of these compounds are lower and higher than that for Ia, respectively.[14]

The fused cyclopropyl derivative of semibullvalene, IV, is predicted to be 9.1 kcal/mol more stable in its delocalized form. The additional stability of the delocalized form seems to be due to three factors: (a) the ability of the $C_2C_1C_8$ angle to open past 109° without angle strain; (b) the weakness of the C_1–C_5 bond (*f* in Table II and *d* in Table III), which is stretched as a consequence of mixing of a symmetrical combination of allyl nonbonding orbitals with the antibonding skeletal orbital; and (c) the availability of a low-lying antibonding skeletal orbital that is a perturbed antibonding Walsh orbital for the fused cyclopropyl ring (see Figure 1).

The fused cyclobutyl derivative, V, provides an interesting contrast to IV. In this case the $C_2C_1C_8$ angle strain ought to be reduced in the homoconjugated form and the C_1–C_5 bond ought to be weakened relative to the corresponding parameters for Ia, although not by as much as for IV. On the other hand, there is no suitable low-lying antibonding orbital of proper symmetry to mix with the symmetrical combination of nonbonding allyl orbitals, as in IV. Any orbital of proper symmetry must be antibonding with respect to two of the cyclobutyl bonds (rather than one C–C bond as in the cases of Ia–e and IV). This last factor seems to be important enough to overcome the first two as the relative energy of the homoconjugated form of V is about the same as that of Ia.

The diaza derivative, III, is, not surprisingly, more stable in its delocalized form as there is no angle strain impediment to forming the planar delocalized diazapentalene, which is a 10π-electron structure. There should, however, be a barrier to the rearrangement of the semibullvalene form to the planar diazapentalene as this process is an 8-electron electrocyclic ring opening that is constrained to occur by a disrotatory process, in violation of the orbital symmetry rules.[15] We expect the complete surface of III, therefore, to be complex. The degenerate Cope rearrangement might successfully compete with the ring-opening process at a low temperature.

Two important questions that have not been resolved by this study because of the CI problems mentioned above are whether a barrier exists between the localized and homoconjugated structures for the cases where the latter are more stable and whether a triplet state of similar or lower energy to the homoconjugated structures exists. A complete understanding of low-temperature NMR data for such systems may not be possible until these questions are answered. We hope to be able to approach these problems in the near future.

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Registry No. Ia, 6909-37-1; Ib, 87351-76-6; Ic, 87351-77-7; Id, 87351-78-8; Ie, 87351-79-9; III, 87351-80-2; IV, 87351-81-3; V, 87351-82-4.

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Selective Ring-Opening Polymerization of Di-O-methylated and Di-O-benzylated 1,4-Anhydro-α-D-ribopyranoses and Structure Proof of Synthetic Cellulose-Type Polysaccharide (1→4)-β-D-Ribopyranan and (1→5)-α-D-Ribofuranan

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Abstract: The cationic polymerization of 1,4-anhydro-2,3-di-*O*-methyl-α-D-ribopyranose (ADMR) for the first time gave two kinds of stereoregular polysaccharide derivatives, 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan and 2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan, by selective ring-opening polymerization with phosphorus pentafluoride as catalyst at low temperatures. The latter polymer was prepared by boron trifluoride etherate and other relatively weak Lewis acids as catalyst. In addition, the polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose by various Lewis acids as catalyst provided stereoregular 2,3-di-*O*-benzoyl-(1→5)-α-D-ribofuranan by the selective 1,5-ring scission. The 2,3-di-*O*-benzyl-(1→5)-α-D-ribofuranan was debenzylated to give a new stereoregular polysaccharide (1→5)-α-D-ribofuranan. The (1→5)-α-D-ribofuranan and formerly synthesized (1→4)-β-D-ribopyranan were methylated into the di-O-methylated ones to prove that the stereostructures of the derived D-ribofuranan and D-ribopyranan are the same as those of the polymerized 2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan and 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan, respectively, using the NMR spectroscopy. ADMR is the second 1,4-anhydro sugar that can give the cellulose-type polysaccharide derivative. The mechanism of selective ring-opening polymerizations is discussed.

Since the ring-opening polymerization of an anhydro sugar was revealed to be an excellent method for providing a stereoregular polysaccharide,[1] a number of 1,6-α-linked polysaccharides have been synthesized from D-glucose, D-mannose, and D-galactose.[2] Syntheses of 1,6-linked polysaccharide models have also been investigated using synthetic bicyclic compounds as monomer.[3]

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Although 1,4-linked polysaccharides such as cellulose and amylose are more widely distributed in nature than 1,6-linked polysaccharides, they have not successfully been prepared by any chemical method.[4] It was reported that polycondensation of a substituted glucose gave a (1→4)-β-D-glucopyranan derivative, but the molecular weight of the polysaccharide was low after deprotection.[5]

Kops and Schuerch investigated the ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-methyl-α-D-galactopyranose and 1,4-anhydro-2,3-di-*O*-methyl-α-L-arabinopyranose, showing that the D-galactan had β-D-furanosidic and β-D-pyranosidic structures and the L-arabinan had similar but variable proportions of β-L-furanosidic units.[6] However, stereoregular polysaccharides were not obtained under any experimental conditions. Micheel and co-workers carried out the cationic polymerization of 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose to aim at the synthesis of cellulose.[7] The polysaccharides obtained were composed of mixed structures of mainly (1→4)-β-linked (cellulose type) and (1→4)-α-linked (amylose type) D-glucopyranosidic units, but the molecular weight was low.

Although there are two possible ring-opening modes in the polymerization of a 1,4-anhydro-α-D-glycopyranose that can be equally regarded as a 1,5-anhydro-β-D-glycofuranose, these researches led to no method to control the ring-opening modes.

Recently, we reported the synthesis of a stereoregular (1→4)-β-D-ribopyranan of high molecular weight by ring-opening polymerization of 1,4-anhydro-2,3-*O*-benzylidene(or isopropylidene)-α-D-ribopyranose and subsequent removal of the protective groups.[8] This is the first synthetic stereoregular polysaccharide that has the cellulose-type (1→4)-β-pyranose backbone. Although D-ribose widely exists as the carbohydrate component of ribonucleic acids, there is no such polyribose in nature. Thus, the determination of the (1→4)-β-D-ribopyranose structure has made on the basis of NMR spectroscopy and optical rotation of polymers and consideration of the mechanism of stereoregular polymerization.

