

the facile oxidations of the 2,5-semidione derived from the cyclopentadiene-*p*-benzosemiquinone Diels-Alder adduct to yield the corresponding *p*-benzosemiquinone.

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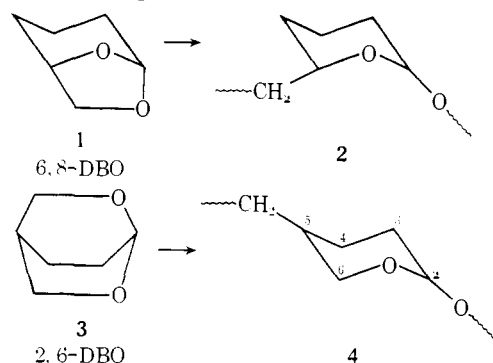
A New Ring System. 2,6-Dioxabicyclo[2.2.2]octane, a Highly Reactive Bicyclic Acetal

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Abstract: A convenient synthesis of 2,6-dioxabicyclo[2.2.2]octane (**3**), the parent compound of a new ring system, has been worked out. This bicyclic acetal is highly reactive, oligomerizing in the solid phase at room temperature and hydrolyzing several orders of magnitude faster than related model compounds. Lewis and proton acids readily polymerized **3** to the 1,4-pyranoose homopolymer **4**, η_{inh} 0.13–1.1. Stereoregular propagation by SN2 displacement on the bicyclic oxonium ion occurred at low temperatures using fluoro acids as initiators. Stereoregular propagation by SN1 reaction of an intermediate carbonium ion was observed at +28° with methanesulfonic or trifluoroacetic acid initiation. The stereochemistries of the polymers obtained under these conditions agreed well with those calculated from conformational considerations for the limiting cases.

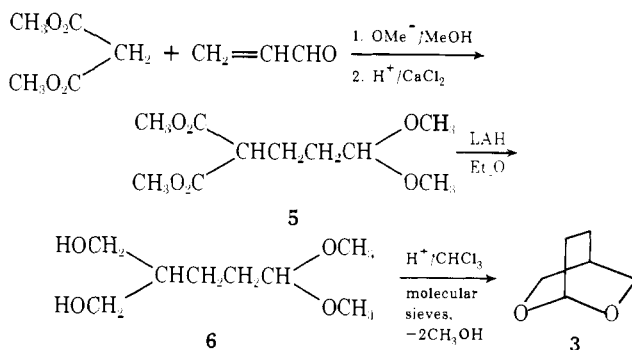
The understanding and chemical synthesis of polysaccharides are of great biomedical interest.¹ The synthesis of stereoregular polysaccharides has been a subject of vigorous study in our laboratories and elsewhere. A stereoregular substituted polysaccharide from 1,6-anhydro-2,3,4-tri-*O*-methyl- β -D-glucopyranose was initially reported by Korshak² and Schuerch.³ Later work by Schuerch and coworkers reported other substituted polysaccharides.³ Most recently, attention has turned toward the synthesis of polysaccharide analogs *via* ring-opening polymerization of unsubstituted bicyclic acetals. Specifically, the cationic ring-opening polymerization of 6,8-dioxabicyclo[3.2.1]octane (6,8-DBO) (**1**) has been shown to proceed at low temperatures *via* a direct displacement-type propagation step to give a completely stereoregular 1,3-linked tetrahydropyranoside **2**.^{4–6} We now report the synthesis and ring-opening polymerization of 2,6-dioxabicyclo[2.2.2]octane (**3**) to give the 1,4-linked analog **4**.



Results

Synthesis. The synthesis of **3** was achieved as described in Scheme I. The synthesis of the required intermediate **6** paralleled that used by earlier workers^{7,8} to prepare the analogous diethyl acetal. Michael addition of sodio dimethyl malonate to acrolein with subsequent acetalization *in situ* gave **5** in 50% yield. Reduction of **5** with lithium aluminum hydride gave a high yield of **6**. The diol acetal, **6**, underwent

Scheme I



intramolecular acid-catalyzed acetal exchange in dilute chloroform solution to afford the camphoraceous bicyclic acetal **3** in up to 35% yield. The monomer proved to be hygroscopic and unstable toward oligomerization under ordinary conditions and had to be stored under nitrogen at Dry Ice temperatures.

