tetrahydrofuran).

Deactivation of butyllithium by coordination: At −75 °C, pivaldehyde (1.1 mL, 0.86 g, 10 mmol) was added dropwise to a solution of butyllithium (10 mmol) in tetrahydrofuran (30 mL) and diethyl ether (50 mL). After 5 min, the mixture was treated with hydrogen chloride (11 mmol) in diethyl ether (10 mL) before being poured into water (20 mL). The aqueous phase was saturated with sodium chloride. The organic layer was separated and analyzed by gas chromatography (30 m, DB-1701, 80 °C; 30 m, DB-FFAP, 80 °C); octan-1-ol as a calibrated "internal standard") revealing the presence of 99% of 2,2-dimethyl-3-heptanol.[50]

In parallel reaction, again conducted at −75 °C, 2,4-dimethylpentan-3-ol (10 mmol) was added to butyllithium (20 mmol) in tetrahydrofuran (30 mL) and diethyl ether (5.0 mL), followed 15 min later by pivalaldehyde (10 mmol). 2,2-Dimethylheptan-3-ol[50] was present this time in 68% yield.

In a third experiment, pentyltriphenylphosphonium bromide (4.1 g, 10 mmol) in tetrahydrofuran (20 mL) was consecutively treated with lithium bromide containing phenyllithium (10 mmol) in tetrahydrofuran (8 mL) and diethyl ether (4 mL) and with heptanol (10 mmol). After decolorization and always at −75 °C, butyllithium (10 mmol) in tetrahydrofuran (5 mL) and, 15 min later, pivalaldehyde (10 mmol) were added. The quantity of 2,2-dimethylheptan-3-ol formed amounted to 16%.

Perdeuterophenyl substituted phosphonium salts:

[$^2H_5$]Iodobenzene: The mixture of [$^2H_6$]benzene (22 mL, 21 g, 0.25 mol; 99% isotopically pure), butyllithium (0.25 mol) in pentanes (25 mL) and potassium *tert*-butoxide (28 g, 0.25 mol) was vigorously stirred for 20 h at 0 °C. At −75 °C, precooled tetrahydrofuran (0.10 mL) was added. After 15 min of continuous stirring a homogeneous solution was obtained. Always at −75 °C, a solution of iodine (64 g, 0.25 mol) in tetrahydrofuran (0.15 L) was added dropwise over the course of 30 min. According to gas chromatographic analysis (30 m, DB-1701, 80 °C; 30 m, DB-FFAP, 80 °C), iodobenzene (34%) was present in the reaction mixture. The solvent and unconsumed benzene were removed by distillation. The residue was dissolved in diethyl ether (50 mL) and thoroughly washed with a saturated aqueous solution of sodium thiosulfate (3 × 50 mL) and with brine (2 × 25 mL), was dried and evaporated. Distillation afforded a colorless liquid; 14.6 g (28%); b.p. 90–92 °C/45 Torr (ref. [51]: b.p. 67–68 °C/16 Torr); n_D^{20} 1.6150.

Tri([$^2H_5$]phenyl)phosphine: At −75 °C, [$^2H_5$]iodobenzene (63 g, 0.30 mol, ~99% isotopically pure) was added dropwise, over the course of 15 min, to *tert*-butyllithium (0.60 mol), from which the commercial solvent (pentanes) had been removed by evaporation and which then was dissolved in precooled diethyl ether (0.30 L). Still at −75 °C and 15 min later, the mixture was treated with triphenyl phosphite (26 mL, 31 g, 0.10 mol). When the temperature had reached 25 °C, the organic layer was washed with a 1.0 M aqueous solution (3 × 0.10 L) of sodium hydroxide and brine (2 × 50 mL) before being dried and evaporated. Recrystallization of the residue from hexanes gave colorless platelets; 21 g (75%); m.p. 74–76 °C (ref. [52]: m.p. 76 °C/16 Torr); ^{13}C NMR: $\delta = 136.9$ (d, $J = 11$ Hz), 133.2 (td, $J = 24$, 5 Hz), 128.1 (t, $J = 25$ Hz), 127.9 ppm (td, $J = 24$, 6 Hz); ^{31}P NMR: $\delta = 5.5$ ppm; elemental analysis calcd (%) for $C_{18}D_{15}P$ (277.38): C 77.94, H 6.06; found: C 78.35, H 5.72.

