



tion of symmetrical ethane-1,2-diphosphonic esters  $[(R^1O)_2P(O)-CH_2-CH_2-P(O)(OR^1)_2]$  arising from **2** via oxidative coupling, even if the quantity of **3** or **4** was varied considerably.

Probably for steric reasons, the coupling reaction of organo-copper derivatives **2** cannot be performed with homologs of **3** and **4** such as chlorotriethylsilane and chlorotributylstannane, the phosphonic esters **1** being recovered unchanged after hydrolysis. In a similar manner, *O,O*-dialkyl alkanephosphonothioates such as **7** undergo the reaction only sluggishly. These observations are in accord with our earlier statements on the effect of steric factors on the reactivity of 1-copper(I) derivatives of alkanephosphonic esters (**2**)<sup>3</sup>.

Since the coupling reaction **2**→**5**, **6** is sensitive to steric hindrance and accordingly relatively slow the yields of diesters **5** obtained from **2** and chlorotrimethylsilane (**3**) could be increased by using a 50% excess of **3**. With chlorotrimethylstannane (**4**), an excess of which is less easy to eliminate from the reaction mixture, the experiments were carried out with stoichiometric amounts of each reagent.

The mol ratio **1** : CuJ (1 : 1 or 1 : 0.5) does not affect the process considerably (e.g., yields of **5a**: 70% and 79%, respectively). On the other hand, replacement of copper(I) iodide<sup>4</sup> by copper(I) chloride appears to decrease the yield (e.g., **5a**: 51%); in this case, the addition of lithium chloride or lithium bromide may raise the yield (e.g., **5a** with LiCl: 67%; **5a** with LiBr: 61%). This effect may be attributed to coordination of the lithium halide to the Cu-atom as a ligand whereby the organocopper derivative **2** is stabilized.

Attempts to perform an analogous reaction of **2** with chlorotrimethylgermane or chlorotriethylgermane were not successful, the phosphonic ester **1** being recovered unchanged. This pronounced difference between chlorotrialkylgermane and its silicon or tin analogs might be explained on the basis of the lower reactivity of the Ge—X bond<sup>2</sup>. Indeed, it is known that the halogermanes are slowly and reversibly hydrolyzed contrary to their silicon and tin analogs and this has been interpreted as a consequence of the lower polarity of the Ge—X bond due to the higher electronegativity of germanium as compared with silicon and tin.

The purity of products **5** and **6** was established by C,H analyses as well as by <sup>31</sup>P-N.M.R. (Table) and <sup>1</sup>H-N.M.R. spectrometry.

# A New Route to Dialkyl 1-(Trimethylsilyl)- and 1-(Trimethylstannyl)-alkanephosphonates

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Several investigators have reported the preparation of diesters of trimethylsilylmethane- or trimethylstannylmethanephosphonic acid, using the Michaelis-Arbuzov or the Michaelis-Becker procedures<sup>1</sup>. However, these two methods are somewhat limited by the availability and reactivity of halomethyltrimethylsilanes or halomethyltrimethylstannanes. They require prolonged refluxing of the reactants and give low yields. Furthermore, diesters of the types **5** and **6**, R<sup>2</sup>=alkyl, i.e., diesters of 1-(trimethylsilyl)- and 1-(trimethylstannyl)-alkane-phosphonic acids having at least a C<sub>2</sub> chain, are not available by these routes for the same reasons.

We have now elaborated a new, more general synthesis of dialkyl 1-(trimethylsilyl)- (**5**) and 1-(trimethylstannyl)-alkane-phosphonates (**6**) which does not show the above-mentioned limitations. Dialkyl alkane-phosphonates (**1**) are first converted into their 1-copper derivatives (**2**) by standard procedures<sup>2</sup>; reaction of derivatives **2** with chlorotrimethylsilane (**3**) or chlorotrimethylstannane (**4**) affords the silylation or stannylation products **5** or **6**, respectively, in good yields.

