Synthesis of carborane-containing phosphates by catalytic phosphorylation

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The catalytic phosphorylation of *o*-carboranylmethanol with different phosphorus acid chlorides has been studied. This method makes it possible to obtain esters of phosphorus acids and esters of the corresponding phosphorus acid chlorides containing carboranylmethyl groups. The catalytic phosphorylation of 1,2-bis(hydroxymethyl)-*o*-carborane affords both acyclic and cyclic phosphate esters. The structure of the synthesized *o*-carborano[1,2-*e*]-1,3,2-dioxaphosphepane was confirmed by X-ray diffraction analysis.

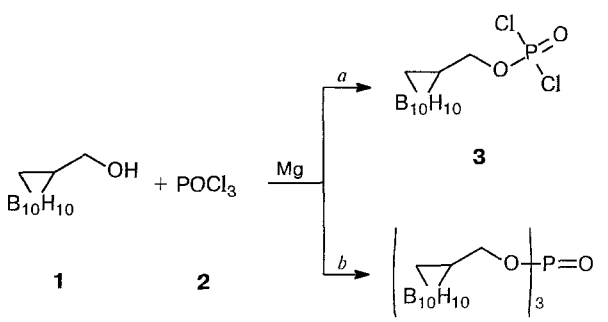
Key words: *o*-carboranylmethanol, 1,2-bis(hydroxymethyl)-*o*-carborane, catalytic phosphorylation; phosphate esters.

At present, two different methods for obtaining *o*-carboranylmethyl esters of oxygen-containing phosphorus acids are known: hydroboration of acetylene esters of phosphoric and phosphonic acids[1] and phosphorylation of *o*-carboranylmethanols by phosphoric acid[2] or PCl_5 in an organic solvent.[3,4]

Previously, we established that *o*-carboranylmethyl esters of phosphorus(v) acids (by analogy with phosphorus esters based on polyfluoroalkanols R_FCH_2OH)[5] can be obtained by catalytic phosphorylation[6] of *o*-carboranylmethanol (**1**). In this work, we studied in detail the catalytic phosphorylation of alcohol **1** and 1,2-bis(hydroxymethyl)-*o*-carborane with different phosphorus(v) acid chlorides in the presence of metallic Mg as the procatalyst.

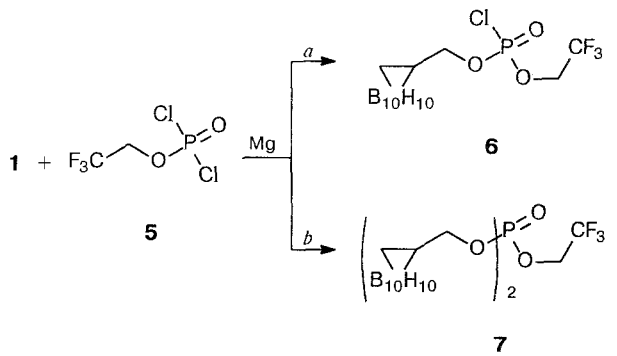
Thus, phosphorylation of alcohol **1** with excess phosphorus oxychloride (**2**) affords *o*-carboranylmethyl dichlorophosphate (**3**) (Scheme 1, *a*). Purely tris(*o*-carboranylmethyl) phosphate (**4**) is formed at 160—200 °C when the alcohol : $POCl_3$ molar ratio 3 : 1 is used (Scheme 1, *b*).

Scheme 1



In a similar manner, acid chloride ester **6** can be obtained by catalytic phosphorylation of compound **1** with excess dichlorophosphate **5** at 140 °C (Scheme 2, *a*). When the alcohol : dichlorophosphate ratio is 2 : 1 at 160—200 °C, ester **7** is formed, which contains two *o*-carboranylmethoxyl substituents at the P atom (Scheme 2, *b*).

Scheme 2



The catalytic phosphorylation of alcohol **1** with monochlorophosphates **8** and **9** affords esters **10** and **11**, respectively (Scheme 3).