In addition, by selective 1,5-ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose (=1,5-anhydro-2,3-di-*O*-benzyl-β-D-xylofuranose), a stereoregular (1→5)-α-D-xylofuranan, which also does not occur in nature, was obtained.[9] In this case, however, a natural wood xylan, which is (1→4)-β-D-xylopyranan, was used to determine the structure of the synthetic xylan.

The purpose of this investigation is to demonstrate that 1,4-anhydro-2,3-di-*O*-methyl-α-D-ribopyranose can be polymerized into the two possible stereoregular polysaccharides, that is, 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan and 2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan, by two kinds of selective ring-opening polymerization. It is also to report that the ring-opening polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose occurs in the selective 1,5-ring-opening mode to give 2,3-di-*O*-benzyl-(1→5)-α-D-ribofuranan, which is then debenzylated into a stereoregular polysaccharide (1→5)-α-D-ribofuranan. The stereostructures of synthetic polysaccharides are identified as the expected ones by converting the (1→4)-β-D-ribopyranan and (1→5)-α-D-ribofuranan into their methylated derivatives and by comparing the structures of the methylated D-ribopyranan and D-ribofuranan with those of the stereoregular 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan and 2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan obtained by polymerization of 1,4-anhydro-2,3-di-*O*-methyl-α-D-ribopyranose.

Table I. Ring-Opening Polymerization of 1,4-Anhydro-2,3-di-*O*-methyl-α-D-ribopyranose by Cationic Catalysts[a]

no.	catalyst kind	catalyst mol %	temp, °C	time, h	yield, %	$[\alpha]_D$,[b] deg	$10^{-3}\overline{M}_n$
1	PF_5	2	−40	0.3	68.4	+42.5	13.0
2	PF_5	2	−60	0.5	77.6	+30.7	10.3
3	PF_5[c]	2	−60	0.5	61.5	+16.8	12.4
4	PF_5	2	−78	0.5	79.0	+20.5	23.2
5	$BF_3 \cdot OEt_2$	1	0	0.5	73.7	+71.0	31.3
6	$BF_3 \cdot OEt_2$	1	−40	2.0	46.1	+131.3	67.5
7	$BF_3 \cdot OEt_2$	2	−40	1.3	87.9	+127.1	110
8	$BF_3 \cdot OEt_2$	1	−60	1.0	29.2	+132.5	124
9	$SnCl_4$	4	−40	1.0	78.0	+130.5	164
10	NbF_5	2	−40	1.0	84.4	+122.4	26.0
11	$SbCl_5$	1	0	0.05	51.5	+23.6	11.7
12	$SbCl_5$	1	−40	0.5	49.5	+31.5	13.9
13	$SbCl_5$	1	−60	1.0	79.9	+91.6	17.4
14	$SbCl_5$	1	−78	1.0	68.3	+66.3	38.5

[a] Monomer, 0.2 g, was polymerized. Monomer concentration, 20 w/v %; solvent, CH_2Cl_2. [b] Measured in chloroform at 25 °C (*c* 1%). [c] Monomer concentration, 10 w/v %.

Results and Discussion

Polymerization of 1,4-Anhydro-2,3-di-*O*-methyl-α-D-ribopyranose. 1,4-Anhydro-2,3-di-*O*-methyl-α-D-ribopyranose (ADMR) was found to be polymerized by various cationic catalysts into polymers with high molecular weights in a short time. The results of polymerizations are summarized in Table I. When the polymerization was carried out with Lewis acids boron trifluoride etherate, stannic chloride, and niobium pentafluoride as catalyst in the temperature range of −40 to −60 °C, polymers with high positive specific rotataions of +122° to +133° and with high molecular weights of 26.0×10^3 ($\overline{DP}_n$ 123)–164×10^3 ($\overline{DP}_n$ 777) were obtained (no. 6–10). The high positive specific rotation clearly indicates that the polymer has an α-configuration.[10]

On the other hand, the polymerization with phosphorus pentafluoride as catalyst afforded polymers with low specific rotations of +42.5° to +16.8° at polymerization temperatures from −40 to −78 °C. Antimony pentachloride exhibited similar catalytic behavior to that of phosphorus pentafluoride, but the specific rotation of the polymers was somewhat higher than that by phosphorus pentafluoride catalyst. The molecular weights of the polymers obtained by phosphorus pentafluoride and antimony pentachloride were in the range of 10.3×10^3 to 38.5×10^3, being lower than those obtained by boron trifluoride etherate and stannic chloride catalyst.

The structures of the polymers with high specific rotation of +127° (Table I, no. 7) and with low specific rotation of +17° (no. 3) or +21° (no. 4) were examined by means of the ^1H and ^{13}C NMR spectroscopy. As shown in Figure 1B, the 400-MHz ^1H NMR spectrum clearly exhibits that the poly(ADMR) with the specific rotation of +21° is exclusively composed of a single repeating unit, since six protons due to the sugar moiety appear as individually separate absorptions except for a H5 proton.

On the other hand, Figure 1C shows that the poly(ADMR) with the specific rotation of +127° is also composed of a single, but completely different, repeating unit. For instance, the H1 proton of the former polymer appears as a singlet at 5.05 ppm, while that of the latter appears as a doublet at 5.09 ppm ($J_{1,2}$ = 3.66 Hz).