Table I. Polymerizations^a of 2,6-Dioxabicyclo[2.2.1]octane (**3**)

Expt	Catalyst	Mol %	Temp, °C	Time, hr	Yield, %	η_{inh}^b	H_{ax}/H_{eq}^c	Fraction SN2 propagation ^d
1	SiF ₄ ^e	0.20	-78	110	19	0.39	3.00	1.00
2	SiF ₄ ^f	0.20	-78	48	18	1.1	1.68	0.45
3	PF ₅ ^e	0.20	-78	43	31	0.51	2.03	0.60
4	PF ₅ ^f	5	-78	16	68 ^l	0.23	0.56	0
5	BF ₃ ^e	0.20	-78	110	2		1.70	0.47
6	FSA ^{f, g}	0.14	-78	60	77	0.51	1.68	0.45
7	I ₂ ^f	0.20	-78	50	59	0.32	1.38	0.33
8	BF ₃ ^f	0.20	-20	24	93	0.29	1.17	0.24
9	SiF ₄ ^f	0.20	-20	80	73	0.40	1.08	0.20
10	FSA ^{f, g}	0.07	-20	60	82	0.23	1.04	0.19
11	BF ₃ ·Et ₂ O ^f	0.20	-20	14	76	0.22	1.00	0.17
12	I ₂ ^f	0.11	-20	80	42	0.23	0.56	0
13	MTF ^{f, h}	0.20	-20	54	86	0.31	0.54	0
14	MSA ^{f, i}	0.20	+28	44	44	0.16	0.64	0
15	TFA ^{f, j}	0.20	+28	87	81	0.13	0.61	0
	None ^k	0	-70, -20	48	0			

^a Monomer weight was 250 mg in each experiment. ^b Inherent viscosity, determined in chloroform solution at 30° and 0.5% concentration. ^c Ratios of areas of pmr absorptions. ^d Calculated from eq 1 in text. ^e Twice distilled monomer. ^f Twice sublimed monomer. ^g Fluorosulfonic acid. ^h Methyl trifluoromethylsulfonate. ⁱ Methanesulfonic acid. ^j Trifluoroacetic acid. ^k Blank experiments. ^l Plus some 5% gel.

Polymerization. Either Lewis or proton acids could be used to polymerize **3** effectively (Table I). Phosphorus pentafluoride and boron trifluoride (and its etherate) have been used in many studies of cyclic acetal and ether polymerization.^{1,3-6} Silicon tetrafluoride has been recommended by Miller as a milder catalyst which is suitable for reactive cyclic monomers.⁹ Iodine served as a still weaker Lewis acid.

Among the proton acids, fluorosulfonic is the strongest acid known,¹⁰ while methanesulfonic and trifluoroacetic acids are progressively weaker. Finally, methyl trifluoromethanesulfonate is a reactive alkylating agent which was expected to give rise to the oxonium ion intermediate required for propagation.

For use in polymerization, the bicyclic acetal was doubly sublimed or doubly distilled at reduced pressure and used immediately. Polymerizations were carried out in ca. 30 wt % solutions of dichloromethane and over a temperature range from -78° to room temperature.

As shown in Table I, homopolymers **4** were obtained in good yields under various conditions of cationic initiation. The most active catalysts were phosphorus pentafluoride, silicon tetrafluoride, iodine, and fluorosulfonic acids, inasmuch as they permitted polymerization at as low temperatures as -78°. Boron trifluoride and methyl trifluoromethanesulfonate were active at -20°, while methanesulfonic and trifluoroacetic acids required +28° to give reasonable yields of polymer.

Blank runs (*i.e.*, without catalyst) showed, while unstable at ordinary conditions, monomer **3** was completely stable under the conditions employed for polymerization.