We used catalytic phosphorylation also for preparing phosphates based on 1,2-bis(hydroxymethyl)carborane (**12**). It was established that the reactions of diol **12** with

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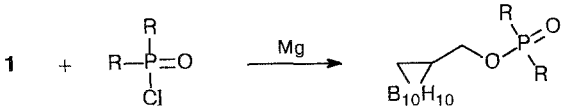
Scheme 3

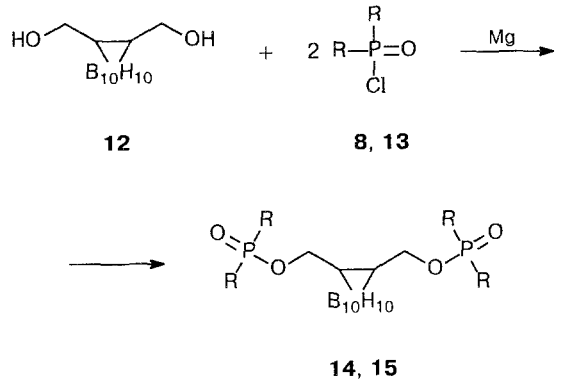


8, 9 **10, 11**

R = CF_3CH_2O (**8**, **10**), PhO (**9**, **11**)

monochlorophosphates **8** and **13** (Scheme 4) afford the products of diphosphorylation (**14** and **15**, respectively).

Scheme 4

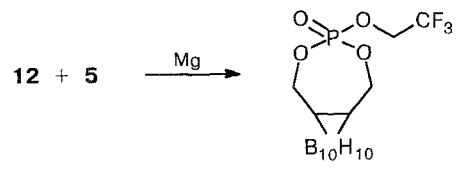


12 **8, 13** **14, 15**

R = CF_3CH_2O (**8**, **14**), $C_4F_9CH_2O$ (**13**, **15**)

However, the catalytic phosphorylation of diol **12** with dichlorophosphate **5** (Scheme 5) gives purely (according to ^{31}P NMR spectroscopy data) *o*-carborano-[1,2-*e*]-1,3,2-dioxaphosphepane (**16**). It should be noted that the formation of analogous 1,3,2-dioxaphosphepane compounds has been observed previously when phosphorylation of diol **12** was performed with phosphorus chlorides, PCl_3 [7] and PCl_5,[4,8] and with hexachlorocyclotriphosphazene.[8]

Scheme 5



16

The crystal and molecular structure of compound **16** was established by X-ray structural analysis. The structure of the molecule is shown in Figs. 1, *a*, and *b*; the bond lengths and principal bond angles are given in Tables 1 and 2; the torsion angles in the cycle are presented in Table 3; atomic coordinates and temperature factors are listed in Table 4.

Table 1. Bond lengths (*d*) in phosphate **16**

Bond	*d*/Å	Bond	*d*/Å
P—O(1)	1.451(2)	B(3)—B(7)	1.774(4)
P—O(2)	1.575(2)	B(3)—B(8)	1.756(4)
P—O(3)	1.572(2)	B(4)—B(5)	1.775(4)
P—O(4)	1.572(2)	B(4)—B(8)	1.766(4)
O(2)—C(13)	1.437(3)	B(4)—B(9)	1.771(4)
O(3)—C(14)	1.431(3)	B(5)—B(6)	1.779(3)
O(4)—C(15)	1.429(3)	B(5)—B(9)	1.782(4)
F(1)—C(16)	1.324(3)	B(5)—B(10)	1.783(4)
F(2)—C(16)	1.324(3)	B(6)—B(10)	1.762(3)
F(3)—C(16)	1.329(3)	B(6)—B(11)	1.764(3)
C(1)—C(2)	1.649(3)	B(7)—B(8)	1.776(4)
C(1)—B(3)	1.722(3)	B(7)—B(11)	1.778(4)
C(1)—B(4)	1.715(3)	B(7)—B(12)	1.772(4)
C(1)—B(5)	1.697(3)	B(8)—B(9)	1.789(4)
C(1)—B(6)	1.738(3)	B(8)—B(12)	1.783(4)
C(1)—C(13)	1.521(3)	B(9)—B(10)	1.785(4)
C(2)—B(3)	1.743(3)	B(9)—B(12)	1.787(4)
C(2)—B(6)	1.717(3)	B(10)—B(11)	1.769(4)
C(2)—B(7)	1.702(3)	B(10)—B(12)	1.786(4)
C(2)—B(11)	1.711(3)	B(11)—B(12)	1.765(4)
C(2)—C(14)	1.523(3)	C(15)—C(16)	1.491(3)
B(3)—B(4)	1.769(4)		

