Phosphane – Tetrahalodiborane(4) Adducts: Formation of *closo*-3,4,5,6-Tetrabromo-1,2-diphosphahexaborane(4)

Willi Keller[*][a][+], **Larry G. Sneddon**[a], **Wolfgang Einholz**[b], and **Armin Gemmler**[b]

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania[a],
Philadelphia, PA 19104-6323, U.S.A.

Institut für Chemie, Universität Hohenheim[b],
Garbenstraße 30, W-7000 Stuttgart 70, F.R.G.

Received December 19, 1991

Key Words: Bis(tribromophosphane) – tetrabromodiborane(4) diadduct / *closo*-3,4,5,6-Tetrabromo-1,2-diphosphahexaborane(4)

Tetrabromodiborane(4), B_2Br_4, forms a 1:2 adduct **1** with PBr_3, which reacts at 350°C to *closo*-1,2-$P_2B_4Br_4$ (**4a**) in 25% yield. Compound **4a** neither rearranges to the 1,6-isomer nor decomposes to an appreciable extent upon heating to 650°C. B_2Cl_4 reacts with equimolar amounts of either tris(trimethylsilyl)phosphane or 1,2-bis(dichlorophosphanyl)ethane to give $B_2Cl_4 \cdot P(SiMe_3)_3$ (**2**) and $B_2Cl_4 \cdot Cl_2PCH_2CH_2PCl_2$ (**3**), respectively. Compound **2** represents the first phosphane – diborane(4) monoadduct with two boron atoms in different coordination environment.

In contrast to the well-established diamine – tetrahalodiborane(4) adducts $R_3N-BHal_2-BHal_2-NR_3$[1], donor – acceptor compounds between phosphanes and tetrahalodiboranes(4) are rare. In fact, preparations of only three such adducts, $B_2Cl_4 \cdot 2\ PH_3$, $B_2Cl_4 \cdot P_2Me_4$, and $B_2Cl_4 \cdot 2\ PCl_3$ have been reported by Wartik and Apple[2] as well as Garrett and Urry[3].

Previously, we have demonstrated that the pyrolysis of a mixture of B_2Cl_4 and PCl_3 at temperatures near 330°C results in the formation of the diphosphahexaborane cluster *closo*-1,2-$P_2B_4Cl_4$ (**4b**)[4]. Similar reactions between tetrahalodiboranes(4) and halogenated hydrocarbons yield different perhalogenated small- and medium-sized *closo*-carboranes like $C_2B_5Hal_7$ (Hal = Cl, Br), $C_2B_7Cl_7$, $C_2B_8Cl_8$[5].

In order to obtain information on the formation of the new phosphaborane cluster and to extend the method for preparing further homologs, we have synthesized different precursory adducts $B_2Hal_4 \cdot n\ PX_3$ (Hal = Cl, Br; X = Cl, Br, $SiMe_3$; $n = 1, 2$) and studied their decomposition in the vapor phase as well as in solution.

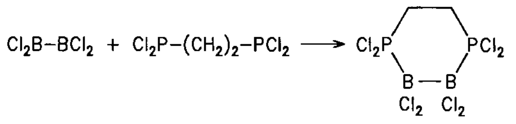
Results and Discussion

Formation of Phosphane – Tetrahalodiborane(4) Adducts

B_2Br_4 reacts with two equivalents of PBr_3 to form the stable adduct $Br_3P-BBr_2-BBr_2-PBr_3$ (**1**) [Eq. (1)]. Unlike B_2Br_4, **1** does not ignite when exposed to air and melts without any appreciable decomposition at 85°C; it sublimes slowly at room temperature under vacuum. Therefore, in contrast to B_2Br_4, stocks of **1** can be stored conveniently in glass tubes under inert gas at room temperature, ideally in the dark, for several months. Since the stability of such phosphane – diborane complexes depends on the strength of the dative B – P bond, **1** is more stable than the previously described homologous adduct $B_2Cl_4 \cdot 2\ PCl_3$[3], which is derived from the less Lewis-acidic B_2Cl_4 and the less Lewis-basic PCl_3 and dissociates above its melting point at −16°C.