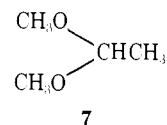
The homopolymers possessed inherent viscosities ranging from 0.13 to 1.1. Clear, coherent films of polymer with $\eta_{inh} \geq 0.4$ could be cast from chloroform solutions. Differential scanning calorimetry measurements showed no detectable thermal transitions through 260°.

Structure and Stereochemistry. Structural proof for **4** was obtained from elemental analysis and pmr spectroscopy. The pmr (60 MHz) spectrum displayed a broad singlet at τ 8.30 and a broad multiplet centered at τ 6.42 which integrated for five and four hydrogens, respectively. The first band was attributed to the methylene hydrogens at C-3 and C-4 and the methinyl hydrogen at C-5; the second absorption was assigned to the C-6 and C-7 hydrogens. The acetal proton at C-2 integrated for one hydrogen and appeared at τ 5.56 (axial) and at τ 5.30 (equatorial).

The ratio (H_{ax})/(H_{eq}) varied from a high of 3.00 (exp 1) to a low of 0.59 ± 0.04 (expt 12-15). As will be discussed

below, these ratios are determined by the stereochemistry of propagation and by the reaction mechanism.

Reactivity. In view of the ease with which 2,6-DBO underwent polymerization relative to the isomeric 6,8-DBO, we measured in a more definitive manner the relative reactivity of these monomers vs. a model compound, 1,1-dimethoxyethane (**7**). Acid-catalyzed hydrolysis in 20% (v/v)



deuterium oxide-acetone was carried out (Table II). The results show that 2,6-DBO is at least two orders of magnitude more reactive than 6,8-DBO and about three orders of magnitude more reactive than an acyclic acetal in acid-catalyzed solvolysis. The difference in rate for the two bicyclic compounds corresponds to the acid-catalyzed polymerization reactivity of these isomeric monomers.

Discussion

The high reactivity displayed by 2,6-dioxabicyclo[2.2.2]octane (**3**) explains in part why this ring system has not been reported previously.

Mechanisms. The mechanisms of cationic polymerization of bicyclic acetals have been reviewed by Schuerch^{1,3} (Scheme II). This scheme shows propagation *via* oxonium or carbonium ions (arrows indicate directions of attack by monomer). Stereoregular polymer will be obtained *via* the

Scheme II

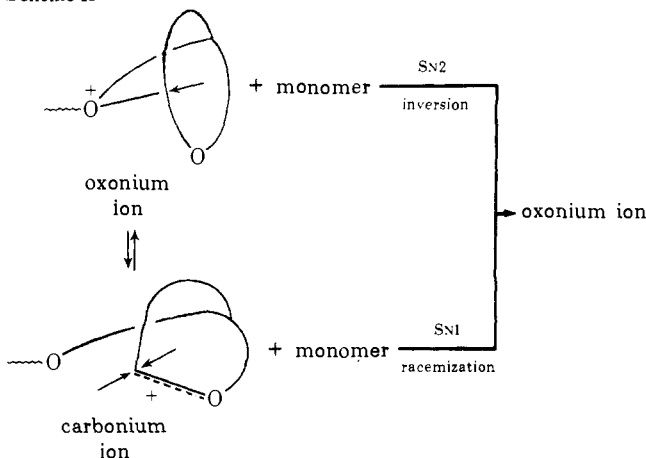


Table II. Reactivity of Acetals toward Solvolysis in D₂O-Acetone^a at 35°C

Acetal	<i>t</i> _{1/2} ^b	Rel reactivity
2,6-Dioxabicyclo[2.2.2]octane	≤ 10 sec	> 3.2 × 10 ³
6,8-Dioxabicyclo[3.2.1]octane	70 min	7.7
1,1-Dimethoxyethane	9 hr	1

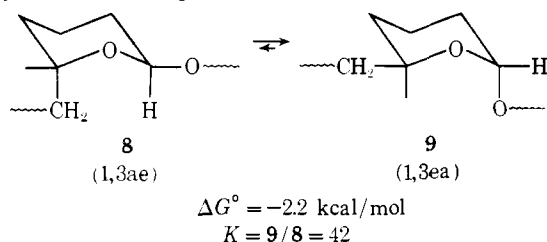
^a 1.4 M acetal and 0.05 M HCl in 20% (v/v) deuterium oxide-acetone. ^b Obtained from pmr analysis (Varian T-60).

