Effect of Alkyl Substitution on the Ease of Oxidation of Bicyclo[1.1.0]butanes. Experimental Verification of PRDDO Calculations for the Nature of the HOMO of Bicyclo[1.1.0]butane

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Abstract: Bicyclo[1.1.0]butane and eight methylated derivatives were synthesized and the oxidative half-wave potentials of each of these nine compounds were measured vs. a saturated calomel electrode by using single sweep voltammetry. The half-wave potentials varied from 1.69 V for bicyclo[1.1.0]butane to 0.93 V for 1,2,2,3,4,4-hexamethylbicyclo[1.1.0]butane. Bridgehead substitution resulted in an average decrease in half-wave potential of 0.29 V per methyl group, while methyl substitution at either the 2- or 4-position resulted in only a 0.05 V average decrease. Molecular orbital calculations using the partial retention of diatomic differential overlap (PRDDO) method gave the wave functions for each of the compounds studied. The vertical ionization potentials for each of the 29 possible methylated bicyclo[1.1.0]butanes and for the parent hydrocarbon were obtained via Koopmans' theorem. In all cases, methyl substitution was found to lower the ionization potential. The largest effect was found for bridgehead substitution and the smallest effect resulted from substitution at the 2- and 4-exo positions. The experimentally obtained oxidative half-wave potentials correlated with the calculated vertical ionization potentials with r = 0.978. These results provide strong evidence in support of the theoretical predictions that the HOMO of bicyclo[1.1.0]butane is localized in the C_1-C_3 bond.

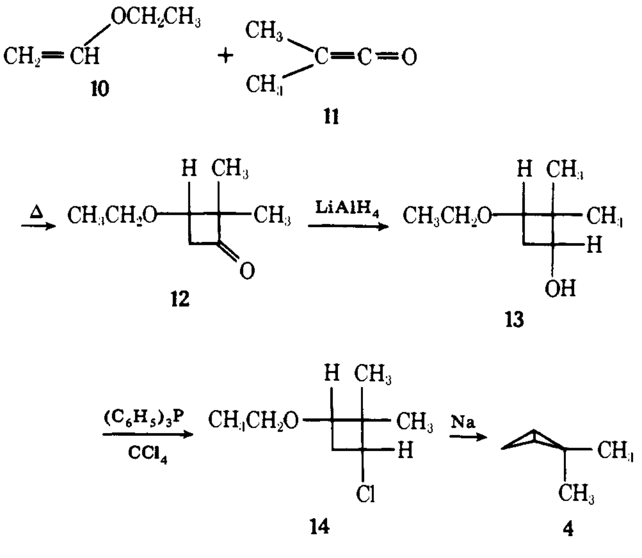
Introduction

The bicyclo[1.1.0]butane nucleus has been the subject of much theoretical interest because of its unusually reactive nature. Theoretical calculations have indicated that the highest occupied molecular orbital (HOMO) of bicyclo[1.1.0]butane (**1**) is localized in the C_1-C_3 region and thus can be associated with the C_1-C_3 carbon-carbon bond.[2] Experimental verifications of these calculations have been difficult to obtain. The reason for the equivocation in substantiating these theoretical predictions is the ease with which the cyclopropylcarbinyl system is equilibrated with the cyclobutyl system. Because of this facile interconversion, most chemical tests fail to establish whether the C_1-C_2 bond or the C_1-C_3 bond of **1** is cleaved in the initial phases of a reaction of **1**. As a result of our recent findings that highly strained polycyclic hydrocarbons are readily oxidized[3] and that their oxidative half-wave potentials reflect the energy of the HOMO of the hydrocarbon,[4] we felt that we could provide an unequivocal experimental test of the theoretical predictions concerning the HOMO of the bicyclo[1.1.0]butane. We now wish to report a systematic study of the oxidation of a series of eight methyl substituted bicyclo[1.1.0]butanes (**2–9**) and of the parent hydrocarbon, **1**. This study verifies that electron transfer occurs from the C_1-C_3 bond of **1**.

We desired to couple this experimental approach with a theoretical molecular orbital study of the properties of these same nine hydrocarbons. For a large series of methylated bicyclo[1.1.0]butane derivatives, it would be prohibitively costly in terms of computer time to do ab initio molecular orbital calculations with large basis sets. Therefore, we utilized the approximate molecular orbital method, partial retention of diatomic differential overlap (PRDDO),[5] to obtain wave functions not only for compounds **1–9** but also for the other 21 methylated bicyclo[1.1.0]butanes which were not studied experimentally. In this manner, we were able to more fully examine the trends suggested by the experiments.

