Semibullvalenes. 2. A MNDO Theoretical Study of the Rearrangements of Semibullvalene and Several of Its Derivatives

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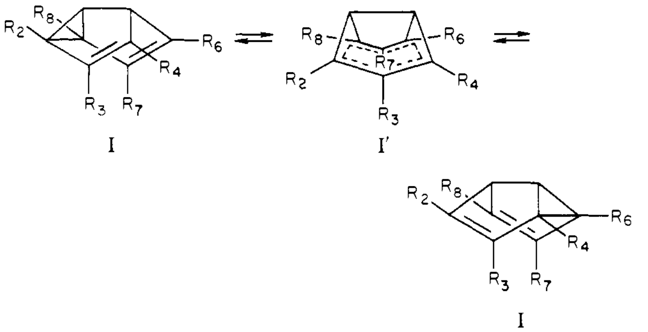
Abstract: The reaction paths for the degenerate Cope rearrangements of semibullvalene and 2,4-dicyano-, 2,6-dicyano-, 3,7-dicyano-, and 2,4,6,8-tetracyanosemibullvalene were calculated by using the MNDO molecular orbital method with full geometrical optimization and 2 × 2 CI (for the homoconjugated structures). The localized and delocalized fully optimized structures for 1,5-diaza-, 1,5-methylene-, and 1,5-dimethylenesemibullvalene were also calculated. The calculated activation energy for semibullvalene is 5.7 kcal/mol, in good agreement with experiment. The differences in the energies between the delocalized and localized structures are 8.9, −0.2, 9.8, and −4.7 kcal/mol, respectively, for the cyano derivatives and −12.4, −9.1, and 5.4 kcal/mol for the others. Thus 2,4,6,8-tetracyanosemibullvalene and 1,5-methylenesemibullvalene are clearly predicted to have homoconjugated ground states. 1,5-Diazasemibullvalene is predicted to be more stable in the diazapentalene form, and 2,6-dicyanosemibullvalene should have classical and delocalized structures of approximately equal energy. The homoconjugated structures of the semibullvalenes are seen to be diallylic in character with additional stabilization due to interaction of the symmetric combination of the allyl nonbonding orbitals with an antibonding skeletal orbital.



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a, $R_{2,3,4,6,7,8} = H$
b, $R_{3,7} = H$; $R_{2,4,6,8} = CN$
c, $R_{3,4,7,8} = H$; $R_{2,6} = CN$
d, $R_{3,6,7,8} = H$; $R_{2,4} = CN$
e, $R_{2,4,6,8} = H$; $R_{3,7} = CN$

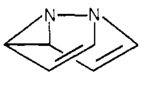
Semibulvalene (Ia), first prepared by Zimmerman et al.,[1] has long been of interest to chemists as its facile degenerate Cope rearrangement has raised the possibility that the delocalized homoaromatic 3 + 3 transition state for the rearrangement could be further stabilized to the point where the symmetric structure might become more stable than the classical structure Ia. Several theoretical papers have appeared,[2] notably those of Hoffmann[2a] and Dewar,[2b] that suggest that substitution of electron-withdrawing groups at R should stabilize the symmetrical structure with respect to I, presumably to give a single minimum on the potential surface. The recent synthesis and crystal structure of the dimethyltetracarbomethoxy derivative, II, is supportive of these suggestions, as the cyclopropane C–C bond is unusually long (1.78 Å).[3] An unexpected feature of the X-ray structure was the total absence of any symmetry elements, particularly in the plane that separates the two double bonds.

Table I. Heats of Formation and Activation Energies for Semibullvalene and Derivatives (kcal/mol)

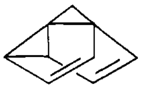
compd	ΔH_f localized	ΔH_f homoconjugated	E_{act}	E_{act} (exptl)
Ia	72.2	77.9	5.7	4.8[a]
Ib	202.3	197.6	−4.7	
Ic	134.3	134.1	−0.2	
Id	134.5	143.4	8.9	
Ie	130.3	140.1	9.8	
III	113.9	101.4	−12.4	
IV	137.0	127.9	−9.1	
V	92.2	97.5	5.4	

[a] Reference 7.