SN₂ reaction using low temperatures and mild catalysts. More vigorous catalysts and higher temperatures favor the SN₁ mechanism and indiscriminate stereochemistry.^{1,3,5,6}

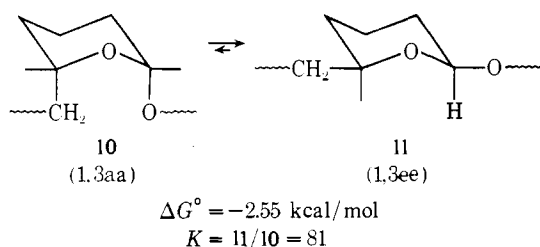
Stereochemistry of Propagation. Polymers **2** and **4** consist of linked 2-alkoxytetrahydropyran units. The conformational behavior of these ring units has been studied extensively.¹¹⁻¹⁶

Briefly, the conformational equilibrium for both cis and trans isomers will be determined by the interplay of two factors: (1) the familiar preference of alkyl substituents (chains) to exist in the equatorial conformation and (2) the preference of the alkoxy group to occupy an axial conformation (anomeric effect). The numerical parameters (kcal/mol) used for our calculations were:^{13,15} OCH_{3ax}-H_{ax}, 0.45; CH_{3ax}-H_{ax}, 0.90; CH_{3ax}-OCH_{3ax}, 2.5; OCH_{3eq}- (anomeric effect) 1.3.

6,8-DBO Propagation. For 6,8-DBO, a stereospecific direct displacement on monomer (which is necessarily cis) would afford a *trans*-1,3-tetrahydropyranoside which could *a priori* exist as a mixture of conformers **8** and **9**. The conformational situation has been given by Anderson and Sepp.¹⁵ Conformer **9** is calculated to be more stable than **8** by 2.2 kcal/mol and would therefore occur almost exclusively (*ca.* 98%) at equilibrium.

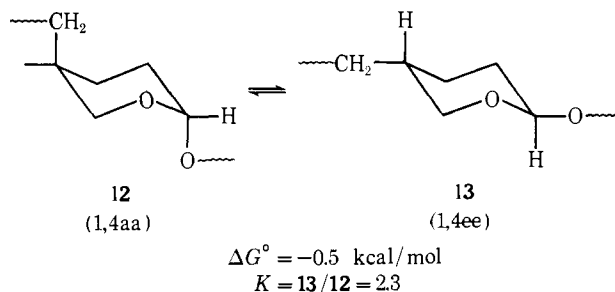


A possible *cis*-1,3-tetrahydropyranoside unit would be distributed between conformers **10** and **11**. The anomeric



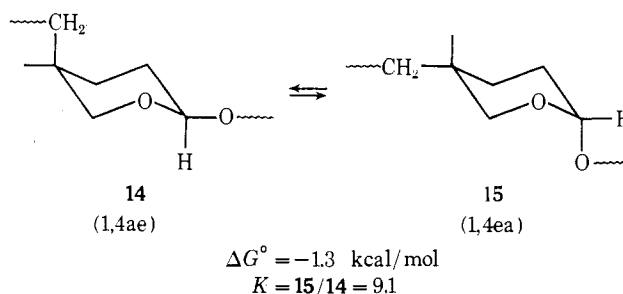
effect favors conformer **10**, but its severe syn-axial interaction between alkoxy and alkyl groups would highly favor **11** (*ca.* 99%). Consequently, any *cis*-1,3-tetrahydropyranoside units would be observable experimentally by pmr as an axial acetal hydrogen (τ 5.56). Only equatorial acetal hydrogen (τ 5.30) is observed experimentally at low temperatures, indicating *trans*-1,3-tetrahydropyranoside polymer and stereospecific SN₂ propagation.^{5,6} At higher temperatures, absorption at τ 5.56 begins to appear, indicating the onset of SN₁ character.