Table 2. Principal bond angles (ω) in phosphate **16**

Angle	ω/deg	Angle	ω/deg
O(1)—P—O(2)	119.7(1)	C(1)—C(2)—C(14)	121.6(2)
O(1)—P—O(3)	110.2(1)	B(3)—C(2)—C(14)	116.1(2)
O(2)—P—O(3)	104.3(1)	B(6)—C(2)—C(14)	120.1(2)
O(1)—P—O(4)	115.7(1)	B(7)—C(2)—C(14)	116.9(2)
O(2)—P—O(4)	97.5(1)	B(11)—C(2)—C(14)	119.8(2)
O(3)—P—O(4)	108.0(1)	O(2)—C(13)—C(1)	113.1(2)
P—O(2)—C(13)	118.7(1)	O(3)—C(14)—C(2)	112.9(2)
P—O(3)—C(14)	120.2(1)	O(4)—C(15)—C(16)	108.7(2)
P—O(4)—C(15)	121.2(2)	F(1)—C(16)—F(2)	106.7(2)
C(2)—C(1)—C(13)	121.9(2)	F(1)—C(16)—F(3)	108.3(2)
B(3)—C(1)—C(13)	119.3(2)	F(2)—C(16)—F(3)	106.3(2)
B(4)—C(1)—C(13)	118.9(2)	F(1)—C(16)—C(15)	112.2(2)
B(5)—C(1)—C(13)	117.0(2)	F(2)—C(16)—C(15)	111.8(2)
B(6)—C(1)—C(13)	117.0(2)	F(3)—C(16)—C(15)	111.2(2)

The C(1), C(2), C(13), and C(14) atoms involved in the C_4O_2P seven-membered heterocycle are coplanar within 0.02 Å; the O(2) and O(3) atoms are displaced from this plane toward opposite sides by 0.569 and 0.867 Å, respectively, whereas the P atom deviates by 0.359 Å (see Fig. 1, *b* and Table 3). The remaining geometric parameters for structure **16** are as expected.

For example, the P=O(1) [1.451(2) Å], P—O(2—4) [aver. 1.573(2) Å], C(13)—O(2) [1.437(3) Å], and C(14)—O(3) [1.431(3) Å] bond lengths are close to those for $O(CH_2)_4OP(O)OH$ tetramethylenephosphoric acid [P=O, 1.471 Å; P—O (aver.), 1.544 Å; and

