2. The reaction of 3-indolethiols with activated acetylenes occurs only on the sulfur atom. The reaction of 3-indolethiols with phenylacetylene takes place stereoselectively, giving the cis isomers, while the reaction with cyanoacetylenes mainly gives a mixture of Z- and E-isomers.

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SYNTHESIS OF 1-SUBSTITUTED 1-VINYLCYCLOALKANES BY ALLYLBORATION OF CARBONYL COMPOUNDS AND ETHOXYACETYLENE WITH DIORGANYLBORYLETHYLIDENECYCLOPENTANE AND A DIORGANYLBORYLETHYLIDENECYCLOHEXANE

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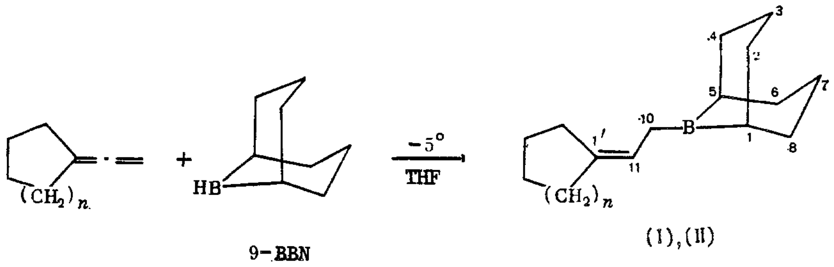
β,γ-Unsaturated (allylic) compounds of boron are useful, and in many instances the only means for the formation of new C—C bonds, and for the cyclization and functionalization of many types of compound [1, 2]. Allylboranes have been already been used with success in organic synthesis for more than two decades.

We here describe the synthesis of two representatives of hitherto unknown β,γ-unsaturated boron derivatives with an exocylic double bond, (I) and (II), and discuss some aspects of their use for the preparation of 1-substituted 1-vinylcyclopentanes and 1-vinylcyclohexanes. The results reported here have been discussed briefly in [3].

One method for the preparation of allylic boranes is by hydroboration of allenic hydrocarbons [1, 8]. This method has, however, many limitations. The reactions are frequently ambiguous, giving mixtures of vinyl and allyl boranes, which are the products of the addition of boron to either the central (C_{sp}) or one of the terminal atoms of the allene system (C_{sp^2}). Allylboranes are readily obtained only from 1,1-disubstituted allenes and $(R_2BH)_2$ [4, 5], the best hydroborating agent being 9-borabicyclo[3.3.1]nonane (9-BBN) [7, 8].

Hydroboration of 1,1-tetra- and 1,1-pentamethyleneallene with 9-BBN in tetrahydrofuran at −5°C has given the boron-containing ethylidenecyclopentane (I) and the ethylidenecyclohexane (II).



(I): $n = 1$, 76%; (II): $n = 2$, 83%,

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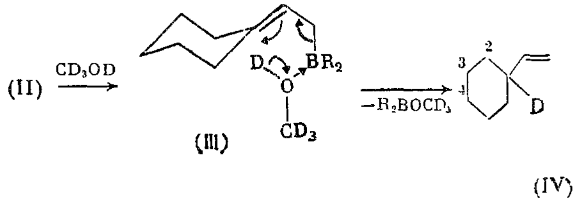
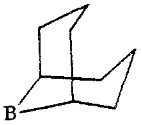
Compounds (I) and (II) are colorless mobile liquids which are monomeric, and stable in an inert atmosphere. In the ^{11}B NMR spectra, the chemical shifts relative to $Et_2O{\cdot}BF_3$ have values of 84.00 and 83.74 ppm, respectively. The IR spectra show weak absorption for the trisubstituted double bond (1665-1670 and 3040 cm^{-1}). PMR spectrum (δ, ppm, J, Hz): (I): 2.27 m ($B{-}CH_2$) and 5.43 t.q (C=CH, $^3J = 7.6$, $^4J = 2.2$), and (II): 2.22 d ($B{-}CH_2$, $^3J = 8.0$) and 5.25 t (C=CH, $^3J = 8.0$). The mean chemical shifts of the $CH_2{-}C{=}$ protons in the rings are 2.18 in (I) and 2.15 ppm in (II). Assignment of the signals in the ^{13}C NMR spectrum of (II) was made as in [9]. At low field, signals for the carbon atoms of the double bond are seen as a singlet at 139.7 for $C^{1'}$ and a doublet at 115.8 ppm for C^{11}; the signals for the carbons bonded to boron are broadened and have shifts of 33.7 (C^{10}) and 31.4 ppm (C^1 and C^5). In addition, the spectrum shows triplets at 33.3 (C^2, C^4, C^6, and C^8), 23.3 (C^3 and C^7), 27.2, 27.9, 28.8, and 29.0 ppm (carbon atoms of the cyclohexane ring).