Synthesis. A large number of methylated bicyclo[1.1.0]butanes have been reported in the literature.[6] Fortunately, we could take advantage of this prior art in the preparation of the desired series.[7] An exception to this approach was provided by compound **4** which had not been previously described. The synthesis is outlined in Scheme I. Treatment of ethyl vinyl ether (**10**) with dimethyl ketene (**11**) gave the cyclobutanone derivative, **12**, in 20% yield. Reduction of **12** with lithium aluminum hydride gave an 84% yield of **13** as a single isomer. After experiencing failure with several approaches to the conversion of **13** to **14**, we found that the use of triphenylphosphine–carbon tetrachloride[8] permitted the reaction to be carried out in 54% yield. Treatment of the chloride, **14** with sodium gave a 40% yield of **4**. The spectral properties of **4** were all consistent with the assigned structure (see Experimental Section).

Scheme I



Oxidative Studies. Listed below in Table I are the half-wave potentials for a series of methyl-substituted bicyclo[1.1.0]butanes. All values were obtained by single sweep voltammetry (sweep rate 100 mV/s) on a Princeton Applied Research

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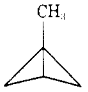
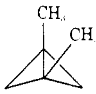
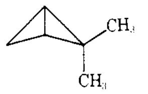
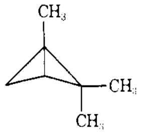
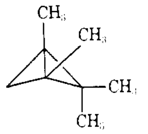
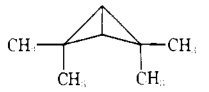
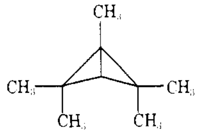
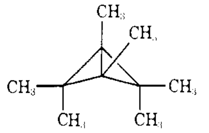
Table I. Half-Wave Oxidation Potentials for Methyl-Substituted Bicyclo[1.1.0]butanes vs. SCE[a]

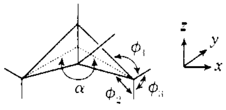
compd no.	compd	$E_{1/2}$ (±0.02 V)
1		1.69
2		1.47
3		1.10
4		1.56
5		1.27
6		1.03
7		1.57[b]
8		1.20
9		0.93

[a] The values cited assume that the measured electrode potentials are kinetically shifted (due to follow-up reactions) relative to the *reversible* potentials for each hydrocarbon. [b] For all values except this, the experimental error was ±0.02 V. For **7**, the margin of error appeared to be slightly larger due to the anomalous instability of **7** under the reaction conditions.

Model 174 polarographic analyzer equipped with platinum electrodes vs. a saturated calomel electrode (SCE). All measurements were made in high purity acetonitrile containing 0.1 M tetraethylammonium fluoroborate as supporting electrolyte and 0.5 mM pyridine as base. Substrate concentration was ca. 10^{-3} M.

As can be seen from Table I, methyl substitution on either one or both bridgehead positions resulted in a major and roughly additive reduction of the oxidative half-wave potential. This can be noted in the series **1-3**, **4-6**, and **7-9**. For these series, both the first and the second addition of a bridgehead methyl group results in an average decrease of 0.29 V in the half-wave potential. In stark contrast, substitution of a methyl group at C-2 or C-4 resulted in an average decrease of 0.05 V per methyl. This is illustrated by the three series: (a) **1**, **4**, **7**, (b) **2**, **5**, **8**, and (c) **3**, **6**, **9**. The relatively large effects of substituents at both the 1- and 3-positions in comparison with the effects of substituents at the 2- and 4-positions leaves little doubt that the oxidation of these bicyclo[1.1.0]butanes involves removal of an electron from the molecular orbital associated with the C_1-C_3 bond. This would appear to provide strong experimental support for the theoretical conclusion discussed below which states that the HOMO of bicyclo[1.1.0]butane is associated with this same bond.