The ^{13}C and ^1H chemical shifts of the monomers and polymers are given in Table II. The C1 carbon of poly(ADMR) with $[\alpha]_D$ +17° appears at lower magnetic field (105.70 ppm) than that with $[\alpha]_D$ +127° (102.07 ppm). Since the C1 carbons of both methyl

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Table II. ^{13}C and ^{1}H Chemical Shifts of 1,4-Anhydro-2,3-di-*O*-methyl(or benzyl)-α-D-ribopyranoses, Their Polymers, and (1→5)-α-D-Ribofuranan[a]

	nucleus	C1, H1	C2, H2	C3, H3	C4, H4	C5, H5	H5′	CH_3 or CH_2Ph	
1,4-anhydro-2,3-di-*O*-methyl-α-D-ribopyranose	^{1}H	5.52 (s)	(3.68 (d))[c]	(3.65 (d))[c]	4.78 (d)	3.46 (q)	3.37 (d)	3.48	
1,4-anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose	^{13}C	100.47	80.22	82.37	78.57	64.91		73.30	73.01
2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan[b]	^{13}C	105.70	81.48[c]	81.95[c]	80.94	70.82		58.82	58.64
	^{1}H	5.05 (s)	3.82 (d)	3.76 (q)	4.11 (m)	3.93 (q)	3.4[d]	3.49	3.39
2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan[e]	^{13}C	102.07	81.35	82.86	79.05	68.02		58.82	58.62
	^{1}H	5.09 (d)	3.87 (d)	3.875 (s)	4.26 (m)	3.78 (q)	3.60 (q)	3.45	3.43
2,3-di-*O*-benzyl-(1→5)-α-D-ribofuranan	^{13}C[f]	101.64	(79.45)[c]	(82.83)[c]	(ca. 77.2[g])[c]	67.37		72.65	71.94
	^{1}H	4.88 (d)	3.85 (q)	4.04 (q)	4.08 (d)	3.72 (q)	3.40 (q)	4.52 (q)	4.17 (q)
(1→5)-α-D-ribofuranan[h]	^{13}C	102.93	71.47	70.37	83.56	68.59			

[a] ppm from internal tetramethylsilane. [b] Proton coupling constants (Hz): $J_{1,2} = 0$, $J_{2,3} = 4.27$, $J_{3,4} = 7.94$, $J_{4,5} = 2.44$, $J_{4,5'} = 7.94$, $J_{5,5'} = 10.53$. [c] The assignment might be interchanged. [d] Overlapped with methoxy protons. [e] Proton coupling constants (Hz): $J_{1,2} = 3.66$, $J_{2,3} = 0$, $J_{3,4} = 0$, $J_{4,5} = 3.05$, $J_{4,5'} = 4.27$, $J_{5,5'} = 11.29$. [f] Measured in $CDCl_3$. [g] Overlapped with the absorption of $CDCl_3$. [h] Carbons 2–4 were assigned according to ref 12.

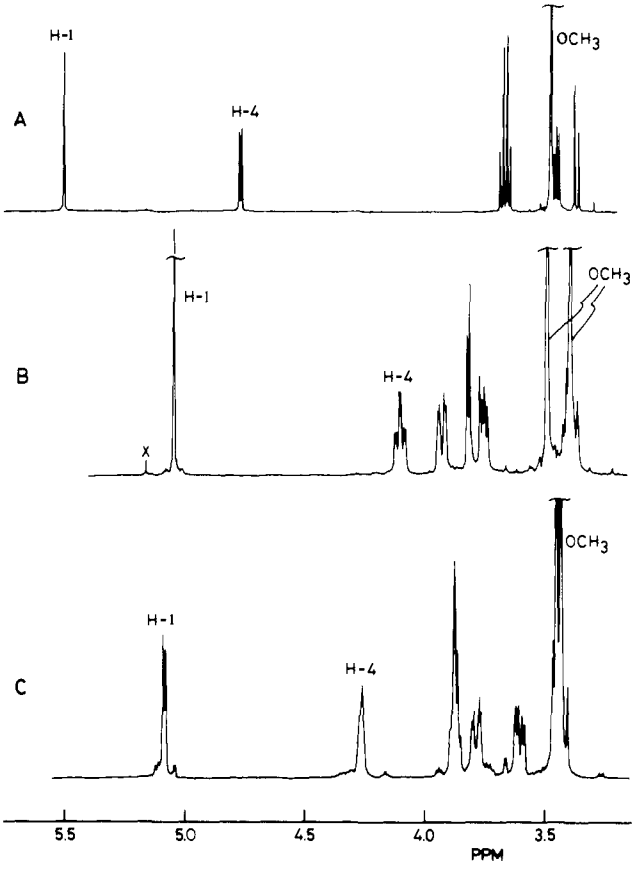
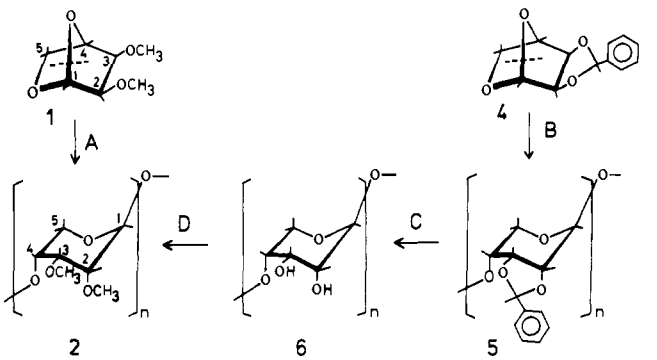


Figure 1. 400-MHz ^{1}H NMR spectra of (A) 1,4-anhydro-2,3-di-*O*-methyl-α-D-ribopyranose, (B) 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan, and (C) 2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan (solvent, $CDCl_3$; reference, $(CH_3)_4Si$).

β-D-ribopyranoside and methyl β-D-ribofuranoside, which can be regarded as low-molecular-weight model compounds, appear at lower magnetic fields (103.85 and 108.0 ppm, respectively) than the C1 of methyl α-D-ribofuranoside (103.1 ppm),[11,12] the former poly(ADMR) is considered to have a β-configuration.

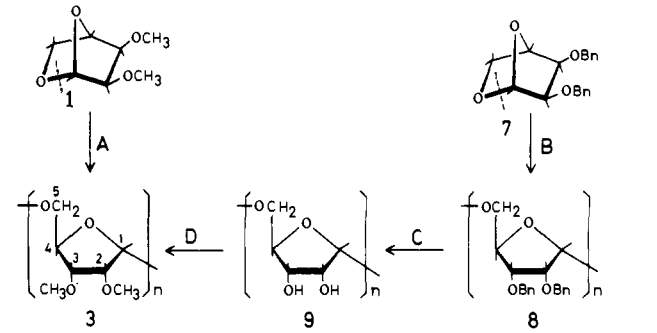
With the ring-opening mode leading to the polymer with β-configuration taken into account, the poly(ADMR) with $[\alpha]_D$ +17° to +21° was concluded to be stereoregular 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan (**2**), which was obtained by selective 1,4-ring-opening polymerization (Scheme I, left part). The latter poly(ADMR) with high positive specific rotation, therefore,

Scheme I[a]



[a] A, PF_5/−78 °C; B, $SbCl_5$/−60 °C; C, $Na/NH_3(l)$; D, NaH/CH_3I.