2,6-DBO Propagation. The case for 2,6-DBO is not as simple, because neither *trans* 1,4-units nor the *cis* 1,4-units would be conformationally homogeneous. For the conformers of the *trans* isomer, calculations show **13** to be more



stable than **12** by only 0.5 kcal/mol, resulting in an equilibrium mixture of 30% of **12** and 70% of **13**. Therefore, polymerization of 2,6-DBO to a *trans*-1,4-tetrahydropyranoside polymer by direct displacement on the trialkyloxonium ion by monomer would be detected by pmr as an (H_{ax})/(H_{eq}) ratio of 2.3.

The conformers of the *cis* isomer have a calculated free energy difference of 1.3 kcal/mol in favor of **15**, which represents an equilibrium mixture of 10% of **14** and 90% of **15**.



A carbonium ion as propagating species suffering attack equally from either side to give equal amounts of *cis* and *trans* units would afford a calculated (H_{ax})/(H_{eq}) ratio equal to 0.67.

The (H_{ax})/(H_{eq}) ratios observed experimentally are in good agreement with these calculated values. Our most stereoregular polymer, that obtained using 0.2 mol % of silicon tetrafluoride at -78° for 110 hr (expt 1), possessed an (H_{ax})/(H_{eq}) ratio of 3.0 as compared with a calculated value of 2.3. This is regarded as indicating pure SN₂ propagation. Similarly, experiments 12-15 gave an (H_{ax})/(H_{eq}) value of 0.59, as compared with the value of 0.67 calculated for pure SN₁ propagation. Intermediate ratio values have been converted in Table I to fractions of SN₂ propagation by the use of eq 1. The results suggested that four factors can influence the stereochemistry of propagation.

fraction SN₂ =

$$\frac{(H_{ax})/(H_{eq}) - 0.59}{3.0 - 0.59} = \frac{(H_{ax})/(H_{eq}) - 0.59}{2.41} \quad (1)$$

The polymerization temperature is the most significant factor. The (H_{ax})/(H_{eq}) ratio decreases uniformly with increasing temperature. This is probably due to a preference of SN₁ over SN₂ propagation at higher temperatures rather than to epimerization of the polymer after it has been formed. To exclude the latter possibility, polymer of run 7 was kept at -20° for 56 hr with 0.07 mol % FSA (conditions similar to run 10). The nmr spectrum showed that the original (H_{ax})/(H_{eq}) ratio had not changed significantly. Accordingly, negligible racemization of the polymer occurs at -78 or -20° at low catalyst concentrations, and these results correspond to kinetic control.

The nature of the catalyst is also important, as expected. The fluorine-containing catalysts tended to give stereoregular polymer, whereas iodine and methyl trifluoromethanesulfonate did not.

A third factor is the catalyst concentration. Comparison of runs 3 and 4 shows that with a high catalyst concentra-

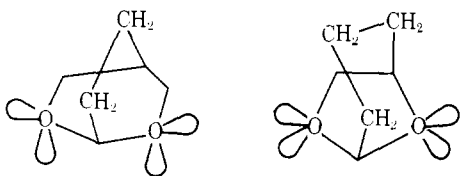
tion no stereoregular polymer is obtained, even at low temperature. Whether the high catalyst concentration favors S_N1 propagation or whether it causes subsequent racemization of the polymer was not established.

Finally, trace impurities may perhaps play a role in determining the precise degree of stereocontrol (compare runs 1 and 2). Monomer purified by distillation in a spinning band column is probably purer than that purified by sublimation.

Strain and Reactivity. Two factors contribute to the high reactivity of 2,6-DBO. The first is its possession of two six-membered rings in the boat form, with accompanying hydrogen eclipsing. This factor alone is enough to make cyclic ethers **16** and **17** polymerize.^{17,18} The second factor is the



anomeric effect, which applies to the monomer as well as to the polymer units (above). Edward¹⁹ ascribed the anomeric effect to a tendency to minimize dipole-dipole repulsions caused by the unshared pairs on oxygen. This is at a maximum when the pairs are parallel (Eliel's "rabbit-ear" effect). The accompanying formulas show that the lone pairs



are much more nearly parallel in 2,6-DBO than in 6,8-DBO. The combination of these two effects explains the high reactivity observed for 2,6-DBO.

