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o-CARBORANYL-CONTAINING ESTERS OF

PENTAVALENT PHOSPHORUS ACIDS*

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Pentavalent phosphorus compounds, in which the P atom is attached to the C atom of the carborane molecule, were synthesized previously [2, 3]. However, up to our investigation [1], esters of pentavalent P acids with a carboranyl group in the ester portion of the molecule were unknown.

We developed methods for the synthesis of the carboranyl esters of phosphinic, phosphonic, and phosphoric acids from the corresponding acetylenic esters, decaborane, and dimethylaniline.

The S-o-carboranylmethyl esters of pentavalent P acids were synthesized as follows. First the reaction of salts of the pentavalent P acids with propargyl chloride in absolute alcohol at $\sim 20^{\circ}$ C gave the corresponding S-propargyl esters, which were then reacted with decaborane in the presence of dimethylaniline.



Compound Id was obtained from crude S-propargyl diphenyldithiophosphinate, which was not isolated analytically pure.

To obtain the O-(o-carboranylmethyl) derivatives we synthesized the corresponding propargyl esters from either the O-thiyl methylchlorophosphonates or O-ethyl methylchlorothiophosphonates and propargyl alcohol in the presence of triethylamine. These esters were converted to the carboranyl-containing compounds by treatment with decaborane.

* See [1] for preliminary communication.

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Similarly, the reaction of 2 moles of propargyl alcohol and triethylamine with the phenyl and methyl dichlorophosphonates or methyl dichlorothiophosphonate gave the bis)propargyl) esters, which when treated with decarborane and dimethylaniline give either O,O-bis(o-carboranylmethyl) phosphonates or O,O-bis(o-carboranylmethyl) thiophosphonates.

The reaction of phosphorus oxychloride with propargyl alcohol leads to tripropargyl phosphate. Tris(ocarboranylmethyl) phosphate was synthesized by reacting the latter with 3 moles of decaborane in the presence of dimethylaniline.

$$Cl_{3}P=O + 3HOCH_{2}C \equiv CH \xrightarrow{3Bt_{3}N} (HC \equiv CCH_{2}O)_{3}P=O \xrightarrow{3Bt_{1}H_{14}} (HC - CCH_{2}O)_{8}P=O$$

$$(V) \qquad (V1)$$

The IR spectra of all of the synthesized phosphates and phosphonates have the characteristic bands of the P = O group in the 1220-1240 cm⁻¹ region. The spectra of the carboranyl-containing esters of pentavalent P contain a broad band in the 2590-2600 cm⁻¹ region (BH). Intense bands of 3230 and 3330 cm⁻¹ are characteristic for acetylenic derivatives (Ia, b, c), (IIIa, c), and (V), which bands are caused by the formation of a hydrogen bond of type $C \equiv C - H$... O = P and π -complexes $C \equiv C - H$ [4]. However, in the spectra of acetylenic com-

$$H - C \equiv C$$

pounds (Ic, d) and (IIIb), which contain the P=S group, only one broad asymmetric band at 3300 cm⁻¹ was detected in the absorption region of the HC \equiv group, which corresponds to the inability of thiono sulfur to form a hydrogen bond.

EXPERIMENTAL

<u>S-Propargyl Esters of Phosphorus Thioacids (Ia-c)</u>. With stirring, to a solution of 0.07 mole of either the Na or K salt of the appropriate pentavalent P acid in EtOH was added 0.07 mole of propargyl chloride and the mixture was stirred for 3-5 h, refluxed for 30 min, let stand overnight, the obtained precipitate was filtered, and the solvent was distilled off. The residue was treated with 15 ml of water, extracted with ether, and the combined extracts were dried over Na₂SO₄. After removal of the ether the residue was vacuum-distilled. Compounds (Ia-c) were obtained. Their constants are given in Table 1.

O-Propargyl Phosphonates (Id-e). A mixture of 0.1 mole of propargyl alcohol and 0.1 mole of Et_3N in 30 ml of ether was added in drops to a solution of 0.1 mole of either O-ethyl methylchlorophosphonate or O-ethyl methylchlorothiophosphonate and the mixture was stirred for 1 h at ~ 20°C, refluxed for 30 min, and let stand overnight. The obtained Et_3N ·HCl was filtered, the ether was removed, and the residue was vacuum-distilled. Compounds (Id-e) were obtained. Their constants are given in Table 1.