Table II. Comparison of Geometries between Bicyclo[1.1.0]butane and the *endo,endo*-Dimethyl-Substituted Derivative



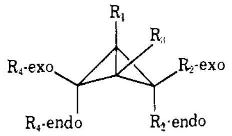
angle	bicyclo[1.1.0]-butane[a]	*endo,endo*-dimethylbicyclo-[1.1.0]butane[b]
α	122° 40 min	135° 48 min
ϕ_1	122° 52 min	116° 40 min
ϕ_2	121° 34 min	131° 02 min
ϕ_3	115° 44 min	112° 18 min

[a] See reference 9. [b] Optimized in this study.

Theoretical Studies. As part of our general program of examining the electronic structure of strained hydrocarbon systems, we have calculated the electronic structure of all 29 different methyl-substituted bicyclo[1.1.0]butanes and of the parent system using the PRDDO molecular orbital method.[5] PRDDO is an approximate molecular orbital method with no empirical parameters that incorporates all electrons with a minimum basis set of Slater orbitals. This methods gives results in good agreement with ab initio methods employing Slater or STO-3G minimum basis sets.[5b] However, it is 10-20 times computationally faster than calculations using the STO-3G basis set. All calculations were carried out using the PRDDO program on a Cyber 74 computer. We employed the experimental geometry[9] for bicyclo[1.1.0]butane in all calculations except as discussed below. The standard molecule basis set of Hehre, Stewart, and Pople[10] for carbon was employed in these calculations while the exponent for the H(1S) orbital was set at 1.2. All methyls were substituted at a C-C distance of 1.54 Å, with C-H distances of 1.09 Å and all methyl group angles tetrahedral. For the monosubstituted and dibridgehead derivatives, rotation barriers for the methyl groups were calculated and found to be small, suggesting that we were not introducing steric crowding. All molecules with two endo methyl groups had their geometry taken from the endo, endo-disubstituted molecule, which was partially geometry-optimized due to steric crowding of these methyl groups. Even after optimization, the endo, endo-disubstituted molecule is still the least energetically stable of the disubstituted isomers. Our optimized results are in good agreement with the results predicted for such substitution patterns by Newton and Schulman[11] using ab initio calculations on bicyclo[1.1.0]butane. In Table II, the bicyclo[1.1.0]butane results are compared with the optimized results for the endo, endo-disubstituted derivative. The flap angle increases upon substitution and the entire CMeH group rocks up.[12]

In Table III, the ionization potentials derived from Koopmans' theorem[13,14] are given as are energy differences between isomers relative to the most stable isomer with the same number of methyl substituents. Although the absolute numerical value of the ionization potential may be in error, we expect that the trends in ionization potentials should be reproduced well.[14] By studying the full set of 30 molecules, trends in ionization potentials can be more easily discerned. Addition of a single methyl group lowers the ionization potential, with the greatest decrease (0.31 eV) occurring for substitution at the bridgehead position. Substitution at the endo position lowers the ionization potential by 0.17 eV, while substitution at the exo position lowers the ionization potential very slightly

Table III. Ionization Potentials and Relative Energy Differences for Methyl-Substituted Bicyclo[1.1.0]butanes



	molecule (substituent position)[a]						IP	ΔE[b]
	R_1	$R_{2\text{-exo}}$	$R_{2\text{-endo}}$	R_3	$R_{4\text{-exo}}$	$R_{4\text{-endo}}$	(eV)	(kcal/mol)
			unsubstituted					
1	H	H	H	H	H	H	8.97	
			monosubstituted					
2	Me	H	H	H	H	H	8.66	0.0
15	H	Me	H	H	H	H	8.92	2.0
16	H	H	Me	H	H	H	8.80	6.6
			disubstituted					
3	Me	H	H	Me	H	H	8.24	0.0
17	Me	Me	H	H	H	H	8.58	2.2
18	H	Me	H	H	Me	H	8.88	3.2
19	Me	H	Me	H	H	H	8.48	6.0
4	H	Me	Me	H	H	H	8.77	7.7
20	H	Me	H	H	H	Me	8.77	8.8
21	H	H	Me	H	H	Me	8.58	16.6
			trisubstituted					
22	Me	Me	H	H	Me	H	8.53	0.0
23	Me	Me	H	Me	H	H	8.20	0.8
24	Me	H	Me	Me	H	H	8.15	1.2
5	Me	Me	Me	H	H	H	8.46	3.6
25	Me	Me	H	H	H	Me	8.44	3.7
26	H	Me	Me	H	Me	H	8.75	4.5
27	Me	H	Me	H	H	Me	8.31	12.6
28	H	Me	Me	H	H	Me	8.58	15.0
			tetrasubstituted					
29	Me	Me	H	Me	Me	H	8.16	0.0
6	Me	Me	Me	Me	H	H	8.12	2.6
30	Me	Me	H	Me	H	Me	8.12	2.7
31	Me	Me	Me	H	Me	H	8.43	4.2
32	Me	H	Me	Me	H	Me	8.02	11.6
7	H	Me	Me	H	Me	Me	8.60	16.2
33	Me	Me	Me	H	H	Me	8.31	17.2
			pentasubstituted					
34	Me	Me	Me	Me	Me	H	8.10	0.0
35	Me	Me	Me	Me	H	Me	8.01	15.7
8	Me	Me	Me	H	Me	Me	8.31	17.9
			hexasubstituted					
9	Me	Me	Me	Me	Me	Me	8.00	