The growing oxonium ion also possesses strain caused by the boat forms of the ring, although it is not clear whether a "rabbit-ear" repulsion is present here as well. However, the tendency for S_N1 propagation indicates that strains in the oxonium ion are sufficient to cause heterolysis to carbonium ion to a significant degree.

Experimental Section

Dimethyl 3,3-Dimethoxypropylmalonate (5). To 500 ml of absolute methanol (dried over Type "3A" molecular sieves) was added with stirring *ca.* 2 g (88 mg-atoms) of freshly cut sodium. The homogeneous solution was cooled to near 0° and 225 g (159 ml, 1.70 mol) of freshly distilled dimethyl malonate was rapidly added. To the mechanically stirred solution at 0° was added 84 g (102 ml, 1.50 mol) of freshly distilled acrolein over 2 hr. The reaction mixture was allowed to warm to room temperature and was stirred for 18 hr. The reaction was monitored by glc analysis using a 5 ft × 0.25 in. column of 3% SE30 on Varaport 30 at 165° with a carrier gas (He) flow of *ca.* 75 ml/min.

To the reaction mixture at 0° were added 10 ml (167 mmol) of glacial acetic acid and 100 g (0.91 mol) of fresh anhydrous calcium chloride. The mixture was allowed to warm to room temperature and vigorously stirred for 24 hr. Acetal formation was followed by glc analysis under the conditions described above.

Rotary evaporation of the reaction mixture gave a solid white mass. The solid was extracted with three 600-ml portions of methylene chloride. The extracts were washed individually with two 200-ml portions of cold water, one 200-ml portion of saturated potassium carbonate solution, and one 200-ml portion of saturated sodium chloride solution. The combined extracts were treated with activated charcoal, dried ($MgSO_4$), and subjected to rotary evaporation.

The crude product, 216 g, was obtained as a yellow oil and subjected to short-path vacuum distillation (bp 135–140° at 2.0 mm). A yield of 130 g of **5** was obtained which represents a 47% yield based on acrolein: bp 79° (0.08 mm); pmr ($CDCl_3$) τ 8.20

(m, 4), 6.72 (s, 6, CH_3O), 6.62 (t, 1, $J = 7$ Hz, $CH(CO_2CH_3)_2$), 6.30 (s, 6, CH_3O_2C), and 5.53 (t, 1, $J = 5.5$ Hz). *Anal.* Calcd for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 51.51; H, 7.74.

5,5-Dimethoxy-2-hydroxymethylpentanol (6). To a mechanically stirred slurry of 9.75 g (257 mmol) of lithium aluminum hydride in 200 ml of anhydrous ether at 0° was added dropwise 50 g (214 mmol) of **5** in 125 ml of anhydrous ether at such a rate so as to maintain a moderate reflux rate. The reaction mixture was allowed to reflux for 6 hr and stir at room temperature for 16 hr. To the reaction mixture was added cautiously 10 ml of ethyl acetate dropwise.

When destruction of the lithium aluminum hydride was complete, work-up was carried out as described by Fieser and Fieser.²⁰ To the reaction mixture were added dropwise and sequentially 9.75 ml of water, 9.75 ml of 15% sodium hydroxide solution, and 29.5 ml of water. A light yellow granular precipitate developed. The reaction mixture was filtered through Celite. The solids were extracted three times with 500-ml portions of ether. The condensed ether extracts were dried ($MgSO_4$) and concentrated by rotary evaporation. A few grains of potassium carbonate was added, and the crude liquid was pumped down to 0.03 mm. Heating was begun and 28 g (75%) of **6** distilled, bp 113–117° (0.03 mm); ir (neat) 3380 (broad), 2950, 2840, 1450, 1380, 1130 and 1050 cm^{-1} ; pmr (CCl_4) τ 8.73 (m, 5), 6.85 (s, 6, CH_3O), 6.77 (broad s, 4, CH_2OH), 6.27 (s, 2, OH), and 5.75 (t (broad), 1, $J \approx 1$ Hz). *Anal.* Calcd for $C_8H_{18}O_4$: C, 53.91; H, 10.18. Found: C, 53.81, 54.16, 54.26; H, 10.18, 10.14, 10.14.