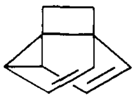
In order to better understand the potential energy surface for these processes, we undertook a study of the tetracyano compound, Ib, with use of the MNDO approximation of molecular orbital theory[4] with 2 × 2 CI and complete geometric optimization in all internal coordinates. Semibullvalene (Ia) itself and three dicyano derivatives, Ic–e, were studied for comparison. Finally, three other derivatives, III–V, were also studied to test a hypothesis suggested by the results.



III



IV



V

Methods

The MNDO[4] approximation to molecular orbital theory was used for this study. Geometrical optimization in all internal coordinates was performed with use of the Fletcher-Powell-Davidon algorithm as incorporated in the MNDO program. The energies of the delocalized, homoconjugated species were recalculated and reoptimized by using 2 × 2 configuration interaction (CI) after a preliminary optimization without CI was accomplished. As the numbers of internal coordinates (42–54) are large, several calculations were performed varying several of the internal coordinates at a time until all were considered. This procedure was particularly necessary for the calculations with CI which were very time consuming. Reaction paths were obtained for semibullvalene (Ia) and each of the cyano derivatives studied. These were calculated by stepping through the appropriate reaction coordinate while optimizing the other internal degrees of freedom. The reaction coordinates considered were the breaking of the cyclopropyl bond and the forming of the new cyclopropyl bond at the other end of molecule. Those delocalized structures that appeared to have symmetric minima were recalculated with imposed symmetry.

The MNDO method has been reported to calculate relative energies better than most commonly used ab initio and semiempirical methods, at a relatively low cost.[5] Few detailed studies of specific reaction paths

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(1) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3316.

(2) (a) Hoffmann, R.; Stohrer, W.-D. *J. Am. Chem. Soc.* **1971**, *93*, 6941. (b) Dewar, M. J. S.; Schoeller, D. W. *Ibid.* **1971**, *93*, 1481. (c) Dewar, M. J. S.; Lo, D. H. *Ibid.* **1971**, *93*, 7201. (d) Iwamura, H.; Morio, K.; Kunii, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 841. (e) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294.

(3) Miller, L. S.; Grohmann, K.; Dannenberg, J. J.; Todaro, L. *J. Am. Chem. Soc.* **1981**, *103*, 6249.

(4) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

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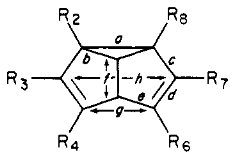
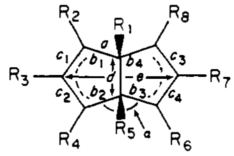
Table II. Geometries for the Localized Structures of Semibullvalene and Derivatives



compd	a^a	b^a	c^a	d^a	e^a	f^a	g^a	h^a
Ia	1.57	1.54	1.50	1.36	1.54	1.57	2.44	3.17
Ib	1.60	1.55	1.50	1.36	1.54	1.56	2.45	3.14
Ic	1.58	1.55	1.51	1.36	1.53	1.57	2.45	3.15
		1.54	1.50	1.37	1.54			
Id	1.58	1.56	1.51	1.36	1.54	1.57	2.44	3.15
		1.54			1.53			
Ie	1.56	1.54	1.51	1.37	1.53	1.56	2.43	3.15
III	1.54	1.52	1.50	1.36	1.48	1.42	2.35	
IV	1.60	1.51	1.51	1.36	1.51	1.60	2.48	
V	1.58	1.53	1.51	1.36	1.52	1.59	2.44	3.17

[a] Angstroms.