O,O-Bis(propargyl) Phosphonates (IIIa-c). Similarly, (IIIa-c) were synthesized from 0.05 mole of the appropriate dichlorophosphonate, 0.1 mole of propargyl alcohol, and 0.1 mole of Et_3N in abs. ether. Their constants are given in Table 1.

	%	Ч	(7,38	2,89	1	8,99	7,38	17,99	16,46	11					%	а	36,49	30,18	Т	26,61	38,59	36,49	50,95	52,95	45,97	57,17
Propargyl Esters of Pentavalent Phosphorus Acids $\frac{R}{R} \rightarrow \frac{X}{P-YCH_{i}C=CH}$	ited,			£5	84	<u>41</u>			22					culated	н	7,14	6, 46	6,77	1	7,54	7,14	1	7,15	6,64	1	
	calcula	н 	45 6,5	99 5,	49 2,	18 7,		•	17 4,						Calc	с	24,31	36,84	24,54	t	25,70	24,31	1	20,57	30,62	1
	<u> </u>	0	40,4	54,9	37,	44,	-	1	44,1	1 1						20	S	\mathbf{S}_{2}	61		s	S	0.	0.		
	Empirical formula		C ₆ H ₁₁ O ₂ PS	C11H13O2PS	$C_7H_{13}O_2PS_2$	C ₆ H ₁₁ O ₃ P	C ₆ H ₁₁ O ₂ PS	$C_7H_9O_3P$	C ₇ H ₉ O ₂ PS						Empirical	formula	$\mathrm{C_6H_{21}B_{10}O_2P}$	$C_{14}H_{23}B_{10}O_2$	$C_7H_{23}B_{10}O_2P$	$C_{45}H_{23}B_{10}PS$	$\mathrm{C_6H_{21}B_{10}O_3P}$	$\mathrm{C_6II}_{21}\mathrm{B_{10}O_2P}$	$\mathrm{C_7H_{29}B_{20}O_2P}$	$C_7H_{29}B_{20}O_3$]	C ₁₂ H ₃₁ B ₂₀ O ₃]	C9H39B30O3I
	Found 7/0	Ч	17,44	12,90	I	18,54	17, 36	17,99	16,44	1 1			. %		Ē	36,23	30,08	1	26,47	38,36	36,60	50,95	52,45	45,85	56,75	
		н	,17	,34	,37	,15	1		,10				— CH	-CH	Found,	н	7,17	6,40	7,21	I	7,56	7,35	1	7,20	6,90	1 .
		a),54 6	t,72 5	,83 5	,37 7		. <u> </u>	,73 5	1 1			YCH ₂ C	́ щ		U U	24,26	36, 43	25,20	I	25,91	24,11	I	20,70	30,62	1
	n ²⁰		1,5018 40	1,5631 54	1,5249 37	1,4418 44	1,4890	1,4662	1,5100 44	1,5314 1,4717			$\operatorname{cids} \frac{R}{2} \operatorname{P}^{-}$	$\operatorname{cids} \frac{R}{R'} \stackrel{h}{\searrow} \stackrel{h}{\longrightarrow}$	1 1	Ap, ^c C	-84 (EtOH)	-62 (EtOH)	I	-89 (hexane)	-58(hexane)	-54 (hexane))-161 (hexane)	2-124 her-hexane)	5-127 etone- nexane)	5–257 (CCl₄)
	Mp,°C p, mm Hg)		87-90 (1)	124 - 126 (1)	1 (1)	(2)	(2)	(1)	(E)	4 (2) 3 (1)			sphorus A		.p		82-	61-		87-	56-	52	16((et)		
					99 - 10	68 20 70	68 - 70	93	7981	142 - 14 116 - 11					Yiel	' ₃ e	61			~; 	6	8	22			
	Y Yield,		69	60	17	63	50	71	50	50 50			t Pho	t Pho		×		S	ŝ	S	0	•	0	0	0	0
			 თ	s	s	0	0		 0 (•		Pentavalent		×	0	0	S	S	<u> </u>	S		0	0	•	
	×		•	0	s	0	s S	0	or o		28.59%			ters of Pentav		R'	OEt	OEt	OEt	Ъћ	OEt	OEt	0CH2CCCCH	OCH,CCCH	0CH ₁ C B ₁₀ H ₁₀	$= CH$ OCH ₃ C $= D_{10}H_{10}$
	R							H2=CH	H ₂ C=CH	H2C=CH	lated: S		sters of													
			OEt	OEt	OE	OEt	OEt	OCI	0CF		alcul		Propargyl Es													
			Me	\mathbf{Ph}	OEt	Me	Me	Me	Me	Ph OCH₂C≞CH	<u>-</u> 28.61. C				μ.	щ	Me	\mathbf{Ph}	OEt	\mathbf{Ph}	Me	Me	Me	Me	Рћ	OCH_C
TABLE 1.		Compound		(I I)	(Ic)*	(Id)	(I e)	(IIIa)	(dIII)	(IIIc)† (V) ⁺	* Found: S		TABLE 2.			nimoduro	(IIa)	(IIb)	(IIc)*	(11d)†	(IIe)	(III)	(IVa)	(q AI)	(IVc)	‡(IV)