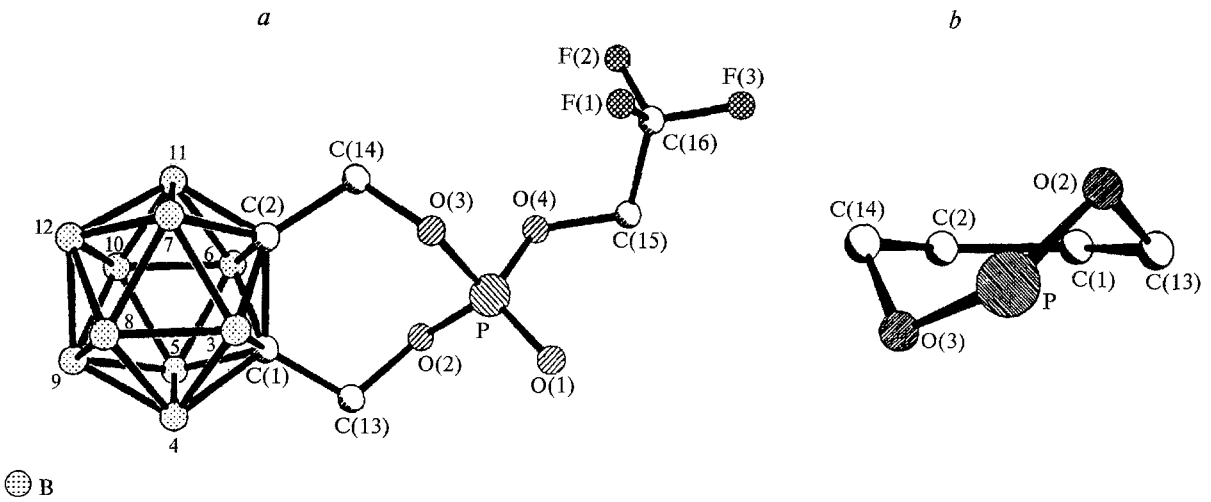


Fig. 1. The structure of the molecule of phosphate **16** (*a*) and the projection of the seven-membered cycle along the C(1)C(2)C(13)C(14) plane (*b*).

C—O (aver.), 1.465 Å].[9] The exopolyhedral C(1)—C(13) [1.521(3) Å] and C(2)—C(14) [1.523(3) Å] bond lengths correspond to the average C—C_{exo} bond length for other carborane structures of different types.[10]

Table 3. Torsion angles (τ) in the seven-membered C_4O_2P heterocycle in phosphate **16**

Angle	τ/deg
O(3)—P—O(2)—C(13)	−62.4
P—O(2)—C(13)—C(1)	89.5
O(2)—C(13)—C(1)—C(2)	−28.9
C(13)—C(1)—C(2)—C(14)	4.5
C(1)—C(2)—C(14)—O(3)	−44.8
C(2)—C(14)—O(3)—P	88.4
C(14)—O(3)—P—O(2)	−37.7

Experimental

The NMR spectra were recorded on a Bruker WP-200SY instrument in $CDCl_3$.

Phosphorylation of *o*-carboranylmethanol (1) and 1,2-bis(hydroxymethyl)-*o*-carborane (12) (general procedure). A mixture of 0.01 mol of alcohol **1** or diol **12**, the corresponding chlorophosphate, and 0.25 mmol of Mg was heated until the evolution of HCl stopped. Compounds **3**, **6**, **10**, **14**, and **15** were obtained by distillation *in vacuo*. Phosphates **4**, **7**, **11**, and **16** were isolated by crystallization. The reaction conditions are given in Table 5; the constants and the results of elemental analysis of phosphates **3**, **4**, **6**, **7**, **10**, **11**, and **14**—**16** are presented in Table 6. The parameters of the NMR spectra of phosphates **3**, **4**, **6**, **7**, **10**, **11**, **14**, and **15** are given in Table 7.

2-Oxo-2-(2,2,2-trifluoroethoxy)-*o*-carborano[1,2-*e*]-1,3,2-dioxaphosphepane (16). ^{1}H NMR, δ: 4.46 (dq, 2 H, CH_2CF_3,

Table 4. Atomic coordinates (×10^4) and equivalent isotropic temperature factors (U_{eq}) in phosphate **16**