Scheme II[a]



[a] A, $BF_3{\cdot}OEt_2$/−40 °C; B, $BF_3{\cdot}OEt_2$/−40 °C; C, $Na/NH_3(l)$; D, NaH/CH_3I.

was concluded to be 2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan (**3**) obtained by selective 1,5-ring-opening polymerization (Scheme II, left part). ADMR is the first 1,4-anhydro sugar that can give the two different, completely stereoregular polysaccharide derivatives.

The polymers having the specific rotations between about +21° and +127° had mixed structures composed of the above two units and possibly one more unit the proportions of which were related to the magnitude of specific rotations.

Since both 2,7-dioxabicyclo[2.2.1]heptane,[13] which is a parent compound of 1,4-anhydropentopyranose, and 2,6,7-trioxabicyclo[2.2.1]heptane[14] showed a tendency to be cationically polym-

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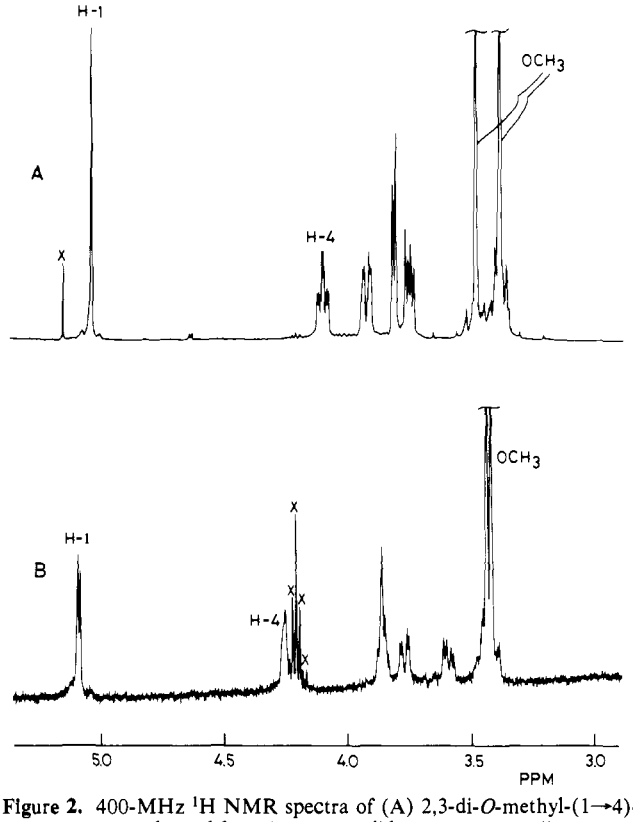

Figure 2. 400-MHz ^{1}H NMR spectra of (A) 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan derived from 2,3-*O*-benzylidene-(1→4)-β-D-ribopyranan and (B) 2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan derived from 2,3-di-*O*-benzyl-(1→5)-α-D-ribofuranan.

erized into polymers with tetrahydrofuran structures, the methoxy groups in ADMR play an important role especially in the stereoregulation leading to the β-D-ribopyranan.

Conversion of (1→4)-β-D-Ribopyranan into 2,3-Di-*O*-methyl-(1→4)-β-D-ribopyranan and Comparison of the Sturctures. In order to confirm the structure of 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan, derivatization was used, as shown in Scheme I. When in the previous investigation 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose (**4**) was polymerized with antimony pentachloride as catalyst to give a stereoregular polymer with large negative specific rotation, the polymer was concluded to be 2,3-*O*-benzylidene-(1→4)-β-D-ribopyranan (**5**).[8] The reasons that led to the conclusion were based on the optical rotation of the polymer, the stereoregular structure revealed by the ^{13}C and ^{1}H NMR spectroscopy, and the consideration of the mechanism of stereoregular polymerization, as in the case of ADMR, because there is no naturally occurring polyribose to be compared. If the presumed 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan with small positive specific rotation that was polymerized by PF_5 catalyst at −60 to −78 °C shows a single, stereoregular structure by the NMR spectroscopy with the same (1→4)-β-D-ribopyranosidic structure as that of **5**, the presumption leading to the conclusion on the polymer structure would be verified.

Thus, (1→4)-β-D-ribopyranan (**6**) was synthesized by polymerizing **4** by $SbCl_5$ catalyst and by subsequent removal of the protective benzylidene group.[8] Then, it was methylated to give a 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan (Scheme I).

As shown in Figure 2A, the derived 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan exhibited completely the same ^{1}H NMR spectrum as that of the polymerized 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan shown in Figure 1B. The specific rotation of the derived polymer was +25.7°, in good agreement with that of the polymerized one. Therefore, the conclusion on the (1→4)-β-D-ribopyranosidic structure of both 2,3-*O*-benzylidene-(1→4)-β-D-ribopyranan and polymerized 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan was proved. The 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan prepared from its monomer is the second, synthetic cellulose-type polysaccharide derivative.