$$Br_2B{-}BBr_2 + 2\ PBr_3 \rightleftharpoons \underset{\mathbf{1}}{Br_3P{-}BBr_2{-}BBr_2{-}PBr_3} \qquad (1)$$

$$Cl_2B{-}BCl_2 + (Me_3Si)_3P \longrightarrow \underset{\mathbf{2}}{(Me_3Si)_3P{-}BCl_2{-}BCl_2} \qquad (2)$$



3

(3)

$$7\ \mathbf{1} \longrightarrow \underset{\mathbf{4a}}{P_2B_4Br_4} + 10\ BBr_3 + 12\ PBr_3 \qquad (4)$$

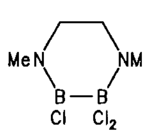
However, in solution the adduct **1** dissociates to an appreciable extent forming a dynamic equilibrium [Eq. (1)], which is depending on the temperature, the kind of solvent, and the sample concentration. By measuring the freezing point depression of benzene solutions with different concentrations of **1** the dissociation degree, i.e. the amount of dissociated complexes per total amount of the dissolved sample **1**, was determined to be approximately 37% (0.39 mol/kg, 2°C), 46% (0.21 mol/kg, 3.5°C), and 54% (0.10 mol/kg, 4.4°C), respectively. The ^{11}B-NMR as well as the ^{31}P-NMR spectra of a 0.1 M CD_2Cl_2 solution show only one signal ($\delta^{11}B = 40.6$ at 22°C, 38.3 at −10°C; $\delta^{31}P = 186.4$ at −10°C). This means that the exchange process according to Eq. (1) is too fast for the NMR time scale, and thus the

---

[+] New address: Fraunhofer-Institut für Produktionstechnik und Automatisierung (IPA), Eierstraße 46, W-7000 Stuttgart 10, F.R.G.

two different species (**1** and free B_2Br_4 or PBr_3, respectively) cannot be detected. Unfortunately, at temperatures below −10°C the adduct **1** starts to precipitate, and NMR spectra could not be taken.

There exist only few diborane compounds with different coordination numbers at the boron atoms. Two examples represent the amine complexes **5**[6] and **6**[7]. However, phosphane–diborane monoadducts were unknown yet. We have now observed that B_2Cl_4 reacts with $P(SiMe_3)_3$ in an equimolar ratio to the 1:1 complex **2** [Eq. (2)]. Its ^{11}B-NMR spectrum consists of 2 signals at $\delta = 69.5$ and -0.9. This clearly shows that the phosphane molecule is coordinated only to one boron atom whilst the other, three-coordinated boron atom is even deshielded compared with B_2Cl_4. This effect of deshielding is also noticed in the analogous monoadducts $Me_3N-BF_2-BF_2$ and $Me_2(Me_3Si)N-BF_2-BF_2$[7]. Like $B_2F_4 \cdot N(SiMe_3)_3$[7], **2** decomposes in solution within several hours.



5

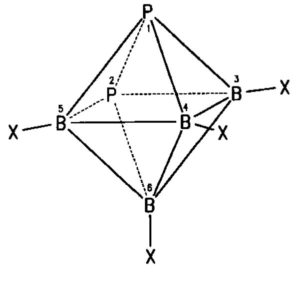
$F_2B-BF_2-NMe_3$

6

B_2Cl_4 adds an equimolar amount of the bifunctional Lewis base $Cl_2P-CH_2-CH_2-PCl_2$ to give the 1:1 complex **3** [Eq. (3)], with each boron atom coordinated to a phosphorus atom ($\delta^{11}B = 57.9$).

Formation of *closo*-3,4,5,6-Tetrabromo-1,2-diphosphahexaborane(4)

Pyrolysis of **1** at 350°C in an evacuated, sealed flask produces *closo*-3,4,5,6-tetrabromo-1,2-diphosphahexaborane(4) (**4a**) in 25% yield based on the consumption of **1** according to the idealized Eq. (4).