The coupling reaction **2**→**5**, **6** was investigated at  $-30^{\circ}\text{C}$ ; in no case did we observe any side reactions such as the forma-

**Table.** 1-(Trimethylsilyl)- and 1-(Trimethylstannyl)-alkanephosphonic Esters (**5**, **6**, **9**)

Prod- uct	Y	R <sup>1</sup>	R <sup>2</sup>	Yield <sup>a</sup> [%]	b.p./torr [°C]	Molecular formula <sup>b</sup> and b.p./torr [°C] reported	<sup>31</sup> P-N.M.R. (CHCl <sub>3</sub> ) δ [ppm]
<b>5a</b>	O	CH <sub>3</sub>	H	70 (79) <sup>c</sup>	88–89°/15	111–114°/21.5 <sup>1b,1</sup>	35.8
<b>5b</b>	O	CH <sub>3</sub>	CH <sub>3</sub>	62	93–94°/15	C <sub>7</sub> H <sub>10</sub> O <sub>3</sub> PSi (210.2)	35.9
<b>5c</b>	O	C <sub>2</sub> H <sub>5</sub>	H	76 (82) <sup>c</sup>	102–105°/15	118.5–121°/22 <sup>1b,1</sup>	33.0
<b>5d</b>	O	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	61 (73) <sup>c</sup>	104–106°/15	C <sub>9</sub> H <sub>23</sub> O <sub>3</sub> PSi (238.3)	33.4
<b>5e</b>	O	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	63	118–121°/16	C <sub>10</sub> H <sub>25</sub> O <sub>3</sub> PSi (252.3)	33.1
<b>5f</b>	O	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	H	82	103–105°/16	C <sub>10</sub> H <sub>25</sub> O <sub>3</sub> PSi (252.3)	28.3
<b>6a</b>	O	CH <sub>3</sub>	H	68	78–80°/1.5	C <sub>6</sub> H <sub>17</sub> O <sub>3</sub> PSn (286.9)	99.6
<b>6c</b>	O	C <sub>2</sub> H <sub>5</sub>	H	78	80–82°/0.7	75–76°/0.1 <sup>1b,1</sup>	36.8
<b>6d</b>	O	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	40	74–76°/0.2	C <sub>9</sub> H <sub>23</sub> O <sub>3</sub> PSn (328.9)	34.1
<b>9</b>	S	CH <sub>3</sub>	H	15	95–98°/16	95–98°/16 <sup>1b,1</sup>	36.1

<sup>a</sup> The reaction components were used in stoichiometric amounts. Yields are based on phosphonic esters **1** as starting materials.

<sup>b</sup> The microanalyses showed the following maximum deviations from the calculated values: C, ±0.40; H, ±0.14.

<sup>c</sup> A 50% excess of chlorotrimethylsilane (**3**) was used.

**Dialkyl Trimethylsilylmethanephosphonates (5a, c, f; R<sup>2</sup> = H) and Dialkyl Trimethylstannylmethanephosphonates (6a, c; R<sup>2</sup> = H); General Procedure:**

A 1.6 molar solution of butyllithium in hexane (0.05 mol + 5%) is placed in a three-necked flask equipped with stirrer, addition funnel, low-temperature thermometer, and nitrogen-inlet tube. An equal volume of tetrahydrofuran (~33 ml) is added to the stirred cooled (–20°C) solution; then, the dialkyl methanephosphonate (**1**; R<sup>1</sup> = CH<sub>3</sub>, 6.2 g; R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>, 7.6 g; 0.05 mol) in tetrahydrofuran (20 ml) is added dropwise at –70°C. After 10 min, the clear mixture becomes turbid; copper(I) iodide (0.05 mol + 5%) is added, the mixture is slowly allowed to warm to –35°C, and stirring is continued at –35°C to –30°C for 60 min. A solution of chlorotrimethylsilane (**3**; 8.2 g, 0.075 mol) or chlorotrimethylstannane (**4**; 10.45 g, 0.0525 mol) in tetrahydrofuran (30 ml) is then added at –30°C. The solution is kept as long possible at that temperature (5–6 h) and allowed to gradually warm to room temperature (overnight). Water (50 mol) is added; the solution is suction-filtered through Celite, and the cake washed with dichloromethane (4 × 50 ml). The solution is filtered again through the same funnel and the cake washed again with dichloromethane (50 ml). The combined layers are dried with magnesium sulfate, the solvent is removed under reduced pressure, and the product purified by vacuum distillation.