Atom	*x*	*y*	*z*	U_{eq}/Å^2
P	6907(1)	2263(1)	4943(1)	24(1)
O(1)	8072(1)	2484(1)	4789(1)	37(1)
O(2)	6501(1)	1007(1)	5045(1)	26(1)
O(3)	6596(1)	2892(1)	5528(1)	26(1)
O(4)	6010(1)	2600(1)	4468(1)	32(1)
F(1)	6225(2)	4877(1)	4600(1)	60(1)
F(2)	4765(1)	4508(2)	4098(1)	59(1)
F(3)	6206(2)	5180(1)	3672(1)	49(1)
C(1)	6402(2)	487(2)	6090(1)	22(1)
C(2)	5709(2)	1652(2)	6262(1)	21(1)
B(3)	4954(2)	420(2)	6108(1)	26(1)
B(4)	5789(2)	−685(2)	6400(1)	30(1)
B(5)	7039(2)	−77(2)	6688(1)	27(1)
B(6)	6985(2)	1420(2)	6595(1)	24(1)
B(7)	4578(2)	1340(2)	6691(1)	20(1)
B(8)	4629(2)	−152(2)	6797(1)	33(1)
B(9)	5919(2)	−475(2)	7165(1)	34(1)
B(10)	6655(2)	826(2)	7282(1)	30(1)
B(11)	5822(2)	1938(2)	6994(1)	28(1)
B(12)	5157(2)	784(3)	7345(1)	34(1)
C(13)	7009(2)	359(2)	5507(1)	28(1)
C(14)	5573(2)	2623(2)	5828(1)	26(1)
C(15)	6304(2)	3300(2)	3981(1)	33(1)
C(16)	5879(2)	4470(2)	4091(1)	30(1)
H(3)	4608(20)	420(21)	5697(10)	35(6)
H(4)	5839(19)	−1425(21)	6153(10)	34(6)
H(5)	7817(19)	−474(20)	6596(10)	29(6)
H(6)	7653(19)	1884(20)	6439(9)	28(6)
H(7)	3839(19)	1917(19)	6608(9)	28(6)
H(8)	3860(23)	−617(22)	6902(10)	46(7)
H(9)	6007(22)	−1132(23)	7482(11)	45(7)
H(10)	7213(21)	1005(21)	7658(10)	41(7)
H(11)	5827(18)	2833(20)	7084(10)	30(6)
H(12)	4722(21)	970(21)	7761(10)	43(7)
H(13)	6925(18)	−416(21)	5374(10)	30(6)
H(13')	7812(20)	588(21)	5556(10)	32(6)
H(14)	5433(21)	3329(23)	6043(10)	40(7)
H(14')	4971(19)	2441(20)	5525(10)	30(6)
H(15)	5976(20)	2989(23)	3654(12)	40(7)
H(15')	7077(25)	3417(24)	3947(12)	53(9)

Table 5. Conditions of catalytic phosphorylation of *o*-carboranylmethanol (**1**) and 1,2-bis(hydroxymethyl)-*o*-carborane (**12**) with chlorophosphates

Alcohol	Chloro-phosphate	Alcohol : chloro-phosphate (mol/mol)	Reaction temperature/°C	Reaction time/h	Product	Yield (%)
1	**2**	1 : 3	120	0.5	**3**	60.8
	2	3 : 1	160—200	5.0	**4**	97.2
	5	1 : 2	140	1.5	**6**	67.7
	5	2 : 1	160—200	5.0	**7**	68.7
	8	1 : 1.1	160	3.0	**10**	57.3
	9	1 : 1.1	200	0.5	**11**	93.5
12	**8**	1 : 2.2	160	2.5	**14**	52.0
	13	1 : 2.2	160	2.0	**15**	51.8
	5	1 : 1.1	160	2.0	**16**	69.0

Note. Mg (2.5 mol. %) was used as the catalyst.

Table 6. Constants and results of elemental analysis of *o*-carborane-containing phosphates **3**, **4**, **6**, **7**, **10**, **11**, and **14—16**

Compound	B.p./°C (*p*/Torr)	M.p./°C (solvent), [n_D^{20}]	Found / Calculated (%)						Molecular formula
			C	H	B	Cl	F	P	
3	167—170 (1)	67—70	12.9 12.4	4.7 4.5	37.4 37.1	23.5 24.3	—	10.2 10.4	$C_3H_{13}B_{10}Cl_2O_2P$
4	—	246—247 (hexane)*	—	—	57.1 57.2	—	—	—	$C_9H_{39}B_{30}O_4P$
6	165—167 (1)	[1.4940]	17.1 16.9	4.3 4.3	30.6 30.5	9.6 10.0	16.4 16.0	8.7 8.7	$C_5H_{15}B_{10}ClF_3O_3P$
7	—	61.5—63.5 (hexane)	19.8 19.5	5.6 5.6	—	—	11.4 11.6	—	$C_8H_{28}B_{20}F_3O_4P$
10	145—149 (1)	[1.4439]	20.2 20.1	4.1 4.1	26.0 25.9	—	26.4 27.2	7.2 7.4	$C_7H_{17}B_{10}F_6O_4P$
11	270—275 (1)	77—78 (hexane)	44.5 44.3	5.8 5.7	26.8 26.6	—	—	7.7 7.6	$C_{15}H_{23}B_{10}O_4P$
14	195—197 (1)	[1.4288]	20.5 20.8	3.3 3.2	15.7 15.6	—	32.5 32.9	9.0 9.0	$C_{12}H_{22}B_{10}F_{12}O_8P_2$
15	207—210 (1)	[1.3710]	22.2 22.3	1.7 1.7	7.8 8.3	—	52.8 52.9	4.8 4.8	$C_{24}H_{22}B_{10}F_{36}O_8P_2$
16	—	76—77 (hexane—ether)	20.4 20.7	4.7 4.6	31.1 31.1	—	15.8 16.4	9.4 8.9	$C_6H_{16}B_{10}F_3O_4P$

