CONCLUSIONS

A simple method has been proposed for the preparation of 1-amino-o-, 1-amino-m, and 1,7-bis(amino)-m-carboranes by the hydrogenation of readily available 1-benzeneazo-o-carborane, 1-benzeneazo-m-carborane, and 1,7-bis(benzeneazo)-m-carborane over Raney nickel.

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SYNTHESIS OF S-(CARBORAN-1-YL)THIOPHOSPHATES AND S-(CARBORAN-1-YL)-THIOPHOSPHONATES

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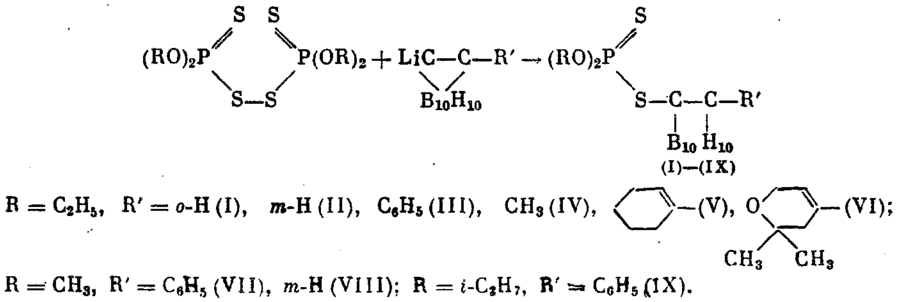
We have proposed methods for the synthesis of carboranyl esters of pentavalent phosphorus acids from phosphorus-containing propargyl esters and decaborane [1] and from the corresponding halo derivatives of pentavalent phosphorus acids and 9-mercaptocarborane [2]. In the present work, we studied the reaction of lithium carboranes with bis(thiophosphoryl)disulfides and lithium mercaptocarboranes with O-ethylmethylchlorophosphonate and thiophosphonate or O,O-diethyl-S-(β-bromoethyl)thiophosphate and the corresponding methyl thiophosphate.

The reaction of bis(dialkoxythiophosphoryl)disulfides with 1-lithium-2-substituted o-carborane in ether—benzene (in benzene for unsubstituted o- or m-lithiumcarboranes) gave the corresponding S-carboranyldithiophosphates.



We should note that, in contrast to o-carborane, disproportionation is not found for the monolithium derivative of m-carborane with the formation of a dilithiumcarborane [3]. Thus, the reaction of equimolar amounts of the starting reagents in ether—benzene unexpectedly gave 1,2-bis(thiophosphorylmercapto)-m-carboranes (X) and (XI). In addition to (XI), the ethoxy derivative gave the corresponding trithiopyrophosphate (mp 42-44°C, δP^{31} 78.8 ppm) [4]. The formation of a similar product was confirmed spectroscopically for the methoxy derivative (δP^{31} 83.5 ppm) [4].

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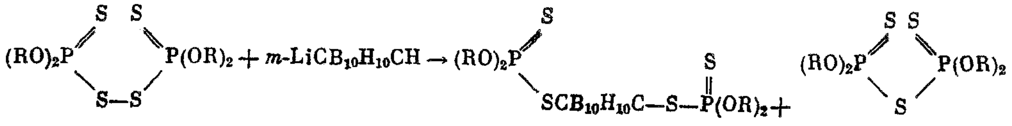
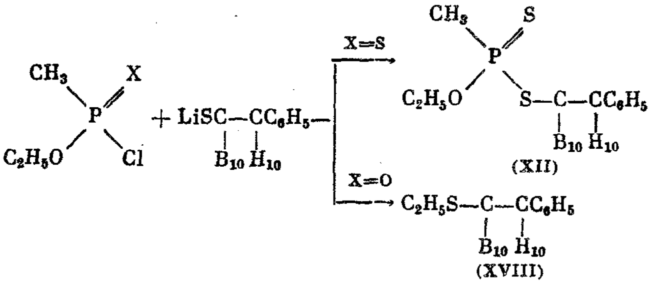
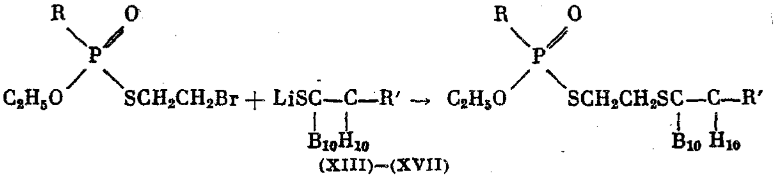


R = CH_3 (X), C_2H_5 (XI).