2,6-Dioxabicyclo[2.2.2]octane (2,6-DBO, 3). A solution of 10 g (56.2 mmol) of **6** and 56 mg (0.30 mmol) of *p*-toluenesulfonic acid monohydrate in 1100 ml of dry, distilled, ethanol-free chloroform was allowed to reflux through a Soxhlet extractor for 16–18 hr; the Soxhlet thimble was charged with *ca.* 100 g of Type "4A" molecular sieves. After the mixture was cooled to room temperature, 15 g of finely ground anhydrous potassium carbonate was added, and the mixture was stirred for 2 hr. The reaction mixture was filtered and concentrated by rotary evaporation at or below room temperature. The crude brown oil was subjected to sublimation (50–55° at *ca.* 25 mm) to give 4.5 g (35%) of **3** which was shown to be pure by glc analysis on three different columns: ir (neat) 2940, 2860, 1420, 1460, 1475, 1370, 1330, 1260, 1200, 1175, 1070, 1005, 995, 926, 880, 860, and 835 cm^{-1} ; pmr (acetone- d_6) τ 7.98 (s, 5), 5.93 (s, 6), and 5.20 (s, 1); mass spectrum (70 eV) *m/e* (relative intensity) 114 (22), 86 (14), 58 (12), 57 (44), 44 (22), 40 (22), 32 (69), 29 (18), 28 (100). *Anal.* Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 63.20; H, 8.91.

Monomer **3** could be redistilled in a semimicro spinning band column, bp 120–121° (160 mm), mp 84.5–86.5° with preliminary softening in the range 70–75°.

Typical Polymerization of 2,6-Dioxabicyclo[2.2.2]octane (3). The monomer, stored at –60°, was purified twice by sublimation and used immediately. Care was exercised not to expose the hygroscopic **3** to atmospheric moisture. Dichloromethane was purified by distillation from calcium hydride and stored over molecular sieves ("3A" type). Polymerization solutions were prepared in an argon-filled polyethylene glove bag.

Two methods were employed to carry out polymerization. (1) In a clear, dry, thick-walled 15-ml polymerization tube, equipped with an 0.5 in. Teflon-coated magnetic stirring bar, were placed 250 mg (2.19 mmol) of **3** and 0.5 ml of dichloromethane. The tube was sealed with a fitted butyl-rubber gasket and a two-holed bottle cap and cooled to –78°; catalyst was introduced by means of either a gas-tight syringe or a prechilled 10- μ l glc syringe directly into the stirring solution. (2) Alternately, in one leg of a clear, dry Pyrex Y tube equipped with a 0.5-in. Teflon-coated magnetic stirring bar were placed 250 mg (2.19 mmol) of **3** and 0.25 ml of dichloromethane. In the other leg was placed 0.25 ml of dichloromethane. The tube was sealed with a rubber serum stopper and cooled. Catalyst was injected by means of a syringe into the solvent leg. Subsequently, the diluted catalyst was mixed with monomer solution to initiate polymerization.

The polymerization reaction was quenched by the addition of 10 ml of *n*-hexane-triethylamine (10:1 v/v). The precipitated polymer **4** was washed three times with 10-ml portions of *n*-hexane and redissolved in *ca.* 4 ml of dichloromethane. Any gel fraction formed during polymerization was separated by centrifugation and the soluble polymer reprecipitated into 40 ml of *n*-hexane. The

polymer was collected on a sintered glass funnel and dried under vacuum at room temperature for 48 hr. The polymer was weighed, and solutions were prepared in chloroform for determination of inherent viscosity (0.5% in chloroform) and pmr spectrum.