As unique allylic derivatives of boron, compounds (I) and (II) show the high chemical reactivity characteristic of this type of compound. For example, they are cleaved by water and alcohols to vinylcyclopentane and vinylcyclohexane respectively. Reaction of (II) with deuteromethanol gives 1-vinyl-1-deuterocyclohexane (IV).

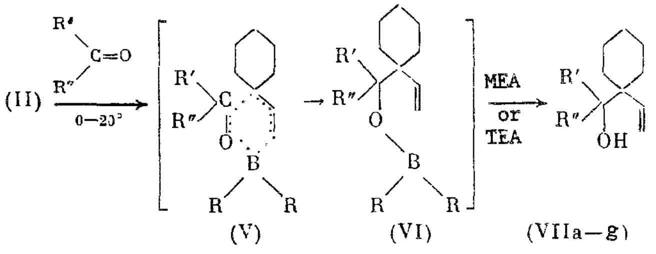


Here and subsequently BR_2=



It follows from these results that alcoholysis (and hydrolysis) proceeds with allylic rearrangement via the six-centered transition state (III). The structure of (IV) was confirmed by its IR, PMR, and ^{13}C NMR spectra. When obtained with complete proton decoupling, the ^{13}C NMR spectrum shows six signals (δ, ppm): 145.7 s (CH=), 112.3 s (CH_2=), 42.6 (C^1, triplet with components of equal intensity, $J_{C-D} = 15.1$ Hz), 33.6 s (C^2), 27.3 s (C^4), and 26.9 s (C^3). The J_{C-D} value provides direct proof of the location of the deuterium atom at position 1.

Like other β,γ-unsaturated boron compounds [1, 2], (I) and (II) add to carbonyl compounds. The reaction of (II) with aldehydes and ketones takes place at 0-20°C with spontaneous evolution of heat to give the esters (VI), transesterification of which with higher alcohols gives the carbinols (VII), which are vinylcyclohexane derivatives



R' = H, R'' = CH_3(a); R' = R'' = CH_3(b); R' + R'' = $(CH_2)_4$(c); R' + R'' = $(CH_2)_5$(d); R' = H, R'' = CH = $CHCH_3$(e); R' = CH_3, R'' = $CH_2CH_2CH{=}CH_2$(f); R' = CH_3, R'' = $CH{=}CH_2$(g).

The esters (VI) were not isolated in the pure state, but were immediately deborylated by treatment with monoethanolamine (MEA) or triethanolamine (TEA). The use of the latter is indicated when the carbinol has a relatively low boiling point; the alcohols (VIIa, b, e-g) were obtained in this way. The esters (VI) obtained from higher ketones were transesterified with MEA (1:1) in hydrocarbon solvents. The resulting intercomplex 9-(2-aminoethoxy)-9-BBN separated as a solid, the carbinol (VII) remaining in solution. After decanting the solution and washing the residue with the same solvent, the alcohol (VIIc, d) was isolated in 50-70% yield by vacuum distillation (Table 1).