The reaction of O-ethylmethylchlorothiophosphonate with 1-lithiummercapto-2-phenyl-o-carborane gave O-ethyl-S-(2-phenylcarboranyl)methyldithiophosphonate (XII). When sulfur in the starting chlorophosphonate is substituted by oxygen, the analogous reaction gave only alkylation product (XVIII). It was not possible to detect O-ethyl-S-(2-phenylcarboranyl)-methylthiophosphonate.



The reaction of S-(β-bromoethyl)-containing esters of thiophosphonic and thiophosphoric acids with derivatives of 1-lithiummercapto-o-carborane gave O-ethyl-S-(β-carboran-1-ylmercaptoethyl)methylthiophosphonates and O,O-diethyl-S-(β-carboran-1-ylmercaptoethyl)thiophosphates.



R = CH_3, R′ = C_6H_5 (XIII), CH_3 (XIV); R = OC_2H_5, R′ = C_6H_5 (XV), CH_3 (XVI), *m*-H (XVII).

Products (XII)-(XVII) are thick oils, which were purified by column chromatography.

EXPERIMENTAL

The previously undescribed starting o-carboranes were synthesized according to Grimes [3] from the corresponding acetylenes and decaborane in the presence of dimethylaniline.

1-Cyclohexenyl-o-carborane was obtained in 72.3% yield, mp 66-68°C (from hexane). Found, %: C 43.09, H 8.93, B 47.90. $C_8H_{20}B_{10}$. Calculated, %: C 42.48, H 8.98, B 48.20.

6,6-Dimethyl-5,6-dihydro-2H-pyran-4-yl-o-carborane was obtained in 81% yield, mp 61-62°C (from hexane). Found, %: C 42.47, H 8.65, B 42.50. $C_9H_{22}B_{10}O$. Calculated, %: C 42.48, H 8.71, B 42.52.

S-Carboran-1-yldithiophosphates (I)-(IX). A solution of BuLi in benzene was added dropwise to a solution of 10 mmoles carborane in 20 ml abs. ether and stirred for 1 h at 20°C. A solution of 10 mmoles bis(dialkoxythiophosphoryl)disulfide in 15 ml abs. ether was added dropwise to the reaction mixture at 0°C. The mixture was warmed to room temperature, stirred for 2-4 h, maintained overnight, treated with water, and dried over Na_2SO_4. Crystallization from hexane or distillation gave (I)-(IX). Thiophosphates (I) and (II) were obtained in benzene.

Reaction of 1-Lithiummercapto-2-phenyl-o-carborane with O-ethylmethylchlorophosphonate and O-ethylmethylchlorothiophosphonate. A sample of 10 mmoles powdered sulfur was added to a solution of 10 mmoles 1-lithium-2-phenyl-o-carborane obtained from phenylcarborane and