4a (X=Br)
4b (X=Cl)

The NMR data and the single-crystal X-ray diffraction study of the analogous cluster $1,2\text{-}P_2B_4Cl_4$[4] (**4b**) confirmed that **4b** adopts a slightly distorted octahedral geometry with the two phosphorus atoms occupying adjacent cage vertex positions [$\delta^{31}P = -187$; $\delta^{11}B = 22.4$ ($h_{1/2} = 101$ Hz) and 2.8 ($h_{1/2} = 106$ Hz)]. The NMR data of **4a** clearly indicate that the P atoms of the tetrabromo derivative are also in *cis*-position to each other. Thus, the ^{11}B-NMR spectrum shows two signals of equal intensity for the two distinct pairs of boron atoms in the molecule, with the resonance line at $\delta = 19.0$ ($h_{1/2} = 110$ Hz) assigned to the boron atoms B4, B6 and the signal at $\delta = 0.0$ ($h_{1/2} = 117$ Hz) to B3, B5. Atoms B3 and B5 are adjacent to both phosphorus atoms and, as a result, this resonance line has a larger line width ($h_{1/2} = 117$ Hz) than the B4, B6 signal ($h_{1/2} = 110$ Hz), which is derived from the boron atoms with only one adjacent P and 3 B atoms. Neither the ^{11}B-NMR signals nor the ^{31}P-NMR resonance line at $\delta = -145.0$ can be resolved upon line narrowing to show B–P coupling.

Compound **4a** shows only minimal fragmentation in its mass spectrum indicating the high stability of the cluster framework. Indeed, a series of thermolysis experiments of **4a** at 450°C, 570°C, and 650°C in evacuated sealed glass tubes resulted neither in an appreciable decomposition nor in a rearrangement to the 1,6-isomer of $P_2B_4Br_4$. This lack of thermal isomerization stands in sharp contrast to the rearrangement reactions of some comparable compounds, such as the corresponding parent carborane $1,6\text{-}C_2B_4H_6$[8] or $1,2\text{-}P_2B_{10}H_{10}$[9], $1,2\text{-}As_2B_{10}H_{10}$[10], $1,2\text{-}B_{10}H_{10}CHP$[11], and $Me_3NCB_{10}H_{10}PPh$[12]. The exceptional stability of the $P_2B_4Hal_4$ cage system has been demonstrated recently by He(I)-photoelectron spectroscopy studies of $1,2\text{-}P_2B_4Cl_4$ under pyrolytic conditions, where it was found that temperatures as high as 950°C were necessary to cause decomposition[13]. These drastic conditions were found to be in accordance with MNDO calculations[13], where the activation gap for dissociation was determined to be as high as 300 kJ/mol.

A byproduct of the thermal decomposition of the complex **1** consisted of an ocher involatile solid which has the formula $B_{1.0}P_{3.6}Br_{1.2}$ and dissolves in protic solvents with the evolution of hydrogen with a smell of phosphane. A similar kind of precipitation was also formed in the pyrolysis of B_2Cl_4 and PCl_3.

Attempts to prepare **4a** in a melt of **1** at 120°C failed owing to the formation of BBr_3 and PBr_3 and the above-mentioned ocher solid. Other efforts to isolate intermediate compounds, by heating samples of **1** in benzene or dodecane at 160°C, yielded, in addition to the ocher solid, only traces of **4a** along with borylated and phosphorylated derivatives of benzene in the former, and mainly BBr_3 and PBr_3 in the latter experiments.

Apparently, the thermal conversion of the adduct $B_2Hal_4 \cdot 2\,PHal_3$ into $P_2B_4Hal_4$ does not occur unless the reactants are in the vapor phase. Since it is known from PE-spectroscopy studies[14] that B_2Hal_4 forms BHal fragments at high temperature in the vapor phase, the initial step of reaction could consist of an attack of BHal on $PHal_3$ to give $B(Hal)_xP(Hal)_y$ intermediates, e.g. $Hal_2B-PHal_2$. Subsequent reactions with either BHal or B_2Hal_4 and $PHal_3$ successively lead to the stable product $P_2B_4Hal_4$.

Further studies were carried out to extend the method of preparing heteroborane clusters to other systems, including reactions by copyrolyzing mixtures of B_2Cl_4 with $TiCl_4$, $SiCl_4$, $SnCl_4$, $AlCl_3$, $SbCl_3$, BrCN, or cyclohexene sulfide, $C_6H_{10}S$. However, these reactions failed, as did attempts to prepare $P_2B_4Hal_4$ or similar phosphaborane clusters by copyrolyzing or UV-irradiating mixtures of $BHal_3$, $PHal_3$ and reducing agents such as Hg or Ag powder.