A number of samples of the homopolymer were selected randomly for elemental analysis. *Anal.* Calcd for $(C_6H_{10}O_2)_n$: C, 63.13; H, 8.83. Found: C, 63.25; H, 8.65; C, 62.78; H, 8.23; C, 63.42; H, 8.94; C, 63.38; H, 9.01.

Hydrolysis of Acetals. A solution of 120 mg (1.05 mmol) of 6,8-DBO in 0.6 ml of acetone-*d*₆ was prepared. To the solution was added a trace of tetramethylsilane as internal standard. The pmr spectrum (Varian T-60) was scanned and integrated. To the solution was added 0.15 ml of D₂O. The spectrum was scanned periodically over a 24-hr period. No reaction could be detected. To the pmr solution, now 1.5 M 6,8-DBO in 20% (v/v) aqueous acetone, was added 1.0 ml [0.038 mmol, (297°K, 699 mm)] of anhydrous hydrogen chloride from a gas-tight syringe to give a solution 0.05 M in HCl. The pmr spectrum was scanned and integrated at specific intervals. The disappearance of acetal was measured and the half-life calculated.

The reaction solution was diluted with *ca.* 2 ml of dichloromethane and stirred with 50 mg of potassium carbonate and 50 mg of anhydrous magnesium sulfate. The mixture was centrifuged and the liquid decanted and concentrated. The infrared spectrum showed a strong broad absorption at 3370 cm⁻¹ but no carbonyl band, indicating that the product of hydrolysis was the cyclic hemiacetal.

Exactly the same procedure was applied to 2,6-DBO. No detectable reaction in the neutral acetone-deuterium oxide occurred during several hours. However, according to a pmr scan taken immediately after the addition of the hydrogen chloride, the hydrolysis reaction to cyclic hemiacetal was complete.

The same procedure was used to determine the reactivity of methyl acetal.

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Crystalline Six-Coordinate Phosphorus Compounds Derived from Spiropentaoxyphosphoranes

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Abstract: Two new types of crystalline substances having six-coordinate phosphorus have been isolated. One of the substances has the charge distribution of a zwitterion and is derived from the reaction of a spiropentaoxyphosphorane with pyridine. The second substance has the charge distribution of an ion pair and is derived from the reaction of the spiropentaoxyphosphorane with phenol and triethylamine. This P(6) adduct differs from previously reported analogs in having two monodentate and two bidentate oxygen ligands attached to P(6).

The literature on organic compounds with P(6)² has been developing in recent years.³ Allcock⁴ described a salt of the type P(6)⁻R₃NH⁺ with six oxygen ligands attached to the phosphorus^{4,5} and more recently⁶ demonstrated the octahedral skeletal symmetry of the anion by X-ray crystallography. Denney⁷ prepared a related type of salt P(6)⁻Na⁺. Wolf⁸ recently described P(6) compounds with three different bidentate oxygen ligands. Barrans⁹ and Burgada¹⁰ have reported a series of salts in which the anion contains one hydrogen and five oxygen ligands, or one hydrogen, one nitrogen, and four oxygen ligands.¹⁰

Derivatives of P(6) with six aromatic carbons as ligands have been known for some time from the work of Wittig¹¹ and of Hellwinkel.¹² The field of the alkyl- and arylfluorophosphates, (RPF₅)⁻ and (R₂PF₄)⁻, has been investigated

by Schmutzler¹³ who also summarized the earlier literature. An interesting type of fluorophosphate zwitterion was described by Brown and Bladon.¹⁴

The most distinctive feature of the P(6) derivatives is their ³¹P nmr chemical shift^{13,15} which appears in general at a much higher magnetic field than the shift of the related P(5) and P(4) structures.³⁻¹⁵

Previous work in this laboratory¹⁶⁻¹⁸ led to the hypothesis that the base-catalyzed exchange of alkoxy ligands, which is observed when oxyphosphoranes are treated with alcohols, proceeds *via* octahedral P(6) species.¹⁶⁻¹⁹ Related observations have been interpreted by Denney, *et al.*,²⁰ in analogous terms. Recent work by Archie and Westheimer²¹ provided support for this hypothesis. Octahedral P(6) intermediates have also been suggested²² to explain the slow ex-