TABLE 1. Properties of Compounds Obtained

Compound	Yield, %	Bp, °C (p, mm, Hg)	n_D^{20}	Found/Calculated, %		IR spectrum ν (C=C), cm^{-1}
				C	H	
(I)	76	117–118(1)	1,5173	82,93/83,33	11,59/11,58	1665
(II)	83	115–116(0,08)	1,5180	83.06/83,48	11,83/11.74	1645. 1670
(VIIa)	52	54–55(2)	1,4824	77,79/77.92	11.81/11.69	1642
(VII b)	71	53–55(2)	1.4872	78.11/78.57	11.93/11.91	1640
(VII c)	68	96–96,5(1)	1,5059	80.22/80.41	11.45/11.34	1635
(VII d)	50	100–101(1) *	–	80,74/80,77	11,53/11,54	1635
(VII e)	68	77–78(1)	1,4932	79,85/80,00	11.24/11.11	1635, 1675
(VIIf)	64	87–89(1)	1.4945	80.98/80.77	11.75/11.54	1640
(VIIg)	65	77–78(1)	1,4961	79.95/80.00	10.96/11,11	1642
(Xa)	65	45–47(1)	1.4780	77,51/77.92	11.67/11.69	1635
(Xb)	65	63–66(1)	1.4982	80.20/80.00	11.20/11.11	1640
(Xc)	50	78–79(6)	1.4829	79.48/79.52	10.99/10.84	1638
(XII)	55	105–106(2)	1,5206	81,81/82,05	11.23/11.11	1635
(XV)	67	62–63(6)	1,4640	79,58/79,52	10.95/10.84	1600, 1645
(XVIII)	73	85–87(9)	1,4719	79,74/80,00	11,16/11.11	1600, 1645

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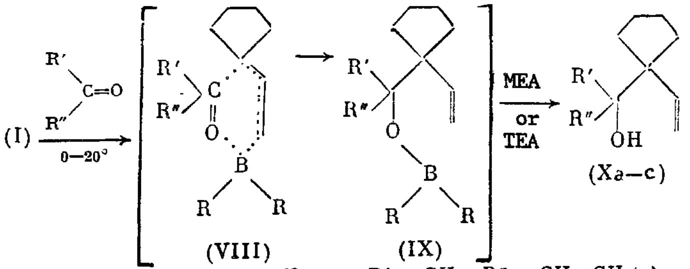
*Mp 47-49°C.

Similarly, from the borane (I) there were obtained three carbinols of the cyclopentane series (X).

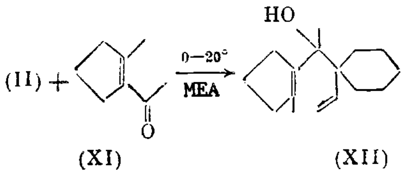


(X): R' = R" = CH_3(a); R' + R" = $(CH_2)_4$(b); R' = CH_3, R" = CH=CH_2(c)

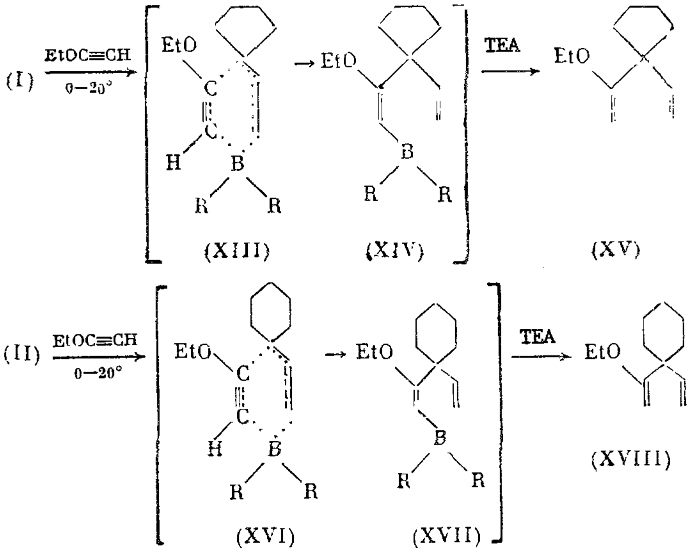
The formation of esters (VI) and (IX) with a vinyl group in the 1-position shows that the addition of the boranes (I) and (II) to the carbonyl group proceeds with allyl rearrangement via the six-membered transition state (V) or (VIII), and is evidently a concerted reaction (2π + 2π + 2σ).