We like to thank Prof. Dr. *W. Haubold* (Institut für Chemie, Universität Hohenheim) for supporting this research, and we are grateful to the *National Science Foundation Materials Research Laboratory at the University of Pennsylvania*, Philadelphia/U.S.A., for the financial support through a fellowship for W.K.

Experimental

The pyrolytic reactions and workup of the obtained products were carried out according to the previously reported method[4]. All other manipulations were performed by using standard high-vacuum or inert-atmosphere techniques as described by Shriver[15].

Materials: Trichloro- and tribromophosphane were freshly distilled and degassed before use. Trichloroborane was purified by vacuum fractionation until the product showed a vapor pressure of 4 Torr at −78°C. Tribromoborane was stirred over mercury, degassed, and condensed into a trap of −80°C prior to use. Tetrachloro- and tetrabromodiborane(4) were prepared by cocondensation of BCl_3 or BBr_3 with copper-vapor onto cooled walls (−196°C) of a metal-vapor reactor similar to that described by Timms[16]. After reaction, B_2Hal_4 was separated from excess $BHal_3$ by repeated fractionation until the condensate exhibited a vapor pressure at 0°C of 44 Torr (B_2Cl_4) or less than 1 Torr (B_2Br_4). Tris(trimethylsilyl)phosphane was synthesized by the method of Becker and Hölderich[17]. 1,2-Bis(dichlorophosphanyl)ethane was purchased from Strem Chemicals and used as received. All reaction solvents were reagent grade, dried, and purified by literature methods.

Physical Measurements: NMR spectra (^1H: 200.1 MHz; ^{11}B: 64.2 MHz; ^{31}P: 81 MHz) were recorded with an IBM AF-200 Fourier transform spectrometer. δ^1H, $\delta^{11}B$, and $\delta^{31}P$ values are referred to internal Me_4Si (^1H), external $BF_3 \cdot OEt_2$ (^{11}B) or H_3PO_4 (^{31}P), respectively. High- and low-resolution mass spectra were recorded with a VG Micromass 7070H mass spectrometer. Cryoscopic measurements were taken with a Knauer cryometer. Elementary analyses were performed by Galbraith Laboratories, Knoxville, TN.

Bis(tribromophosphane)—Tetrabromodiborane(4) Diadduct (**1**): In a typical reaction, 1.00 g (2.93 mmol) of B_2Br_4 and 1.58 g (5.86 mmol) of PBr_3 were condensed into a 100-ml round-bottomed flask equipped with a teflon stopcock. The flask was sealed, removed from the vacuum line and allowed to warm slowly with vigorous shaking. Upon thawing of the reactants, the white adduct started to precipitate as a fine powder, and the reaction was completed by warming to room temperature. The ^{11}B-NMR spectrum indicated a quantitative formation of $B_2Br_4 \cdot 2\,PBr_3$ (**1**); yield 2.51 g (97%), m.p. 78°C (sealed tube). The ^{11}B-NMR spectrum of a sample heated at 85°C for 5 min showed no peaks resulting from decomposition products. Upon exposure to air, **1** slowly decomposed. — ^{11}B NMR: δ = 40.6 (0.1 M in CD_2Cl_2, 22°C), 38.3 (0.1 M in CD_2Cl_2, −10°C), 40.1 (toluene, 25°C), 40.2 (benzene, 25°C), 66.2 (*n*-hexane, 25°C). — ^{31}P NMR: δ = 186.4 (0.1 M in CD_2Cl_2, −10°C). — The dissociation degree of **1** in benzene was determined by measuring the freezing-point depression of benzene solutions (Table 1).