[a] Me = methyl group. [b] ΔE is calculated relative to the most stable isomer with the same number of methyl substituents.

(0.05 eV). These general effects basically determine the variation in ionization potential. Addition of a second methyl group at the bridgehead position lowers the IP by 0.42 eV, the largest change, while addition of a second endo group to the endo-monosubstituted derivative lowers the IP an additional 0.22 eV. However, addition of a second exo-methyl group only lowers the IP by 0.04 eV. As can be seen for the other mixed disubstituted derivatives, these general trends are followed. For the trisubstituted derivatives, the lowest IP is found, as expected, by extrapolation of the above discussion, for the endo, dibridgehead trisubstituted isomer, **14** (8.15 eV), while the highest IP would be found for the endo, exo, exo trisubstituted species, **17.** In the trisubstituted isomers, an interesting lowering of the IP is found for the bridgehead, exo, exo derivative, **12,** which shows a decrease of 0.13 eV when compared with the monosubstituted bridgehead derivative. In this instance, the exo substituents give an additive effect rather than no effect and the IP is lowered. These general trends continue with the higher substituted derivatives. The lowest IP is found for the hexamethyl substituted derivative.

Since no extensive geometry optimization was carried out, the ΔE values for a group of isomers with the same number of substituents (Table III) are not accurate but should give a correct prediction of the qualitative features. Thus, adding a bridgehead substituent tends to give the most stable configuration, while addition of endo substituents gives the least stable configuration. Much of the destabilization of adding two endo groups is due to the necessity of increasing the value of the flap angle, α, to relieve the steric crowding. As shown in Table III, there is no direct correlation between decreasing energetic stability and decreasing ionization potential for a given number of substituents.

In order to help in obtaining a simple physical picture for these results, we have investigated the atomic orbital character of the HOMO and have examined the dependence of the IP on the flap angle, α, for the parent hydrocarbon, bicyclo[1.1.0]butane. The IP is found to increase as the angle decreases. This result has also been predicted by Bischof, Gleiter, and Müller[15] using the MINDO/3 method. At the experimental geometry, the HOMO (in the canonical molecular orbital sense) is found to be localized in the region of the bridgehead bond with about 50% P_y character (σ) which is directed on the C-C axis and 50% P_z character (π) corresponding to density perpendicular to this axis (Table II). Thus, the bond is significantly bent and contains significant π-type character. It is also interesting to note that in bicyclo[1.1.0]-

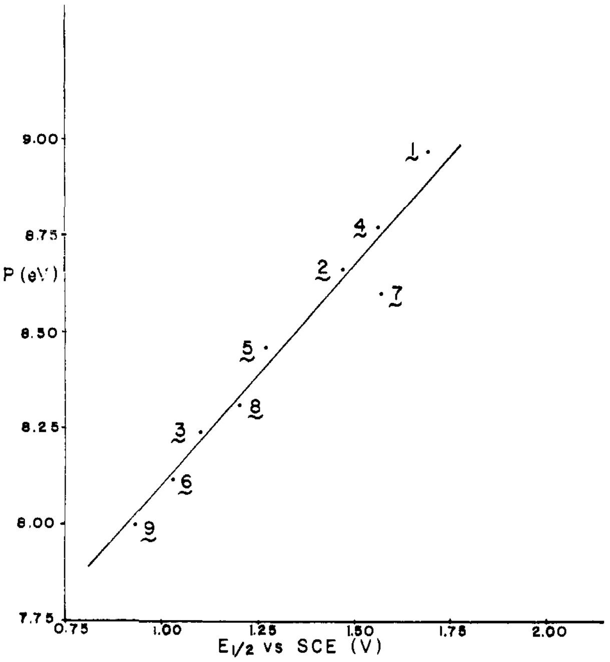


Figure 1. Plot of calculated vertical ionization potentials vs. measured oxidation half-wave potentials.