As in the cases of other allyl(dialkyl)boranes [1, 2], the reaction of (I) and (II) with α,β-unsaturated carbonyl compounds (crotonaldehyde and methyl vinyl ketone) takes place at the $>C=O$ group only. In no case were 1,4-addition products found.

Both open-chain and cyclic unsaturated carbonyl compounds react in this way. For example, the ketone (XI) and borane (II) give the diene alcohol (XII).



We then used (I) and (II) to prepare 1,1-divinyl derivatives of cyclopentane (XV) and cyclohexane (XVIII). The key step in this two-stage reaction, carried out in the same flask, is the cis-allylboration of the alkoxyacetylene. The reaction of boranes (I) and (II) with ethoxyacetylene takes place at 0-20°C to give the adducts (XIV) and (XVII), with boryl and ethoxy groups having the trans orientation.



The adducts (XIV) and (XVII) were likewise not isolated, but their formation is shown by IR spectroscopy. The IR spectra of the products of the reaction of (I) and (II) with ethoxyacetylene show very strong absorption at 1590 cm^{-1} characteristic of the B—CH═C—O fragment. The B-C$_{sp}{}^2$ bond in (XIV) and (XVII) is strongly polarized [10], and is readily cleaved by alcohols. The products of protolytic deborylation are the dienes (XV) and (XVIII).

The structures of the carbinols (VII), (X), and (XII) and the dienes (XV) and (XVIII) were confirmed by their elemental analyses and by spectral methods (Tables 1 and 2). The IR spectra of all the compounds showed absorption for the terminal double bond in the regions 910-920, 1635-1645, and 3080-3085 cm^{-1}, and absorption for the OH group in (VII), (X), and (XII) at 3200-3600 cm^{-1}. The IR spectra of 1-vinyl-1-(1-ethoxyvinyl)cycloalkanes (XV) and (XVIII) also show very strong absorption at 1600 cm^{-1} (CH_2═COEt). The NMR spectra also confirm the structures of the carbinols and dienes. The spectral parameters are given in Table 2, from which it will be seen that the protons at the double bond have characteristic chemical shifts and coupling constants. The vinyl protons (CH═C) give signals at 5.6-6.1 ppm, and the termainal protons (CH_2═C) at 5.0-5.4 ppm, the signal for the proton in the cis position to the substituent being seen at lower field, as will readily be seen from the coupling constants, J_{trans} being in the range 15-20 Hz, and J_{cis} 10-12 Hz. The geminal coupling constants for these compounds are small (1.5-1.8 Hz). According to its PMR spectrum, the carbinol (VIIe) is the E-isomer.

EXPERIMENTAL

All operations with organoboron compounds were carried out under dry argon.

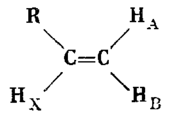
The ^{1}H NMR spectra were obtained on a Bruker WM-250 and ^{13}C and ^{11}B spectra on a Bruker AM-300 spectrometer in the impulse mode, with total and partial decoupling from protons, solvent $CDCl_3$.

1,1- Tetra- and 1,1-pentamethyleneallenes were synthesized as described in [11], by reaction of the appropriate 1-chloro-1,1-ethynylcycloalkanes with the zinc—copper couple.

9-(3,3-Pentamethyleneallyl)-9-borabicyclo[3.3.1]nonane (II). In a three-necked flask, fitted with a magnetic stirrer, thermometer, and dropping funnel, was placed 8.25 g of 9-BBN in 120 ml of dry THF, and 7.3 g of 1,1-pentamethyleneallene in 20 ml of THF was added with cooling at −5°C over 40 min. The mixture was stirred at ambient temperature for 4 h, and kept overnight. After removal of the solvent, distillation of the residue gave 12.85 g (83%) of (II), bp 115-116°C (0.8 mm), n_D^{20} 1.5180.