A similar procedure is used for the conversion of *O,O*-dimethyl methanephosphonothioate (**7**) into *O,O*-dimethyl trimethylsilylmethanephosphonothioate (**9**) in low yield.

The reactions of the copper(I) derivatives **2** prepared using copper(I) chloride are carried out in the same manner except that dry lithium chloride or dry lithium bromide (0.05 mol) are previously dissolved in tetrahydrofuran (~35 ml) and added to the stirred and cooled (–20°C) solution of butyllithium. The procedure described above is then followed; chlorotrimethylsilane (**3**) is used in excess (50%) and chlorotrimethylstannane (**4**) in stoichiometric amounts.

**Dialkyl 1-(Trimethylsilyl)- (5b, d, e) and Dialkyl 1-(Trimethylstannyl)-alkanephosphonates (6d); General Procedure:**

A 1.6 molar solution of butyllithium in hexane (0.05 mol + 5%) is placed in a three-necked flask fitted with stirrer, addition funnel, and nitrogen-inlet tube. An equal volume of tetrahydrofuran (~33 ml) is added to the stirred and cooled (–20°C) solution; then, the dialkyl methanephosphonate (**1**; R<sup>1</sup> = CH<sub>3</sub>, 6.2 g; R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>, 7.6 g; 0.05 mol) in tetrahydrofuran (20 ml) is added dropwise at –70°C. After 10 min, the clear mixture becomes turbid; the alkyl iodide (R<sup>2</sup> = CH<sub>3</sub>, 7.8 g; R<sup>2</sup> = C<sub>2</sub>H<sub>5</sub>, 8.6 g; 0.055 mol) in tetrahydrofuran (15 ml) is added dropwise at –70°C and the mixture is allowed to slowly warm to room temperature. After 10 min at room temperature, the mixture is cooled to –45°C and a solution of butyllithium (0.05 mol + 5%) in hexane is added. Stirring is continued for 20 min at –45°C, copper(I) iodide

(0.05 mol + 5%) is added, the mixture is slowly allowed to warm to –35°C, and the procedure described above is followed.

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- <sup>1</sup> (a) W. H. Keeber, H. W. Post, *J. Org. Chem.* **21**, 509 (1956).
- (b) V. A. Ginsburg, A. Y. Yakubovich, *Zh. Obshch. Khim.* **28**, 728 (1958); *C. A.* **52**, 17091 (1958).
- (c) A. E. Canavan, C. Eaborn, *J. Chem. Soc.* **1959**, 3751.
- (d) D. Seyferth, *Angew. Chem.* **72**, 36 (1960).
- (e) D. Seyferth, S. O. Grim, *J. Am. Chem. Soc.* **83**, 1610 (1961).
- (f) E. F. Bugarenko, E. A. Chernyshev, A. D. Petrov, *Izv. Akd. Nauk SSSR, Ser. Khim.* **2**, 286 (1965); *C. A.* **62**, 14721 (1965).
- (g) R. J. Hartle, *J. Org. Chem.* **31**, 4288 (1966).
- (h) M. I. Aliev, S. Z. Israfilova, N. I. Podobaev, D. R. Israelyan, *Vop. Neftekkim.* **3**, 78 (1971).
- (i) Z. S. Novikova, S. N. Zdorova, I. F. Lutsenko, *Zh. Obshch. Khim.* **42**, 112 (1972); *J. Gen. Chem. USSR* **42**, 108 (1972).
- (j) M. G. Voronkov et al., *Zh. Obshch. Khim.* **45**, 2010 (1975); *J. Gen. Chem. USSR* **45**, 1974 (1975).
- (k) A. Sekiguchi, W. Ando, *Tetrahedron Lett.* **1978**, 1385.
- (l) H. Weichmann, B. Ochsler, J. Dichek, A. Tzschach, *J. Organomet. Chem.* **182**, 465 (1979).
- <sup>2</sup> F. Mathey, P. Savignac, *Synthesis* **1976**, 766.
- <sup>3</sup> F. Mathey, P. Savignac, *Tetrahedron* **34**, 649 (1978).
- <sup>4</sup> Copper(I) iodide and copper(I) chloride were furnished by Merck and used without any purification.
- <sup>5</sup> F. A. Cotton, G. Wilkinson, in: *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 1980.