Table III. Ring-Opening Polymerization of 1,4-Anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose by Cationic Catalysts[a]

no.	catalyst kind	catalyst mol %	temp, °C	time, h	yield, %	$[\alpha]_D$,[b] deg	$10^{-3}\overline{M}_n$
1	PF_5	1	0	0.5	16.5	+47.8	5.9
2	PF_5	1	−40	0.5	76.5	+136.2	23.5
3	PF_5	1	−60	0.5	78.9	+140.5	35.0
4	PF_5	1	−78	0.5	78.5	+128.9	36.7
5	$SbCl_5$	2	0	0.05	47.6	+60.0	7.7
6	$SbCl_5$	2	−40	1.0	94.7	+134.0	30.1
7	$SbCl_5$	2	−60	0.5	82.6	+133.2	46.6
8	$SbCl_5$	2	−78	0.5	49.9	+118.9	37.7
9	$BF_3{\cdot}OEt_2$	2	0	0.5	79.5	+135.9	41.1
10	$BF_3{\cdot}OEt_2$	2	−40	0.5	88.9	+153.4	542
11	$BF_3{\cdot}OEt_2$	2	−60	0.5	87.0	+147.9	346
12	$BF_3{\cdot}OEt_2$	2	−78	0.5	85.1	+150.4	356
13[c]	TaF_5	4	0	0.3	9.3	+39.5	5.6
14[c]	TaF_5	4	−40	0.5	88.8	+149.0	33.0
15[c]	NbF_5	3	−60	2.0	78.2	+144.0	319
16[c]	NbF_5	3	−78	0.5	73.9	+140.7	31.0
17[c]	$NbCl_5$	3	−20	10	60.7	+142.2	9.0
18[c]	SiF_4	*d*	−40	43	75.8	+158.9	36.8

[a] Monomer concentration, 20 w/v %; solvent, CH_2Cl_2. [b] Measured in chloroform at 25 °C (*c* 1%). [c] Monomer concentration, 10 w/v %. [d] Silicon tetrafluoride gas was introduced by bubbling for 3 min.

The fact that in the NMR spectrum of 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan the H1 proton appears as a singlet indicates that there is not a diaxial relationship between H1 and H2, because the H1 proton that is in diaxial relationship with H2 must appear as a doublet with a splitting of more than 7 Hz.[15] Thus, the conformation of 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan is 1C in which H1 and H2 are both equatorial. This is unexpected, but similar phenomena are observed in a number of pentopyranoses in which the C1 and 1C conformations are known to be of comparable energy.[16]

Polymerization of 1,4-Anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose into Stereoregular 2,3-Di-*O*-benzyl-(1→5)-α-D-ribofuranan. In the previous investigation,[8] the polymerization of 1,4-anhydro-2,3-*O*-benzylidene(or isopropylidene)-α-D-ribopyranose with phosphorus pentafluoride and boron trifluoride etherate as catalyst gave a polymer composed of two kinds of repeating units; one is a (1→4)-β-D-ribopyranosidic unit and the other is a unit having an α-configuration which could not be determined to be a (1→5)-α-D-ribofuranosidic or (1→4)-α-D-ribopyranosidic unit, although the former unit was considered to be more probable. In addition, a stereoregular (1→5)-α-D-ribofuranan has not been prepared by any catalyst.

Thus, to determine the structure of the unit with the α-configuration and to synthesize a stereoregular (1→5)-α-D-ribofuranan, the polymerization of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose (ADBZR) (**7**) was attempted.

Table III outlines the results of polymerizations of ADBZR. The polymerization of ADBZR with almost all catalysts employed resulted in the formation of polymers in high yields. The rate of polymerization was very fast. For instance, with boron trifluoride etherate as catalyst at −60 °C, the yield of poly(ADBZR) was 87.0% in 0.5 h (Table III, no. 11), while the yield of poly(ADMR) was 29.2% in 1 h (Table I, no. 8). However, when the polymerization temperature was relatively high, around 0 °C, the yields were low except for with mild Lewis acid boron trifluoride etherate as catalyst, suggesting that degradatioin of the polymer chain might occur during polymerization at higher temperatures. The molecular weights of polymers obtained by boron trifluoride etherate and niobium pentafluoride catalysts were extremely high in the range of 346 × 10^3 to 542 × 10^3 ($\overline{DP}_n$ 1110–1740). Polysaccharide derivatives with such high molecular weights have only been obtained by the ring-opening polymerization of 1,6-

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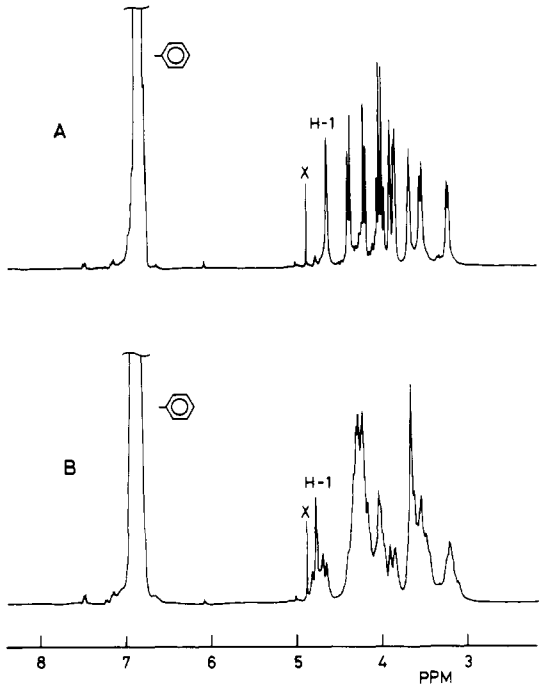


Figure 3. 400-MHz ^{1}H NMR spectra of (A) 2,3-di-*O*-benzyl-(1→5)-α-D-ribofuranan and (B) nonstereoregular poly(1,4-anhydro-2,3-di-*O*-benzyl-D-ribopyranose) polymerized by $SbCl_5$ catalyst.

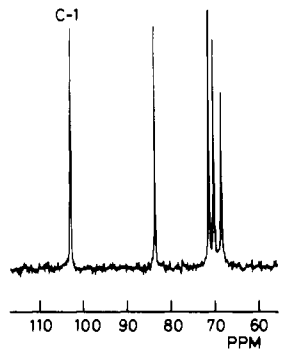


Figure 4. 25-MHz ^{13}C NMR spectrum of (1→5)-α-D-ribopyranan (solvent, D_2O; reference, external tetramethylsilane dissolved in CH_2Cl_2).