Table III. Geometries for Delocalized (Homoconjugated) Structures of Semibullvalene and Derivatives



compd	a^a	b^a	c^a	d^a	e^a	angle $(\alpha)^b$
Ia	2.46	1.51	1.40	1.59	3.72	109
Ib	2.50	1.52	1.40	1.60	3.71	111
Ic	2.52	1.51	1.39	1.60	3.80	113
		1.52	1.41			
Id	2.36	1.51	1.41	1.59	3.63	103
Ie	2.37	1.51	1.40	1.59	3.63	103
III	2.65	1.41	1.41	1.37		140
IV	2.47	1.47	1.41	1.64	3.78	113
V	2.41	1.51	1.39	1.61	3.69	107

[a] Angstroms. [b] Degrees.

have been carried out.[6] Our own experience indicates that MNDO with 2 × 2 CI is very useful for calculating the activation energies for reactions that involve radical or biradicaloid transition states.[6a,b]

Results

The energies of the species calculated are collected in Table I and the main geometric features in Tables II and III. Table IV compares the present work with previous calculations on semibullvalene. The energies of the homoconjugated structures were lowered by 7–15 kcal/mol upon recalculation with CI. Semibullvalene was calculated to have a symmetric homoallylic transition state and an E_{act} of 5.7 kcal/mol, in good agreement with the experimental value of 4.8 kcal/mol.[7] The preferred reaction path was found to be bond breaking with a C_2–C_8 distance of 2.46 Å. The tetracyano derivative, Ib, is predicted to exist preferably in the delocalized form by 4.7 kcal/mol, while the 2,6-dicyano derivative, Ic, is predicted to prefer the delocalized structure by an insignificant amount (0.2 kcal/mol). The other two dicyano derivatives are both predicted to have higher barriers to rearrangement than the parent semibullvalene, 8.9 and 9.8 kcal/mol for Id and Ie, respectively.

The reaction paths for the rearrangement of Ia–e were uneventful except for that of Ib. In this case the reaction path suggested that there may be a barrier between the semibullvalene structure and the delocalized structure, which is of lower energy. After many hours of computer time, we were not able to completely optimize the *col* that corresponds to this barrier. The problem is further complicated because CI is necessary to correctly calculate the energies of the homoconjugated structures. Although CI is not generally used to calculate ground states of normal molecules, it usually significantly affects neither the energies nor the geometries of these molecules. However, molecules that have degenerate HOMO's and LUMO's cannot be adequately described with less than 4 × 4 CI. Fewer configurations cannot give equal weights to each of the HOMO's and LUMO's in the final ground state. This problem has been discussed at length by Borden and Davidson, particularly with respect to the trimethylenemethane diradical.[8] Unfortunately Ib has accidently degenerate HOMO's and LUMO's due to the equivalent π-bonding and antibonding orbitals of the equivalent C–C double bonds. The localized structure cannot, therefore, be correctly described by using the 2 × 2 CI necessary to calculate the delocalized structure. The apparent barrier between the two structures may be due partly or entirely to a discontinuity on the potential surface that results from the CI problem.

Since Ia has an unusual structure even in its ground state, the possibility that CI would lower its calculated energy much more than a normal molecule was considered. The energy of the previously optimized structure of Ia, recalculated by using 2 × 2 CI, was lowered by only 0.5 kcal/mol, indicating no unusual stabilization.

As seen from Table III, the optimized homoconjugated structures for Ib–c, which have energies lower than the localized structures, have $C_2C_1C_8$ angles that slightly exceed the tetrahedral angle. Although these deviations are small ($\leq 4°$), they suggest that the angle strain resulting from larger distortions of this angle could be an impediment to further reductions in energy of the delocalized structures. To test this hypothesis, the energies of 1,5-diazasemibullvalene, 1,5-methylenesemibullvalene, and 1,5-dimethylenesemibullvalene (III–V) in their localized and delocalized forms were calculated. The energies and geometries for these species are included in the relevant tables. No attempt was made to calculate the reaction paths for these species. This will be the subject of a later study. Both III and IV, which have delocalized structures of lower energy, also have large $C_2C_1C_8$ angles (140° and 113°, respectively). The delocalized structure of II is the known diazapentalene, which is a 10 π-electron aromatic species.

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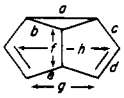
(5) (a) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5558. (b) Halgren, T. A.; Kleier, D. A.; Hall, J. H., Jr.; Brown, L. D.; Lipscomb, W. N. *Ibid.* **1978**, *100*, 6595.