butane there is some contribution (0.1*e*) to the HOMO from the endo hydrogens. It is not surprising, then, that the endo substituents cause a larger lowering than do the exo substituents. Examination of the character of the HOMO as the flap angle is varied shows that, for smaller flap angles (large IP), the P_y character increases at the expense of the P_z orbitals giving more σ bonding than π bonding. Thus, decreasing the π character of the HOMO leads to a stabilization of this orbital, while increasing the flap angle leads to an increase in the π character and a destabilization of the HOMO.

Discussion

It is interesting to note that, in highly strained hydrocarbon systems, the HOMO is normally associated with C-C bonding, while, in unstrained alkanes, the HOMO is associated with C-H bonding. This is clearly due to a raising of the C-C bonding molecular orbital and not to a lowering of the C-H bonding molecular orbital. The ease of oxidation of the series of nine hydrocarbons discussed above is consistent with this picture.

In order to correlate theory with experimental data, we have related the calculated vertical ionization potentials with the measured half-wave potentials. Figure 1 shows a plot of our measured oxidative half-wave potentials vs. the calculated vertical ionization potentials (IP) as determined from Koopmans' theorem. As can be seen from the figure, a reasonable correlation exists (r = 0.978). From these data it can be seen that IP = $1.16E_{1/2} + 6.94$. While several correlations of this type have been previously reported (oxidation potentials vs. ionization potentials),[4] we believe that this particular correlation emphasizes the corroboration of theory and experiment to establish what many had believed, but no one had proven. Overall, we feel that this study leaves little doubt but that the HOMO of bicyclo[1.1.0]butane and many of its derivatives is associated with the C_1-C_3 bond.

We are continuing to explore the role of substituents in influencing the energy levels of a variety of highly strained polycyclic hydrocarbons using both experimental and theoretical methods.

Experimental Section

Bicyclo[1.1.0]butanes. Compounds **1**, **2**, **5**, **6**, **7**, **8**, and **9** were prepared according to literature procedures.[6]

1,3-Dimethylbicyclo[1.1.0]butane (3). A solution of *n*-butyllithium in *n*-octane was prepared by removal of the hexane from a commercial sample of 5.0 mL of a hexane solution of 2.4 M *n*-butyllithium, followed by addition of 5 mL of *n*-octane. To this solution were added 12.0 mmol of tetramethylethylenediamine and 464 mg of 1-methylbicyclo[1.1.0]butane (**2**)[6] at 0 °C. The reaction mixture was stirred at 25 °C under a nitrogen atmosphere for 48 h. The reaction mixture was cooled to 0 °C and 12.0 mmol of methyl iodide was added dropwise over a 10-min period. The reaction mixture was stirred at 0 °C for 30 min. The reaction mixture was washed with two 2-mL portions of saturated copper sulfate solution, three 2-mL portions of water. The reaction mixture was dried over anhydrous potassium carbonate and the product was isolated by distillation from the drying agent to give 487 mg of distillate, bp 54-65 °C. The sample used in the oxidation studies was further purified by preparative GC on a 5% OV-101 on 60-80 Chromosorb W column (5 ft × 0.25 in.). The spectral properties of **3** prepared by this method were identical with those given by Doering and Coburn.[6]

1-Ethoxy-2,2-dimethylcyclobutan-3-one (12). Compound **12** was prepared in 20% yield according to the procedure of Hasek et al.[16]

1-Ethoxy-3-hydroxy-2,2-dimethylcyclobutane (13). A solution of 8.17 g of **12** in 20 mL of diethyl ether was added dropwise to a stirred suspension of 1.33 g of lithium aluminum hydride in 50 mL of diethyl ether at 0 °C under nitrogen. After stirring for 1 h at 0 °C the reaction mixture was quenched by the sequential dropwise addition of 1.3 mL of water, 1.3 mL of 3.8 M sodium hydroxide solution, and 3.9 mL of water. The suspended salts were removed by filtration and the filtrate was distilled to yield 6.95 g (84%) of **13**, bp 93 °C (25 mm): IR (neat) 3400, 2980, 2950, 2875, 1462, 1343, 1215, 1109, 1078, 1029, and 987 cm^{-1}; NMR (CCl_4) δ 3.30 (2 H, q, J = 7 Hz), 3.20 (2 H, m), 2.40 (2 H, m), 1.70 (1 H, m), 1.11 (3 H, t, J = 7 Hz), 1.09 (3 H, s), 0.92 (3 H, s).