$B_2Br_{10}P_2$ (882.6) Calcd. B 2.45 P 7.02 Found B 2.22 P 7.19

Tris(trimethylsilyl)phosphane—Tetrachlorodiborane(4) Adduct (**2**): At −78°C 0.30 g (1.20 mmol) of $P(SiMe_3)_3$ in 5 ml of CH_2Cl_2 was pipetted into a stirred solution of 0.29 g (1.80 mmol) of B_2Cl_4 in 5 ml of CH_2Cl_2. The reaction mixture was warmed up to room temperature within 30 min without any precipitation. The ^{11}B-NMR spectrum of the clear solution indicated the consumption of 1.2 mmol of B_2Cl_4 ($\delta^{11}B$ = 61.1) and the formation of the adduct **2**. — ^{11}B NMR: δ = 69.7 ($h_{1/2}$ = 540 Hz, 1 B, BCl_2), −0.9 ($h_{1/2}$ = 340 Hz, 1 B, $P-BCl_2$). — After the sample had been stored at room temperature for 30 min, it showed slight changes in the intensities of the ^{11}B-NMR signals. While the B_2Cl_4 resonance line remained constant, the intensities of the signals at δ = 69.7 and −0.9 decreased, and a signal at δ = 3 assigned to $BCl_3 \cdot P(SiMe_3)_3$ appeared. — After stirring for 12 h, the clear solution took on a deep orange color. The ^{11}B-NMR spectrum of this solution showed a signal for BCl_3 at δ = 47 and a very broad absorption area between δ = +20 and −30. Attempted vacuum distillation between room temperature and 200°C gave excess B_2Cl_4 ($\delta^{11}B$ = 62.1) and BCl_3 ($\delta^{11}B$ = 46.3) as the only volatile boron-containing compounds. A brown powder remained in the flask as a residue.

Table 1. Freezing-point depression of benzene solutions of **1**

Molality of **1** in benzene [mol/kg]	ΔT [K]	Dissociation degree (%)
0.3933	3.46	37
0.2108	2.08	46
0.1042	1.10	54

1,2-Bis(dichlorophosphanyl)ethane—Tetrachlorodiborane(4) Adduct (**3**): 0.22 g (1.35 mmol) of B_2Cl_4, 0.31 g (1.35 mmol) of $(CH_2PCl_2)_2$, and 10 ml of *n*-pentane were condensed into a 50-ml round-bottomed flask and allowed to warm to room temperature with vigorous shaking. The white adduct $B_2Cl_4 \cdot (CH_2PCl_2)_2$ (**3**) precipitated; yield 0.51 g (96%). — ^{11}B NMR ($CDCl_3$): δ = 57.9 ($h_{1/2}$ = 120 Hz).

$C_2H_4B_2Cl_8P_2$ (395.2) Calcd. C 6.07 H 1.01 B 5.47 P 15.68
Found C 6.63 H 1.17 B 5.32 P 15.85

closo-3,4,5,6-Tetrabromo-1,2-diphosphahexaborane(4) (**4a**): 1.80 g (2.04 mmol) of **1** was pyrolyzed at 350°C for 5 h. Fractional condensation gave 1.50 g BBr_3 and PBr_3 as volatile products at room temperature under high vacuum. From the residue **4a** sublimed upon heating with a heat gun and condensed as a white solid; yield 0.03 g [24% according to eq. (4)], m.p. 104–107°C (sealed tube). — ^{11}B NMR (C_6D_6): δ = 19.0 ($h_{1/2}$ = 110 Hz, 2 B, B-4, B-6), 0.0 ($h_{1/2}$ = 117 Hz, 2 B, B-3, B-5). — ^{31}P NMR (CD_2Cl_2): δ = −145.0.

$B_4Br_4P_2$ (424.8) Calcd. B 10.17 P 14.58
Found B 10.21 P 14.73

$^{11}B_4{}^{81}Br_4{}^{31}P_2$ Calcd. 429.650 Found 429.654 (MS)

Thermolysis of **4a**: 0.050 (0.118 mmol) of **4a** which was heated at 450°C for 6 h in an evacuated, sealed pyrex tube of 20 ml volume showed, as monitored by ^{11}B-NMR spectroscopy and mass spectrometry, no decomposition. Heating of 0.045 (0.106 mmol) of **4a** at 570°C or 650°C resulted in some decomposition, producing very thin homogeneous golden depositions at the walls (presumably boron phosphide). However, workup gave 0.035 g (78%) or 0.025 g (56%), respectively, of unchanged **4a**. Neither the 1,6-isomer of **4a** nor other homologs of $P_2B_nBr_n$ or B_nBr_n could be detected by ^{11}B-NMR spectroscopy.

Pyrolysis of **1** *at 120°C:* 2.50 g (2.83 mmol) of **1** was placed under inert gas into a 100-ml round-bottomed flask equipped with a seal constriction and a break-seal joint. The flask was evacuated, sealed, and heated to 120°C for 16 h. An orange solid precipitated at the spot of the melted puddle. The flask was opened to the vacuum line, and all volatile compounds vacuum-distilled at room temperature into a −196°C trap (2.20 g; $\delta^{11}B$ = 38). The residue was extracted with hexane. The undissolved orange powder was filtrated off and dried in vacuo (yield 0.15 g). — Elementary analysis: Found B 4.56, Br 41.46, P 46.79.