9-(3,3-Tetramethyleneallyl)-9-borabicyclo[3.3.1]nonane (I) was obtained as in the foregoing from 4.3 g of 9-BBN in 70 ml of dry THF and 3.3 g of 1,1-tetramethyleneallene in 20 ml of THF, to give 5.77 g (76%) of (I), bp 117-118°C (1 mm), n_D^{20} 1.5173.

TABLE 2. PMR Spectral Parameters of Carbinols (VII), (X), (XII) and Dienes (XV) and (XVIII)



(δ, ppm., J, Hz)

Compound	H_A	H_B	H_X	CH_3	J_{AB}	J_{AX}	J_{BX}	Signals for other protons*
(VIIa)	5,08	5,34	5,62	1,08	1,8	17,3	10,7	3.44 q (1H, OCH, J = 6.5), 1.1-1.9 m (11 H, CyH and OH)
(VIIb)**	5,05	5.37	5,63	1,12	1,7	15.6	9,7	1.2-1.77 m (12H, CyH and OH)
(VIIc) **	5.07	5.33	5,61	–	2,0	18,0	11,0	1.0-1.9 (19H, CyH, CyP, and OH)
(VIId)	5,02	5,35	5,60	–	1,85	18.1	11,25	0.90-1.85 m (21H, CyH and OH)
(VIIe)	5.08	5,32	5,63	1,7	1,7	18.5	11,3	5.45 d.d.q (1H, $CH_3CH{=}CH{-}C$), 5.60 d.d.q (1H, $CH_3CH{=}CH{-}C$, J_{trans} = 16.1, J = 7.2, J = 1.6), 3.68 m (1H, OCH), 1.1-1.7 m (11H, CyH and OH)
(VIIf)	5,05	5,37	5,62	1,08	1,9	18,6	11,4	5.01 d.q (1H_{trans}, $CH_2{=}C$), 4.92 d.q (1H_{cis}, $CH_2{=}C$, J_{gem} = 1.8, J_{trans} = 16.5, J_{cis} = 9.8), 2.13 m (2H, $CH_2{-}C{=}C$), 1.2-1.77 m (11H, CyH and OH)
(VIIg)	5,07	5,38	5,58	1,18	1,8	18,0	11,1	5.17 d.d (1H_{trans}, $CH_2{=}C$), 5.07 d.d (1H_{cis}, $CH_2{=}C$), 6.01 d.d (1H, CH=C, J_{gem} = 1.8, J_{trans} = 17.5, J_{cis} = 11.0), 1.0-1.9 m (11H, CyH and OH)
(Xa)	5,03	5,05	5.83	1,13	1,6	17.8	11.0	1-3-1.9 m (9H, CyP and OH)
(Xb)	5.10	5.15	5.89	–	1,7	17.7	10.7	1.4-1.9 m (17H, CyP and OH)
(Xc) ***	4.98	5.07	5.85	1,17	1,5	17,5	11.0	5.27 d.d (1H_{trans}, $CH_2{=}C$ 5.04 d.d (1H_{cis}, $CH_2{=}C$),5.98 d.d (1H, CH=C, J_{gem} = 1.9, J_{trans} = 17.3, J_{cis} = 10.9), 1.3-1.95 m (9H, CyP and OH)
(XII)	5.08	5,37	5,62	1.28	1,8	17,5	10,7	1.88 s (3H, $CH_3{-}C{=}C$), 2.33 m (4H, $C{=}C{-}CH_2$), 0.95-1.8 m (13 H, CyH, OH, and $C{-}CH_2{-}C$
(XV)	5.04	5.02	5.90	–	1,8	16,7	10,4	3.88 d (1H, $C{=}CH_2$), 3.98 d (1H, $C{=}CH_2$, J_{gem} = 2.0), 3.7 q (2H, OCH_2, J = 6.7), 1.28 t (3H, CH_3), 1.5-2.0 m (8H, CyP)
(XVIII)	5,0	4.80	5,80	–	1,5	18,0	10,0	3.9 d (1H, $C{=}CH_2$), 4.0 d (1H, $C{=}CH_2$, J_{gem} = 2.0), 3.70 q (2H, OCH_2, J = 7.0), 1.3 t (3H, CH_3), 1.5-2.0 m (10H, CyH)