Butyl(tri[$^2H_5$]phenyl)phosphonium bromide: Tri([$^2H_5$]phenyl)phosphine (6.8 g, 25 mmol), 1-bromobutane (3.0 mL, 3.8 g, 28 mmol), and toluene (10 mL) were mixed and heated 6 h to 125 °C. At 25 °C, the syrup formed was dissolved in dichloromethane, and warm ethyl acetate was added until the solution became turbid. Upon scratching with a glass rod, crystallization set in. Recrystallization from dichloromethane and ethyl acetate gave colorless granules. 9.1 g (88%); m.p. (decomp) 230–232 °C; ^{1}H NMR: $\delta =$ 3.7 (m, 2H), 1.6 (m, 4H), 0.92 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR: $\delta = 134.4$ (d, $J = 12$ Hz), 133.0 (dt, $J = 12$, 5 Hz), 129.8 (td, $J = 12$, 6 Hz), 117.8 (d, $J =$ 86 Hz), 24.4 (d, $J = 5$ Hz), 23.5 (d, $J = 17$ Hz), 22.4 (d, $J = 51$ Hz), 13.6 ppm (s); ^{31}P NMR: $\delta = 24.7$ ppm; elemental analysis calcd (%) for $C_{22}H_9D_{15}BrP$ (414.40): C 63.76, H 6.24; found: C 64.03, H 6.11.

Acknowledgement

This work was supported by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, Bern (grants 20-49′307-96 and 20-55′303-98). The authors also wish to express their appreciation to Professor Yu-fen Zhao at the Chemistry Departments of Tsinghua University, Beijing, and of Xiamen University. She offered Q.W. the opportunity to pursue his graduate studies during two years in Lausanne.

[1] M. Schlosser, K. F. Christmann, *Liebigs Ann. Chem.* **1967**, *708*, 1–35.
[2] M. Schlosser, T. Huynh Ba, B. Schaub, *Tetrahedron Lett.* **1985**, *26*, 311–314.
[3] M. Schlosser, *Top. Stereochem.* **1970**, *5*, 1–30.
[4] M. Schlosser, K. F. Christmann, *Synthesis* **1969**, 38–39.
[5] M. Schlosser, K. F. Christmann, A. Piskala, D. Coffinet, *Synthesis* **1971**, 29–31.
[6] M. Schlosser, D. Coffinet, *Synthesis* **1971**, 380–381.
[7] M. Schlosser, D. Coffinet, *Synthesis* **1972**, 575–576.
[8] M. Schlosser, B. Schaub, J. de Oliveira-Neto, S. Jeganathan, *Chimia* **1986**, *40*, 244–245.
[9] B. Schaub, S. Jeganathan, M. Schlosser, *Chimia* **1986**, *40*, 246–247.
[10] M. Schlosser, K. F. Christmann, A. Piskala, *Chem. Ber.* **1970**, *103*, 2814–2820.
[11] W. S. Johnson, *Angew. Chem.* **1976**, *88*, 33–41; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 9–25.
[12] M. B. Gravenstock, W. S. Johnson, B. E. McCarry, R. J. Parry, B. E. Ratcliffe, *J. Am. Chem. Soc.* **1978**, *100*, 4274–4282.
[13] W. S. Johnson, L. R. Hughes, J. A. Kloeck, T. Niem, A. Shenvi, *J. Am. Chem. Soc.* **1979**, *101*, 1279–1281.
[14] W. S. Johnson, B. E. McCarry, R. L. Markezich, S. G. Boots, *J. Am. Chem. Soc.* **1980**, *102*, 352–359.
[15] W. S. Johnson, C. Newton, S. D. Lindell, *Tetrahedron Lett.* **1986**, *27*, 6027–6030.
[16] W. S. Johnson, Y. Q. Chen, M. S. Kellogg, *J. Am. Chem. Soc.* **1983**, *105*, 6653–6656.
[17] K. Issleib, R. Lindner, *Liebigs Ann. Chem.* **1967**, *707*, 120–129.
[18] F. G. Bordwell, *Acc. Chem. Res.* **1988**, *21*, 456–463.
[19] T. A. Mastryukova, A. G. Matveeva, A. A. Grigoreva, G. F. Litovchenko, E. I. Matrosov, I. M. Aladzheva, O. V. Bukhovskaya, I. V. Leonteva, M. I. Kabachnik, *Zh. Obshch. Khim.* **1991**, *61*, 2427–2433; *Russ. J. Gen. Chem.* **1991**, *61*, 2253–2257; *Chem. Abstr.* **1992**, *116*, 194449k.
[20] V. Patil, M. Schlosser, *Synlett* **1993**, 125–126.
[21] X.-p. Zhang, M. Schlosser, *Tetrahedron Lett.* **1993**, *34*, 1925–1928.
[22] X.-p. Zhang, Ph.D. thesis, Université de Lausanne, **1994**, pp. 17–24.
[23] M. Schlosser, B. Schaub, *J. Am. Chem. Soc.* **1982**, *104*, 5821–5823.
[24] G. Wittig, G. Geißler, *Liebigs Ann. Chem.* **1953**, *580*, 44–57.