* *Cf.* Ref. 1: m.p. 255—257 °C (CCl_4).

Table 7. Parameters of NMR spectra for carborane-containing phosphates **3**, **4**, **6**, **7**, **10**, **11**, **14**, and **15**

Compound	^{1}H NMR							^{31}P {^{1}H} NMR, δ (s)
	CH, δ	$POCH_2C_nF_{2n+1}$ δ	$J_{H,P}$/Hz	$J_{H,F}$/Hz	CH_2OP δ (d)	$J_{H,P}$/Hz	C_6H_5, δ	
3	3.86 (br.s)	—	—	—	4.67	9.7	—	8.08
4	3.77 (br.s)	—	—	—	4.45	7.5	—	−4.42
6	3.86 (br.s)	*	*	*	4.59	8.5	—	4.60
7	3.81 (br.s)	4.40 (dq)	8.1	8.1	4.47	7.3	—	−3.81
10	3.85 (br.s)	4.41 (dq)	8.2	8.2	4.48	7.2	—	−3.32
11	3.80 (br.s)	—	—	—	4.47	5.8	6.36—6.75 m	−13.16
14	—	4.41 (dq)	8.1	8.1	4.63	6.8	—	−3.54
15	—	4.54 (dt)	8.7	13.1	4.65	7.0	—	−3.34

* For $POCH(A)H(B)CF_3$: δH(A) 4.51, δH(B) 4.47, $J_{H(A),H(B)}$ = 12.4 Hz, $J_{H(A),F}$ = 7.7 Hz, $J_{H(B),F}$ = 7.7 Hz, $J_{H(A),P}$ = 10.0 Hz, and $J_{H(B),P}$ = 10.0 Hz.

$J_{H,F}$ = 7.9 Hz, $J_{H,P}$ = 9.6 Hz); 4.60 (dd, 2 H, CH(A)C<u>H</u>(B)OP, $J_{H(A),H(B)}$ = 13.3 Hz, $J_{H(B),P}$ = 18.0 Hz); 4.71 (dd, 2 H, C<u>H</u>(A)CH(B)OP, $J_{H(A),P}$ = 17.9 Hz). ^{31}P NMR {^1H}, δ: 0.92 (s).

Crystals of phosphate **16** are orthorhombic, at −120 °C a = 11.880(6) Å, b = 11.790(6) Å, c = 22.841(10) Å, V = 3199(3) Å^3, d_{calc} = 1.446 g cm^{-3}, Z = 8. $C_6H_{16}B_{10}O_4F_3P$. The space group is *Pbca*.

The unit-cell parameters and intensities of 2741 independent reflections with $F^2 \geq 4\sigma$ were measured on a four-circle automated Syntex $P2_1$ diffractometer (−120 °C, Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, $\theta \leq 28°$).

The structure was solved by the direct method and refined by the full-matrix least-squares method first isotropically and then anisotropically. All H atoms were located from the difference Fourier synthesis, and were included in the refinement with isotropic thermal parameters. The final R factor was 0.0394; the weighted R_w factor was 0.0532. All calculations were carried out on an IBM PC/AT computer using the SHELXTL-PC program package.

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