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*CyH is the cyclohexane ring, and CyP the cyclopentane ring.

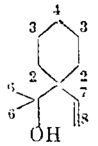
**For the ^{13}C NMR spectra, see Experimental.

***The PMR spectrum was obtained in C_6D_6.

1-Vinyl-1-deuterocyclohexane (IV). In a distillation apparatus was placed 1.95 g of the borane (II), and 3 ml of CD_3OD added at −10°C. The mixture was warmed to room temperature, and the (IV) distilled off to give 0.58 g (68%) of product, bp 125-126°C, n_D^{20} 1.4463. The PMR spectrum was similar to that described in [12].

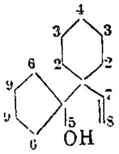
1-Vinyl-1-(1-hydroxy-1-methylethyl)cyclohexane (VIIb). In a distillation apparatus was placed 2.96 g of the borane (II), cooled to 0°C, and 1.5 ml of acetone added with shaking. The mixture was warmed to room temperature, excess acetone distilled off, and the boron-containing residue treated with 5 ml of TEA. After 1 h, the alcohol (VIIb) was distilled from the mixture. Yield 1.5 g (71%). ^{13}C NMR spectrum (δ, ppm): 142.6 d (C^7), 117.0 t (C^8), 74.1 s

(C^5), 47.6 s (C^1), 29.1 t (C^2), 26.3 (C^4), 22.4 t (C^3), and 24.9 q (C^6).



1-Vinyl-1-(1-hydroxybut-2-en-1-yl)cyclohexane (VIIe) (E-Isomer). In a distillation apparatus was placed 2.96 g of the borane (II), cooled to 0°C, and 0.9 g of crotonaldehyde added with shaking. The mixture was gradually warmed to room temperature, and the boron-containing residue treated with 5 ml of TEA. After 0.5 h, the carbinol (1.6 g) was distilled from the reaction mixture, and purified by chromatography on silica (100/160 μ) (eluent was hexane:ether, 2:1). Redistillation gave 1.35 g (68%) of (VIIe). Alcohols (VIIa, f, g) and (Xa, c) were obtained similarly.

1-Vinyl-1-(1-hydroxycyclopent-1-yl)cyclohexane (VIIc). In a three-necked flask fitted with a magnetic stirrer, thermometer, and dropping funnel was placed 3.2 g of the borane (II) in 10 ml of pentane, and 1.18 g of cyclopentanone in 4 ml of pentane added at 0-10°C. The mixture was warmed to 20°C and stirred for 1 h, then treated with 0.85 g of MEA. The crystalline 9-(2-aminoethoxy)-9-BBN which separated was filtered off and washed with pentane. Redistillation gave 1.84 g (68%) of the carbinol (VIIc), bp 96-96.5°C (1 mm), ^{13}C NMR (δ, ppm): 142.7 d (C^8), 116.8 t (C^7), 86.3 s (C^5), 47.0 s (C^1), 29.8 t (C^2), 26.4 t (C^4), 22.2 t (C^3), 34.5 t (C^6), and 23.8 t (C^9). The alcohols (VIId), (Xb), and (XII) were obtained similarly.