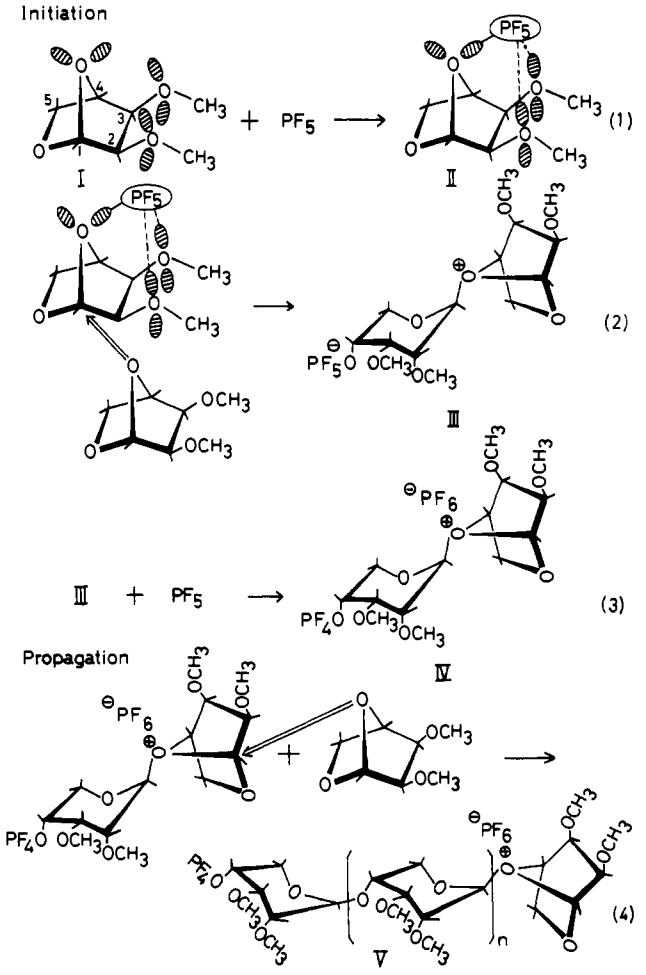
anhydroglucose[17,18] and -mannose derivatives.[2a]

The specific rotations of the polymers that were prepared by all the catalysts in the temperatures below −40 °C were very high, in the range of +119° to +159°, indicating that the polymer has an α-configuration. The ^{1}H (Figure 3) and ^{13}C NMR spectra exhibit that the poly(ADBZRs) with high positive specific rotation were composed of a single repeating unit. Therefore, the resulting stereoregular poly(ADBZR) was concluded to be 2,3-di-*O*-benzyl-(1→5)-α-D-ribofuranan (**8**). The ^{13}C and ^{1}H chemical shifts of **8** are given in Table II.

On the other hand, poly(ADBZRs) that were prepared by various Lewis acids at higher temperatures, around 0 °C, showed low specific rotations ranging from +39.5° to +60.0° except for polymers prepared by boron trifluoride etherate. The H1 proton absorption of the polymer with $[\alpha]_D$ +60.0° clearly indicates the existence of possibly four structural units (Figure 3).

Conversion of 2,3-Di-*O*-benzyl-(1→5)-α-D-ribofuranan into 2,3-Di-*O*-methyl-(1→5)-α-D-ribofuranan and Comparison of the Structures. As depicted in Scheme II, the 2,3-di-*O*-benzyl-(1→5)-α-D-ribofuranan with high positive specific rotation was converted into 2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan by debenzylation and subsequent methylation. The ^{13}C NMR spectrum

Scheme III



of the (1→5)-α-D-ribofuranan (**9**) is shown in Figure 4, indicating that the free polysaccharide with $[\alpha]_D$ +164° consists of a single repeating unit that is different from the (1→4)-β-D-ribopyranan.[8] Since the chemical shifts of individual carbons of **9** were completely the same as those of the structural unit with the α-configuration that was seen in the polyribose with mixed structure,[8] the unit with the α-configuration was revealed to be the (1→5)-α-D-ribofuranosidic unit.

The ^{1}H NMR spectrum of the derived 2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan (Figure 2B) is in good agreement with that of the 2,3-di-*O*-methyl-(1→5)-α-D-ribofuranan polymerized from the monomer (Figure 1C) except for impurity signals. As a result, the (1→5)-α-D-ribofuranosidic structures of both polymers and the occurrence of stereoregular polymerization via selective 1,5 scission were also proved.

Mechanism of Polymerization. It was revealed that in the stereoregular polymerization of the 1,4-anhydro-α-D-ribopyranose the substituents at C2 and C3 positions play a major role in the formation of the β-D-ribopyranan and α-D-ribofuranan. The benzylidene and isopropylidene groups led to the former, while the benzyl group gave to the latter. On the other hand, the methyl group gave both polymers depending on the polymerization conditions. Moreover, in spite of the same polymerization conditions, that is, with phosphorus pentafluoride as catalyst at −78 °C, ADMR gave the β-D-ribopyranan, while ADBZR gave the α-D-ribofuranan.

As shown in Scheme III, for the 2,3-di-*O*-methyl-(1→4)-β-D-ribopyranan to be formed, two factors must be satisfied, that is, (1) in the initiation step, the complexation of Lewis acid occurs at the 1,4-linked oxygen O4 and (2), in the propagation step, the 1,4-linked oxygen of the monomer attacks to the propagating end from the backside direction of the C1–O4 bond. Since the methoxy groups at C2 and C3 might be considered to be con-

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formationally rigid at low temperature, the oxygens may participate in the complexation of a strong Lewis acid, phosphorus pentafluoride, with the O4 oxygen. Once the propagating species IV is formed, the exchange between complexes IV and VIII (Scheme IV) might not occur at low temperature, and the selective 1,4 scission would be continued to give the β-D-ribopyranan.

In the case of di-*O*-benzylated 1,4-anhydro-ribopyranose, steric and electronic effects of the two benzyloxy groups may not allow such a complexation of PF_5 with the O4 oxygen. In addition, both O2 and O3 oxygens might be necessary for the complexation, because 1,4-anhydro-2,3-di-*O*-methyl-α-L-arabinopyranose in which the two methoxy groups are in the trans position gave almost no (1→4)-β-pyranosidic unit.[19]

Accordingly, in this series of monomers that have the identical 2,7-dioxabicyclo[2.2.1]heptane structure except for the substituents, it can be concluded that the selection of the bond to be cleaved, that is, the C1–O4 or C1–O5 bond, is to a large extent controlled by which oxygen is subject to complexation with a Lewis acid. In contrast to the stereoregular polymerization of 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose by antimony pentachloride,[8] it might be ascribed to the prevention of such complexation by steric hindrance that the antimony pentachloride did not give a completely stereoregular poly(ADMR).