  0947-6539/03/0902-0573 $ 20.00+.50/0

[25] D. Seyferth, M. A. Eisert, J. K. Heeren, *J. Organomet. Chem.* **1964**, *2*, 101 – 108.
[26] D. Seyferth, J. K. Heeren, W. B. Hughes, *J. Am. Chem. Soc.* **1965**, *87*, 2847 – 2854.
[27] D. Seyferth, W. B. Hughes, J. K. Heeren, *J. Am. Chem. Soc.* **1965**, *87*, 3467 – 3474.
[28] M. Schlosser, *Angew. Chem.* **1962**, *74*, 291 – 291; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 266 – 266.
[29] B. Schaub, T. Jenny, M. Schlosser, *Tetrahedron Lett.* **1984**, *25*, 4097 – 4100.
[30] M. Schlosser, *J. Organomet. Chem.* **1967**, *8*, 9 – 16.
[31] M. Schlosser, *Pure Appl. Chem.* **1988**, *60*, 1627 – 1634.
[32] M. Schlosser, *Mod. Synth. Methods* **1992**, *6*, 227 – 271.
[33] M. Schlosser in *Organometallics in Synthesis: A Manual*, 2nd ed. (Ed.: M. Schlosser), Wiley, Chichester, **2002**, pp. 1 – 352, specifically pp. 21 – 22.
[34] T. L. Brown, J. A. Ladd, G. N. Newman, *J. Organomet. Chem.* **1965**, *3*, 1 – 6.
[35] H. Dietrich, D. Rewicki, *J. Organomet. Chem.* **1981**, *205*, 281 – 289.
[36] M. Marsch, K. Harms, L. Lochmann, G. Boche, *Angew. Chem.* **1990**, *102*, 334 – 335; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 308 – 309.
[37] G. T. DeLong, D. K. Pannell, M. T. Clark, R. D. Thomas, *J. Am. Chem. Soc.* **1993**, *115*, 7013 – 7014.
[38] B. Goldfuss, S. I. Khan, K. N. Houk, *Organometallics* **1999**, *18*, 2927 – 2929.
[39] H. Gilman, B. J. Gaj, *J. Org. Chem.* **1957**, *22*, 1165 – 1168.
[40] R. Waack, M. A. Doran, *J. Org. Chem.* **1967**, *32*, 3395 – 3399.
[41] G. Wittig, *Angew. Chem.* **1940**, *53*, 242 – 247.
[42] H. Gilman, J. W. Morton, *Org. React.* **1954**, *8*, 258 – 304, specifically p. 286.
[43] M. Schlosser in *Organometallics in Synthesis: A Manual*, 2nd ed. (Ed.: M. Schlosser), Wiley, Chichester, **2002**, p. 100.
[44] C. Bobbio, M. Schlosser, *Eur. J. Org. Chem.* **2001**, 4533 – 4536.
[45] H. C. Brown, D. Basavaiah, *J. Org. Chem.* **1982**, *47*, 754 – 756.
[46] G. Wittig, M. Schlosser, *Chem. Ber.* **1961**, *94*, 1373 – 1383.
[47] E. Vedejs, W.-f. Huang, *J. Org. Chem.* **1984**, *49*, 210 – 212.
[48] J. Závada, M. Pankova, J. Sicher, *Collect. Czech. Chem. Commun.* **1973**, *38*, 2102 – 2120.
[49] J. Závada, M. Pankova, J. Sicher, *Collect. Czech. Chem. Commun.* **1972**, *37*, 2414 – 2435.
[50] W. F. Foley, F. J. Welch, E. M. LaCombe, H. S. Mosher, *J. Am. Chem. Soc.* **1959**, *81*, 2779 – 2784.
[51] T. Joh, K. Doyama, K. Fujiwara, K. Maeshima, S. Takahahi, *Organometallics* **1991**, *10*, 508 – 513.
[52] M. A. Bennett, D. L. Milner, *J. Am. Chem. Soc.* **1969**, *91*, 6983 – 6994.

Received: July 5, 2002 [F4230]

  0947-6539/03/0902-0574 $ 20.00+.50/0