TABLE 1. Carboranyl Esters of Pentavalent Phosphorus Acids

Compound	Yield, %	n_D^{20}	Mp, °C, bp, °C (p, mm Hg)	Found, %			Chemical formula	Calculated, %		
				B	C/H	P		B	C/H	P
(I)	50	—	160–162	32,85	—	9,37	$C_6H_{21}B_{10}O_2PS_2$	32,95	—	9,45
(II)	68	—	31–33	32,90	—	9,47	$C_6H_{21}B_{10}O_2PS_2$	32,95	—	9,45
(III)	73	—	95–97	—	$\frac{35,65}{6,22}$	7,97	$C_{12}H_{25}B_{10}O_2PS_2$	—	$\frac{35,62}{6,23}$	7,65
(IV)	71	1,5719	158–160 (1)	31,16	—	8,81	$C_7H_{23}B_{10}O_2PS_2$	31,59	—	9,04
(V)	72	—	76–77	26,26	—	7,88	$C_{12}H_{29}B_{10}O_2PS_2$	26,47	—	7,58
(VI)	74	—	88–90	24,29	—	7,07	$C_{11}H_{27}B_{10}O_3PS_2$	24,67	—	7,06
(VII)	68	—	106–109	—	$\frac{32,03}{5,58}$	8,21	$C_{10}H_{21}B_{10}O_2PS_2$	—	$\frac{31,91}{5,58}$	8,24
(VIII)	65	—	58–60	36,08	—	10,09	$C_4H_{17}B_{10}O_2PS_2$	36,00	—	10,33
(IX)	72	—	98–100	25,03	—	7,11	$C_{14}H_{33}B_{10}O_2PS_2$	26,00	—	7,17
(X)	35	—	79–83	23,96	—	13,49	$C_6H_{22}B_{10}O_4P_2S_4$	23,65	—	13,59
(XI)	34	1,5836	—	21,10	—	11,98	$C_{10}H_{30}B_{10}O_4P_2S_4$	21,09	—	12,10
(XII)	72	—	106–108	—	$\frac{35,35}{6,21}$	7,90	$C_{11}H_{23}B_{10}OPS_2$	—	$\frac{35,28}{6,19}$	8,27
(XIII)	68	1,6049	—	25,76	$\frac{37,05}{6,43}$	—	$C_{12}H_{27}B_{10}O_2PS_2$	26,15	$\frac{37,32}{6,45}$	—
(XIV)	67	1,5706	—	30,57	—	—	$C_8H_{25}B_{10}O_2PS_2$	30,34	—	—
(XV)	65	1,5841	—	—	$\frac{36,91}{6,30}$	6,93	$C_{14}H_{29}B_{10}O_3PS_2$	—	$\frac{37,48}{6,45}$	6,92
(XVI)	67	1,5531	—	—	$\frac{27,59}{7,10}$	8,08	$C_9H_{27}B_{10}O_3PS_2$	—	$\frac{27,97}{6,99}$	8,03
(XVII)	70	1,5581	—	28,58	—	8,06	$C_8H_{25}B_{10}O_3PS_2$	29,03	—	8,33

butyllithium in benzene—ether and stirred for 2 h at 20°C. A corresponding acid chloride in abs. ether was added to the suspension formed and heated at reflux for 1-2 h. The mixture was treated with water and dried over Na_2SO_4 to give (XII) or (XVIII).

1-Phenyl-2-ethylmercapto-o-carborane (XVIII) was obtained in 28% yield, mp 220-222°C. Found, %: B 38.23. $C_{10}H_{20}B_{10}S$. Calculated, %: B 38.57.

S-(β-Carboran-1-ylmercaptoethyl)phosphonates and S-(β-carboran-1-ylmercaptoethyl)phosphates (XIII)-(XVII). Analogously, the reaction of 10 mmoles lithiummercapto-o-carboranes and 10 mmoles S-(β-bromoethyl)thiophosphonate or S-(β-bromoethyl)thiophosphate in benzene—ether and subsequent purification by column chromatography on silica gel L 40/100 with elution by 8:4:1 hexane—benzene—acetone to give (XIII)-(XVII). The physical indices for (I)-(XVII) are given in Table 1.

CONCLUSIONS

New S-(carboran-1-yl)thiophosphates and S(carboran-1-yl)thiophosphonates were obtained by the reaction of derivatives of lithiumcarboranes with bis(dialkoxythiophosphoryl)disulfides or halo derivatives of pentavalent phosphorus.

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REACTION OF SULFUR PENTAFLUORIDE CHLORIDE WITH ACRYLIC ACID DERIVATIVES

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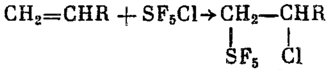
547.391.1'261

The addition of sulfur pentafluoride chloride at the C=C double bond is a convenient method for the introduction of pentafluorothio group into organic molecules. This was shown for many unsaturated and polyhaloolefins [1]. On the other hand, the reaction with olefins containing functional substituents has virtually not been studied.

We have established that sulfur pentafluoride chloride smoothly adds upon moderate heating to methyl acrylate to form methyl 1-chloro-2-pentafluorothiopropionate as the major product. Under analogous conditions, acrylonitrile gives largely solid, unidentified polymerization products, while the expected 1-chloro-2-pentafluorothiopropionitrile was isolated in small amounts:



$$CH_2{=}CHR + SF_5Cl \rightarrow \underset{SF_5}{CH_2}{-}\underset{Cl}{CHR}$$

(Ia, b) (IIa, b)

R = COOMe (Ia), (IIa), CN (Ib), (IIb).

Products (IIa) and (IIb) are colorless, mobile liquids, whose structures were confirmed by NMR and IR spectroscopy.

EXPERIMENTAL

A mixture of 4 g (0.033 mole) (Ia) and 5.5 g (0.033 mole) sulfur pentafluoride chloride in freon-113 was heated in a hermetically sealed metal test tube for 20 h at 120°C with pe-

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