* n_D^{20} 1.5657. Found: P 9.34%. Calculated P 9.34%. † The yield is based on the starting sodium diphenyl-dithiophosphinate. ‡ Cf. [6].

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Carboranyl Phosphates, Phosphonates, and Phosphinates (IIa-f), (IVa-c), and (VI). a) A mixture of 0.02 mole of propargyl derivative (I), 0.02 mole of decaborane, and 0.04 mole of dimethylaniline in 50 ml of toluene was heated until the hydrogen evolution ceased, cooled, and treated with dilute HCl solution. The toluene was removed and 30 ml of EtOH was added to the residue. The mixture was refluxed until the hydrogen evolution ceased. After removal of the alcohol the residue was either recrystallized or passed through an SiO_2 column, using a 2:1 hexane-acetone mixture as the eluent. Compounds (IIa-f) were obtained.

b) Similarly, from decaborane, dimethylaniline, and either (IIIa-c) (mole ratio 2:4:1) or tripropargyl phosphate (V) (3:6:1) were synthesized either (IVa-c) or (VI).

The constants of (IIa-f), (IVa-c), and (VI) are given in Table 2.

CONCLUSIONS

Some new carboranyl esters of pentavalent phosphorus acids were synthesized from the appropriate propargyl esters and decaborane.

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TELOMERIZATION OF TRIMETHYLVINYLSILANE

WITH METHYL PROPIONATE

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The telomerization of vinylsilanes by oxygen-containing telogens has not been described. The addition of butyraldehyde and benzaldehyde to trimethylvinylsilane (TVS) to give adducts is known [1, 2]. The addition of ethyl bromoacetate at the C-Br bond to TVS in the presence of benzoyl peroxide [3], and of methyl trichloroacetate to methyldichlorovinylsilane, initiated by ruthenium complexes [4], has been described. An attempt to effect the radical addition of ethyl bromoacetate and acetoacetic ester to phenyldichlorovinylsilane proved unsuccessful [5], which is explained by the effect of electron-acceptor substituents on the silicon atom on the reactivity of the double bond.

A study of the telomerization of vinylsilanes with carboxylic acids and their derivatives is of interest from the standpoint of studying the reactivity of $R_3 Si\dot{C}$ = radicals in chain growth and transfer reactions, and as a method for the synthesis of organosilicon monomers that contain carbofunctional groups.

In the present paper we studied the telomerization of TVS with methyl propionate, initiated by tert-butyl peroxide (TBP), which leads to the formation of telomers of general formula $H[(CH_3)_3SiCHCH_2]_nCH(CH_3)CO_2CH_3$ (T_n) , with n = 1, 2. Telomer T, was isolated in the pure state and characterized (Table 1). The structure of T_1 was confirmed via the ¹³C NMR spectra based on the signals characteristic for the monomer and the telogen. Together with the ¹³COO and OCH₃ signals, the corresponding signals of the ¹³CH₃CH and ¹³CH groups [6] are present. The monomeric portion of the molecule is represented by the ¹³CH₃Si and ¹³CH₂Si (13.6 ppm) signals,

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