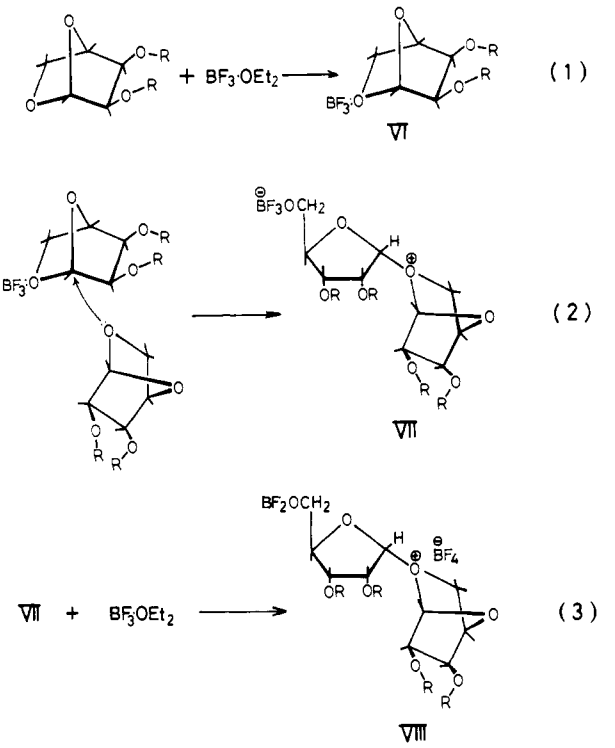
The complexation of Lewis acids to the oxygens of α,β-unsaturated carbonyl compounds was examined by NMR spectroscopy to reveal the structure of the complexes and the relative coordination power[20] and was used for the regio- and stereospecific synthesis in Diels–Alder reactions.[21] In reference to the complexation of Lewis acid to the C–O bond in the cyclic compound, selective complexation of antimony pentachloride with an oxygen in bicyclic ozonides, which caused the stereoselective C–O bond fission, was reported.[22] The coordination of Lewis acids with the O2 and O3 oxygens of 1,4-anhydroribose is suggested by the finding that the cationic polymerization of *anti*- and *syn*-1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose was accompanied by isomerization.[23] Besides, the complexation of titanium tetrachloride with two oxygens in tetra-*O*-benzylated D-glucopyranose accounted for the very rapid anomerization of the compound.[24]

In order to explain the mode of bond scission in cyclic compounds having more than two labile C–O bonds, Deslongschamps proposed the stereoelectronic control theory that, in the case of specific cleavage of a C–O bond in cyclic acetals and glycosides, the cleavage of a C–O bond occurs if the oxygen has an electron pair oriented antiperiplanar to the C–O bond to be cleaved.[25] In the case of the ring-opening polymerization of 2,7-dioxabicyclo-[2.2.1]heptane, Hall and co-workers elucidated the ring-opening mode leading to the formation of the five-membered ring according to theory.[13] However, it is not the case in the selective ring-opening polymerization of the 1,4-anhydro-2,3-di-*O*-methyl-α-D-ribopyranose, because the bicyclic compound shows the two kinds of selective scissions by variation of the polymerization conditions, and therefore the mode of scission is not inherent to the bicyclic anhydro sugar.

As shown in Scheme IV, a mild Lewis acid such as boron trifluoride causes the complexation with 1,5-linked oxygen of the methylated monomer ADMR probably because of a little higher basicity of the O5 oxygen than the O4 oxygen. In the case of the benzylated monomer ADBZR, it is also reasonable to consider that in the initiation step the complexation of Lewis acid occurs solely at the O5 oxygen possibily because of no participation of the benzyloxy oxygens to the complexation. Then a stable propagating species including the $O5^+$ oxonium ion and anion pair is formed, which causes the selective 1,5 scission after the attachment of approaching monomer.

Scheme IV

Initiation



In conclusion, it was found that the special combinations of sugar configuration, substituent, and catalyst can form stereoregular polyriboses (1→4)-β-D-ribopyranan and (1→5)-α-D-ribofuranan through the selective ring-opening polymerizations.

Experimental Section

1,4-Anhydro-α-D-ribopyranose. D-Ribose (240 g) was pyrolyzed under vacuum.[26] A dark brown syrup was dissolved in an aqueous (1.5 L) solution of $Ba(OH)_2 \cdot 8H_2O$ (120 g), followed by heating at 90 °C for 6 h. The solution was neutralized by dry ice and concentrated to dryness. After extraction 3 times by hot ethanol, the solution was concentrated and crystallized from ethanol: yield 14.1 g (6.7%); mp 107.0–108.0 °C (lit.[26] mp 109–110 °C).

1,4-Anydro-2,3-di-*O*-methyl-α-D-ribopyranose (ADMR). 1,4-Anhydro-α-D-ribopyranose was methylated according to the method of Hakomori.[27] 1,4-Anhydro-α-D-ribopyranose (5 g) in 30 mL of dimethylformamide was added dropwise to a dimethylformamide (30 mL) solution of 3.3 g sodium hydride and reacted for 1 h. Then, methyl iodide (7 mL) in 30 mL of dimethylformamide was added dropwise and allowed to stand for 12 h at room temperature. The reaction mixture was poured into ice water and extracted with chloroform. The methylated compound was chromatographed on a column of silica (250 g) eluting twice with benzene–methanol (95:5), followed by concentration to dryness to give clear syrup: yield 4.0 g (65.9%); $[\alpha]^{25}_D$ −76.0° (*c* 1%, $CHCl_3$).

1,4-Anhydro-2,3-di-*O*-acetyl-α-D-ribopyranose.[26] Pyridine (300 mL) and acetic anhydride (200 mL) were added to the 1,4-anhydro-α-D-ribopyranose (syrup, 30 g) held in a flask: the solution was kept at room temperature for 12 h. After the solution was concentrated, the acetylated compound was recrystallized from ethanol: yield 46 g (94%); mp 71.0–72.5 °C (lit.[26] 68–70 °C).