(6) (a) Dannenberg, J. J.; Rocklin, D. *J. Org. Chem.* **1982**, *47*, 4529. (b) Decoret, C.; Royer, J.-L.; Dannenberg, J. J. *Ibid.* **1981**, *46*, 4074. (c) Dannenberg, J. J.; Bunch, B.; Brown, N., unpublished results. (d) Frenking, G.; Schmidt, J.; Schwarz, H. *Z. Naturforsh., B: Anorg. Chem., Org. Chem.* **1980**, *35*, 3513. (e) Burkholder, D.; Jones, W. E.; Ling, K. W.; Wasson, J. S. *Theor. Chim. Acta* **1980**, *55*, 325.

(7) Cheng, A. K.; Anet, F. A. L.; Mioduski, J.; Meinwald, J. *J. Am. Chem. Soc.* **1976**, *98*, 5014. For the barrier in the solid state, see: Miller, R. D.; Yanoni, C. S. *Ibid.* **1980**, *102*, 7396, Macho, V.; Miller, R. D.; Yanoni, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3735.

(8) Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* **1982**, *38*, 737.

Table IV. A Comparison of Calculated and Experimental Geometries for Semibullvalene



method	E_{act}[a]	a[b]	b[b]	c[b]	d[b]	e[b]	f[b]	g[b]	h[b]	ref
MNDO	5.7	1.57	1.54	1.50	1.36	1.54	1.57	2.44	3.17	
MINDO/2	2.3	1.54	1.49	1.48	1.35	1.51	1.53	1.93		2b, 2c
MINDO/2	0.6	1.51	1.51	1.48	1.34	1.53		2.15		2d
MINDO/3		1.57	1.53	1.53	1.36	1.51	1.57			2e
exptl		1.60	1.53	1.53	1.35	1.53	1.49	2.26		9

[a] kcal/mol. [b] Angstroms.

Discussion

In order to have confidence in the ability of the MNDO method to adequately predict the properties of the potential surfaces for the various semibullvalene derivatives that we have studied, we shall first consider the potential surface for the parent molecule, Ia. The barrier to the Cope rearrangement is calculated to be within 1 kcal/mol of the experimentally observed value obtained from low-temperature ^{13}C NMR by Anet.[7] The only experimental study on the structure of semibullvalene is the gas-phase electron-diffraction determination by Wang and Bauer.[9] The geometries calculated by MNDO agree quite well with the experimental data except for two distances, f and g in Table IV. The experimental distance between C_1 and C_5 of 1.49 Å is unusually small for a C–C bond length, an observation that caused Wang and Bauer to try (unsuccessfully) to fit their data to a structure with a longer bond. The structures of several substituted semibullvalenes that have been determined by X-ray crystallography suggest that the C_1–C_5 distance may in fact be longer. The distances of 1.55 and 1.58 Å reported for 1-cyano-[10] and 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene[3] (II), respectively, are in much better agreement with our calculated distance of 1.57 Å.

The distance g is a nonbonded distance, therefore, the potential surface is likely to be quite flat in this direction. We have calculated the energies and geometries for Ia with g fixed at 2.30 and 2.35 Å with all other parameters optimized. The geometry hardly changes, and the energy increases by no more than 1.5 kcal/mol. Despite these two minor discrepancies, the MNDO geometry agrees, at least as well as any other reported calculations, with the experimental report.[2b–e]

The calculated geometries for the various cyano-substituted semibullvalenes listed in Table II exhibit very little difference in most of the geometric parameters. Although no symmetry elements were imposed upon the optimized structures, the calculated lengths for all bonds that could be related by imposing C_{2v} symmetry differed by no more than 0.01 Å. This is in marked contrast to the crystal structure of II which is remarkably unsymmetrical,[3] suggesting that crystal packing forces acting upon a molecule that is easily distorted, due to a relatively flat potential surface, may have caused the deviation from the symmetrical structure.

The C_2–C_8 bond lengths vary from 1.56 to 1.60 Å in Ie and Ib, respectively, in accord with the predicted interaction of a cyano group with the Walsh orbitals of the cyclopropyl ring of semibullvalene.[2a] All the cyclopropyl bonds that have cyano groups directly attached to at least one carbon are longer than those that are unsubstituted. The effect is greatest in Ib.