Anal. Calcd for $C_8H_{16}O_2$: C, 66.61; H, 11.19. Found: C, 66.81; H, 11.13.

1-Ethoxy-3-chloro-2,2-dimethylcyclobutane (14). A solution of 6.75 g of **13** in 100 mL of carbon tetrachloride containing 18.4 g of triphenylphosphine was refluxed under nitrogen for 16 h. The solvent was distilled from the reaction followed by direct distillation of the product to give 4.35 g (54%) of **14**, bp 63-65 °C (25 mm): IR (neat) 2980, 2940, 2880, 1465, 1345, 1125, 1080, 1047, 976, and 856 cm^{-1}; NMR (CCl_4) δ 3.95 (1 H, m), 3.65 (1 H, m), 3.30 (2 H, q, J = 7 Hz), 2.30 (2 H, m), 1.12 (3 H, s), 1.11 (3 H, t, J = 7 Hz), 1.07 (3 H, s).

Anal. Calcd for $C_8H_{15}OCl$: C, 59.05; H, 9.30. Found: C, 58.84; H, 9.29.

2,2-Dimethylbicyclo[1.1.0]butane (4). A 100-mL, three-necked flask was equipped with a dropping funnel, thermometers and 30-cm Vigreaux column. A stirred suspension of 5.0 g of sodium in 50 mL of freshly distilled 1,4-dioxane was heated to reflux and 4.15 g of **14** was added dropwise over a 0.5-h period. During this time, a slow nitrogen flow was passed through the dropping funnel and out through the distillation column and into a receiver which was cooled to −78 °C. After an additional 30 min of refluxing, the reaction was stopped and the material in the receiver flask was redistilled to yield 1.0 g (40%) of **4**, bp 65-80 °C. This material was contaminated with traces of 1,4-dioxane. An analytical sample was obtained by preparative GC on a 10 ft × 0.25 in., 3% Amine 220 on 60-80 Chromosorb G column at 60 °C: IR (CCl_4) 2980, 2955, 2925, 1459, 1377, 1348, 1076, 1050, 987, and 858 cm^{-1}; NMR (CCl_4) δ 1.60 (1 H, m), 1.20 (3 H, m), 1.05 (3 H, s), 0.80 (3 H, s), high resolution mass spectrum m/e calcd for C_6H_{10}: 82.0782. Found: 82.0789.[17]

Electrochemical Procedures. Acetonitrile (Aldrich Chemical Co. or Fisher Scientific Co. ACS grade) was refluxed with calcium hydride under a slight positive nitrogen pressure for several hours and distilled, followed by a similar treatment with phosphorus pentoxide. A center fraction was taken in each distillation.

Tetraethylammonium tetrafluoroborate was prepared by neutralizing tetraethylammonium hydroxide with tetrafluoroboric acid, recrystallizing three times from ethanol-water, followed by drying in a vacuum oven at 60 °C for 24 h.

The electrochemical instrumentation consisted of a Princeton Applied Research Corporation Model 174 polarographic analyzer equipped with a Houston 2000 XY recorder. A Tektronix Model 564 storage oscilloscope was used for relatively fast sweep (>100 mV/s) experiments. An undivided cell was used with a saturated calomel electrode isolated by two bridges, the first a saturated potassium chloride solution, the second a solution of 0.1 M tetraethylammonium tetrafluoroborate in acetonitrile. No adjustment was made for junction potential effects. No contamination of the substrate solution by chloride was observed during the typical analysis time of less than 30 min. The stationary platinum wire anode (6 × 0.57 mm) was preconditioned according to the following procedure before each sample was examined: (1) 30-s wash with 1 M chromium trioxide in concentrated sulfuric acid, then distilled water rinse; (2) 30 s wash with 1 M ferrous ammonium sulfate in 1 M sulfuric acid, water rinse, and dry; (3) 60 s with 0.00 V vs. SCE applied to the electrode immersed in the electrolyte solution with stirring followed by 60 s without stirring. The last treatment was repeated before each run. Each reported half-wave potential is an average of at least four runs using a sweep rate of 100 mV/s.