1,4-Anhydro-2,3-di-*O*-benzyl-α-D-ribopyranose (ADBZR). 1,4-Anhydro-2,3-di-*O*-acetyl-α-D-ribopyranose (10 g) was benzylated with 120 mL of benzyl chloride and 24 g of KOH at 95–100 °C for 1 h and then for a further 1.5 h after addition of 60 mL of benzyl chloride and 12 g of KOH.[28] After evaporation, chloroform and water were added to the reaction mixture, followed by separation of the chloroform layer. ADBZR was purified by recrystallization from ethanol 3 times and finally from *n*-butyl chloride. Yield 3.3 g (45%) mp 65.0–66.5 °C; $[\alpha]^{25}_D$ −35.9° (*c* 1%, $CHCl_3$).

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Polymerization of ADMR and ADBZR. High-vacuum technique was used for polymerization.[17] Monomer (0.2 g) was polymerized by cationic catalyst in 1 mL of methylene chloride. Syrupy monomer ADMR was transfered into the polymerization ampule by distillation under vacuum just before polymerization. After termination by the addition of methanol, polymers were purified by reprecipitations using chloroform–petroleum benzin several times and subsequent freeze-drying from benzene. Polymerization of 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose was carried out by antimony pentachloride catalyst according to the previous paper.[8]

Debenzylation. To 60 mL of liquid ammonia containing 0.4 g of sodium, a solution of 0.5 g of 2,3-di-*O*-benzyl-(1→5)-α-D-ribofuranan with $[\alpha]_D$ +148.4° in 20 mL of dimethoxyethane was added dropwise at −78 °C under nitrogen. After the mixture was stirred for 2 h, anhydrous ammonium chloride and a small amount of water were added. The aqueous solution was washed with methylene chloride and dialyzed with running water. The solution was concentrated and finally freeze-dried from water. The (1→5)-α-D-ribofuranan showed $[\alpha]^{25}_D$ +164.1° in water (yield about 50%). Debenzylidenation of 2,3-*O*-benzylidene-β-D-ribopyranan (0.39 g) was performed using the same method (yield 0.11 g (45%)).

Methylation of Free Polysaccharides. To a 3 mL of dimethyl sulfoxide solution containing (1→4)-β-D-ribopyranan (30 mg) was added a 3-mL portion of carbanion solution, which was prepared by reacting 5.7 g of sodium hydride with 50 mL of dimethyl sulfoxide for 3 h, followed by the addition of 3 mL of methyl iodide. After it had reacted overnight, the reaction mixture was worked up (yield 23.6 mg (65%)). When (1→5)-α-D-ribofuranan was methylated using the same procedure, the yield was over 100%, because it contained impurities that were distinguishable from the product by the NMR spectroscopy.

Measurements. 400-MHz ^{1}H and 100-MHz ^{13}C NMR spectra were measured on the solutions in $CDCl_3$ and CD_2Cl_2, respectively, by means of a JEOL GX-400 spectrometer. 25-MHz ^{13}C spectrum of a free polysaccharide was measured by means of a JEOL PS-100 spectrometer. The peak assignments of ^{1}H and ^{13}C spectra were performed by the decoupling method and the heterospin decoupling method, respectively. Specific rotations were measured by means of a Perkin-Elmer 241 polarimeter.

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Proton [1,5] Shifts in P-Unsubstituted 1*H*-Phospholes. Synthesis and Chemistry of 2*H*-Phosphole Dimers

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Abstract: The protonation of four representative phospholyl anions has been studied at low temperature. In each case, the primary protonation product is the P-unsubstituted 1*H*-phosphole. Among the products described is the parent phosphole C_4H_4PH. Between −70 °C and room temperature according to the substitution pattern, the 1*H*-phospholes rearrange through proton [1,5] shifts to give 2*H*-phospholes, which instantly dimerize. Such an evolution can be frozen out by P-complexation with $W(CO)_5$ in the case of 1,2,3,4-tetraphenyl-1*H*-phosphole. The 2*H*-phosphole dimers are generally [4 + 2] Diels–Alder endo dimers in which one 2*H*-phosphole unit acts as a diene and the other as a dienophile through its P=C double bond. In the case of 1,2,3,4-tetraphenyl-2*H*-phosphole, the dimerization takes another path, however. The P—H bond of the 1*H*-phosphole adds onto the P=C double bond of the 2*H*-phosphole to give a 1-phospholylphospholene, this type of dimerization being probably less sensitive to steric hindrance than the normal [4 + 2] dimerization. Around 100 °C, the [4 + 2] endo dimers give the more stable [4 + 2] exo dimers. At higher temperature, 1,1′-biphospholyls are obtained through loss of hydrogen. UV irradiation of the [4 + 2] endo dimers, on the other hand, gives pentacyclic cage compounds. Mixed [4 + 2] dimers are also described together with some reactions in which the 2*H*-phospholes act as dienes (with acetylenes) and as dienophiles (with conjugated dienes). A tentative theoretical explanation of the observed proton [1,5] shifts is presented; it relies on a σ(P–H)/π hyperconjugative interaction, which has been proposed previously by Schweig as one of the major stabilizing mechanisms within the phosphole nucleus.

The synthesis and properties of phosphaalkenes are currently under active investigation in many laboratories working on organophosphorus chemistry.[1] The stability of phosphaalkenes is generally achieved through steric crowding or cyclic delocalization. In both cases, the reactivity of the P=C double bond is significantly reduced. For instance, Diels–Alder reactions in which P=C double bonds act as dienophiles remain scarce in the literature.[2] We have recently shown that 2*H*-phosphole [4 + 2] dimers can be easily obtained by protonation of phospholyl anions.[3,4] These dimers can yield monomeric 2*H*-phospholes by heating at moderate temperatures (~100 °C). The 2*H*-phospholes thus obtained are stabilized neither by steric crowding nor by cyclic delocalization. They appear to be very reactive both as dienes and dienophiles. Therefore, we decided to perform a thorough study of these species. The results of this study are described hereafter.

Results and Discussion

Protonation of Phospholyl Anions at Low Temperature. Synthesis of P-Unsubstituted 1*H*-Phospholes. Theoretical investigations[5-7] on the phospholyl anion have established that it is fully aromatic as the isoelectronic thiophene. As a consequence, the initial protonation site could be either phosphorus or α- or β-carbons. Thus, we decided to perform a ^{31}P NMR study of this protonation at very low temperature in order to observe the

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