Thermolysis of **1** *in Benzene at 150°C:* A solution of 0.050 g (0.057 mmol) of **1** in 1 ml of benzene was heated in a sealed NMR tube at 150°C for 17 h. An orange solid precipitated. The solution was shown by ^{11}B-NMR spectroscopy to contain only very small amounts of **4a** along with $PhBBr_2$. No intermediates of the formation of **4a** could be detected.

Thermolysis of **1** *in Dodecane at 160°C:* After 16 h an ochre solid precipitated, and the ^{11}B-NMR spectrum of this slurry showed the formation of BBr_3 with traces of a degradation product at δ = 28. Further heating at 160°C over a period of 5 d resulted in a total consumption of BBr_3. The only signal observed in the ^{11}B-NMR spectrum was at δ = 28.

Pyrolysis of **1** *at 170°C under Hydrogen:* A 200-ml Fischer-Porter pressure vessel was charged with 0.56 g (0.63 mmol) of **1** and 0.50 atm of hydrogen gas (4.50 mmol). The flask was heated in an oil bath at 170°C for 16 h. A transparent ocher material deposited at the glass wall. After cooling, all volatile compounds were pumped into the vacuum line (0.43 g) and shown by IR (gas) and ^{11}B-NMR analysis to be HBr, BBr_3, and PBr_3. The ocher deposition was peeled of the glass wall by rinsing with 50 ml of *n*-pentane. After stripping off the solvent, 0.12 g of an ocher-brown material remained as a residue. — Elementary analysis: Found B 3.78, P 53.06.

---

[1] N. N. Greenwood, *The Chemistry of Boron*, Pergamon Press, Oxford, **1975**, p. 982.
[2] T. Wartik, E. F. Apple, *J. Am. Chem. Soc.* **1958**, *80*, 6155−6158.
[3] A. G. Garrett, G. Urry, *Inorg. Chem.* **1963**, *2*, 400−405.
[4] W. Haubold, W. Keller, G. Sawitzki, *Angew. Chem.* **1988**, *100*, 958−959; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 925−926.
[5] W. Haubold, W. Keller, *J. Organomet. Chem.* **1989**, *361*, C54−C56.
[6] W. Haubold, J. Hrebicek, G. Sawitzki, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39*, 1027−1031.
[7] W. Haubold, U. Kraatz, W. Einholz, *Z. Anorg. Allg. Chem.* **1991**, *592*, 35−41.
[8] R. N. Grimes, *Carboranes*, Academic Press, New York, **1970**.
[9] J. L. Little, J. G. Kester, J. C. Huffman, L. J. Todd, *Inorg. Chem.* **1989**, *28*, 1087−1091.
[10] J. L. Little, S. S. Pao, K. K. Sugathan, *Inorg. Chem.* **1974**, *13*, 1752−1756.
[11] L. J. Todd, J. L. Little, H. T. Silverstein, *Inorg. Chem.* **1969**, *8*, 1698−1703.
[12] W. F. Wright, J. C. Huffman, L. J. Todd, *J. Organomet. Chem.* **1978**, *48*, 7−15.
[13] B. Solouki, H. Bock, W. Haubold, W. Keller, *Angew. Chem.* **1990**, *102*, 1099−1100; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1044−1046.
[14] B. Solouki, H. Bock, R. Weinmann, W. Haubold, *unpublished results*; citation in R. Weinmann, Dissertation, Univ. Stuttgart, **1985**.
[15] D. F. Shriver, M. A. Drezdzon, *The Manipulation of Air-Sensitive Compounds*, 2nd ed., Wiley, New York, **1986**.
[16] P. L. Timms, *Adv. Inorg. Chem. Radiochem.* **1972**, *14*, 121−171.
[17] G. Becker, W. Hölderich, *Chem. Ber.* **1975**, *108*, 2484−2485.

[491/91]

CAS Registry Numbers

1: 142981-22-4 / **2**: 142981-23-5 / **3**: 142981-24-6 / **4a**: 142981-21-3 / B_2Br_4: 14355-29-4 / B_2Cl_4: 13791-67-2