The geometries of the homoconjugated cyano-substituted derivatives (Table III) indicate that these structures, which were optimized without imposed symmetry, also are as symmetrical as their substitution patterns allow.

The two allylic systems separate the most for those systems that have the lower energy homoconjugated structures, as can be seen from the distance a and the angle α in Table III. These systems have cyano groups that stabilize the diallylic character of the transition state. Gajewski[11] has suggested that Cope rearrangements can proceed via transition states that vary in character from diallylic to 1,4-cyclohexanediyl. The nature of the transition state for Ia and the delocalized ground states for Ib and Ic are definitely diallylic in character, so much so that the allyl groups separate as much as the remaining molecular skeleton will allow without introducing undue strain. Examination of the HOMO of semibullvalene (Figure 1) shows it to be composed of the symmetrical combination of the two nonbonding allyl orbitals *which is stabilized by interaction with an antibonding skeletal orbital of correct symmetry.* This interaction has an analogy in the "through-bond coupling" of the tetramethylene diradical first discussed by Hoffmann,[12] although the symmetries of the HOMO's are different. This phenomenon should be general for all divinyl cyclopropane derivatives and may be the cause for the anomalous kinetic isotope effects observed for compounds of this type.[13] A more detailed study of the rearrangements of molecules of this kind will be the topic of a future study.

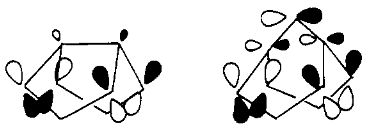

Ia IV

Figure 1. HOMO's for Ia and IV in their homoconjugated states.

The three isomeric dicyanosemibullvalenes, Ic–e, have markedly different predicted E_{act}'s, −0.2, 8.9, and 9.8 kcal/mol, respectively. Examination of Table I indicates that Ie has a heat of formation that is 4.0–4.2 kcal/mol lower than that of the other isomers. This ground-state stabilization is clearly due to the fact that only Ie has both cyano groups simultaneously on vinyl carbons where they can stabilize the C–C double bonds. On the other hand, they do less to stabilize the homoconjugated transition state whose HOMO has a node at carbons 3 and 7. Their effect upon the transition state can be estimated to be 4.1 kcal/mol which is the difference between the E_{act} of 13.9 kcal/mol expected if only ground-state stabilization were operative (about 8.2 kcal/mol for the stabilization due to two CN's plus 5.7 for the E_{act} of Ia) and the calculated E_{act} for Ie, 9.8 kcal/mol.

The other two isomers, Ic,d, have about the same ground-state energies, but very different energies for the delocalized structures. The 2,6 derivative, Ic, forms a delocalized structure with two equivalently substituted allyl groups, thereby allowing maximum stabilization due to the interaction of the two nonbonding allyl orbitals. The 2,4 derivative, Id, forms a delocalized structure where the allyl group that has both CN's is significantly lower in energy than the other allowing less interactive stabilization. Since the completion of this work, we have learned that the 1,5-dimethyl derivatives of both Ic[14a] and Ie[14b] have been synthesized. Preliminary results indicate the barriers for the Cope rearrangement

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(9) Wang, W. C.; Bauer, S. H. *J. Am. Chem. Soc.* **1972**, *94*, 5651.

(10) Christoph, G. C.; Beno, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 3156.

(11) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693; **1978**, *100*, 6268.

(12) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(13) Gajewski, J. J., personal communication.

(14) (a) Quast, H., personal communication. (b) Quast, H.; Sauer, J., personal communication.

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.

Acknowledgment. This work was supported in part by a PSC-BHE grant.

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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(15) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim/Bergstr., Germany, and Academic Press: New York, 1970.

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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(1) (a) Korshak, V. V.; Golowa, O. P.; Sergeev, V. A.; Merlis, N. M.; Shneer, R. Ya. *Vysokomol. Soedin.* **1961**, *3*, 477. (b) Tu, C.-C.; Schuerch, C. *J. Polym. Sci., Part B* **1963**, *1*, 163. (c) Ruckel, E.; Schuerch, C. *J. Am. Chem. Soc.* **1966**, *88*, 2605.

0002-7863/83/1505-6865$01.50/0