1-Vinyl-1-(1-ethoxyvinyl)cyclopentane (XV). In a distillation apparatus was placed a solution of 1.2 g of the borane (I) in 5 ml of pentane, and a solution of 0.55 ml of ethoxyacetylene in 2 ml of pentane added dropwise at 0-10°C. The mixture was warmed to 20°C, and the pentane and excess ethoxyacetylene removed. The residue was treated with 3.5 ml of TEA, and after 0.5 h the diene (XV) was distilled off in vacuo to give 0.6 g (67%), bp 62-63°C (6 mm).

1-Vinyl-1-(1-ethoxyvinyl)cyclohexane (XVIII). In a three-necked flask, fitted with a magnetic stirrer, thermometer, and dropping funnel, was placed 3.65 g of the borane (II) in 10 ml of pentane, and 1.12 g of ethoxyacetylene in 3 ml of pentane added at 0-10°C. The mixture was warmed to 20°C, and stirred for a further 0.5 h. MEA (0.98 g) was added, and the crystalline 9-(2-aminoethoxy)-9-BBN which separated was filtered off and washed with pentane. Removal of the solvent and distillation gave 2.05 g (73%) of the diene (XVIII), bp 85-87°C (9 mm).

CONCLUSIONS

1. Hydroboration of 1,1-tetra- and 1,1-pentamethyleneallene with 9-borabicylo[3.3.1]-nonane has given 9-(3,3-tetramethyleneallyl)- and 9-(3,3-pentamethyleneallyl)-9-borabicyclo-[3.3.1]nonanes.

2. A new method has been developed for the synthesis of 1-substituted 1-vinylcycloalkanes by allylboration of carbonyl compounds and ethoxyacetylene with diorganylborylethylidenecycloalkanes.

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SYNTHESIS AND STRUCTURE OF THE UNSYMMETRICAL P-DIASTEREOISOMER OF 1,6-DICHLORO-1,6-DIDESOXY-2,4;3,5-BIS-O-(PIPERIDINOPHOSPHORYL)-D-MANNITOL*

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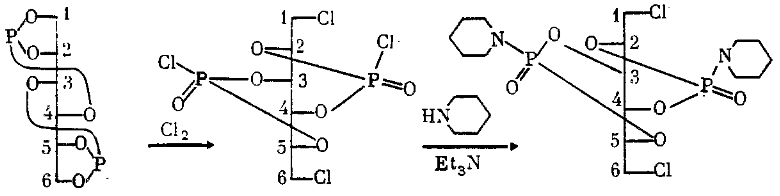
Chlorination of 1,2,4;3,5,6-bis-O-(phosphintriyl)-D-mannitol (I), which contains two cis-condensed 2,7,8-trioxa-1-phosphabicyclo[3,2,1]octane fragments [2], is known to give 1,6-dichloro-1,6-didesoxy-2,4;3,5-bis-O-(chlorophosphoryl)-D- manniol [3]. In examining the properties of the latter, we have carried out its reaction with piperidine. Chromatography of the reaction products on silica gel has given two of the three possible RpRp-, SpSp-, and RpSp-diastereoisomers of 1,6-dichloro-1,6-didesoxy-2,4;3,5-bis-O-(piperidinophosphoryl)-D-mannitol (III). Although possessing the same elemental composition and ^{31}P NMR spectra, the compounds obtained (IIIa, IIIb) differ in their melting points and chromatographic mobility. They were obtained in an overall yield of 64.5%, in a ratio of ~1:2.



(I) (II) (III)

X-ray structural examination has shown the chromatographically less mobile isomer (IIIb) to contain two six-membered 1,3,2-dioxaphosphorinane rings which are cis-condensed at the C^3—C^4 bond (see Fig. 1).

The $P^1O^2C^2C^3C^4O^4$ ring exists in the boat conformation, the $P^1O^4C^3C^2$ fragment being planar to within 0.014(3) Å, and atoms O^2 and C^4 departing from this plane by −0.51 and −0.63 Å, respectively. The phosphoryl (P═O) and chloromethyl ($ClCH_2$) groups are in the trans positions, the chloromethyl group and the piperidine ring being oriented pseudoequatorially. The chiral atom P^1 has the S-configuration.

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*For previous communication, see [1].

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