No cathodic waves were observed at scan rates up to 20V/s.[18]

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References and Notes

(1) Alfred P. Sloan Foundation Research Fellow (1977–1979), Camille and Henry Dreyfus Teacher-Scholar Awardee (1978–1983), and Du Pont Young Faculty Grantee (1978).

(2) M. D. Newton in "Modern Theoretical Chemistry: Applications of Electronic Structure Theory", Vol. 3, H. F. Schaeffer III, Ed., Plenum, New York, 1977, p 223.

(3) P. G. Gassman, R. Yamaguchi, and G. F. Koser, *J. Org. Chem.* **43,** 4392 (1978).

(4) P. G. Gassman and R. Yamaguchi, *J. Am. Chem. Soc.*, **101,** 1308 (1979).

(5) (a) T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.*, **58,** 1569 (1973); (b) T. A. Halgren, D. A. Kleier, J. H. Hall, Jr., L. D. Brown, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **100,** 6595 (1978).

(6) Most of the bicyclo[1.1.0]butanes which were studied as part of this investigation have been previously described in the literature: **1,** D. M. Lemal, F. Menger, and G. W. Clark, *J. Am. Chem. Soc.*, **85,** 2529 (1963); J. B. Sieja, *ibid.*, **93,** 130 (1971); **2** and **7,** H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkovsky, and J. B. Sieja, *ibid.*, **93,** 121 (1971); P. G. Gassman and R. R. Reitz, *J. Organomet. Chem.*, **52,** C51 (1973); **3,** W. von E. Doering and J. F. Coburn, *Tetrahedron Lett.*, 991 (1965);[7] **5** and **6,** L. Skattebøl, *ibid.*, 2361 (1970); W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *ibid.*, 2365 (1970); **8,** D. P. G. Hamon, *ibid.*, 3143 (1969); D. P. G. Hamon, *Aust. J. Chem.*, **28,** 2641 (1975); L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Am. Chem. Soc.*, **94,** 7780 (1972); **9,** D. P. G. Hamon, *ibid.*, **90,** 4513 (1968); D. P. G. Hamon, *Aust. J. Chem.*, **27,** 153 (1974); L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Am. Chem. Soc.*, **94,** 7780 (1972).

(7) Compound **3** was prepared in our laboratory by the methylation of 1-methylbicyclo[1.1.0]butane rather than according to the literature method. In both cases, the spectral data were identical with those in the literature.

(8) I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind.* (*N.Y.*) 900 (1966).

(9) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50,** 1976 (1969).

(10) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51,** 2657 (1969).

(11) M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.*, **94,** 767 (1972).

(12) Comparison of total energies for addition of a methyl group to form the most stable isomer for a given number of substituents showed only small variations, i.e., $E(\mathbf{2}) - E(1) = -39.00988$ au as compared with $E(\mathbf{5}) - E(\mathbf{2}) = -39.00839$ au. This suggests that we are not introducing steric effects by adding substituents.

(13) T. Koopmans, *Physica* (*Utrecht*), **1,** 104 (1934).

(14) Justification of the vertical ionization potentials derived from the use of Koopmans' theorem was obtained in a preliminary study through the calculation of the energies of selected bicyclo[1.1.0]butyl cation radicals using the PRDDO method. Utilizing the experimental geometry for bicyclo[1.1.0]butane[9] the incremental differences in vertical ionization potential energies calculated by Koopmans' theorem (KT) and the PRDDO values for the cation radicals relative to the parent system are: *exo*-2-methylbicyclo[1.1.0]butyl, $KT = -0.05$ eV, PRDDO = −0.13 eV; *endo*-2-methylbicyclo[1.1.0]butyl, $KT = -0.17$ eV, PRDDO = −0.26 eV; 1-methylbicyclo[1.1.0]butyl, $KT = -0.31$ eV, PRDDO = −0.38 eV.

(15) P. Bischof, R. Gleiter, and E. Müller, *Tetrahedron*, **32,** 2769 (1976).

(16) R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, **29,** 1239 (1964).

(17) Standard elemental analysis failed to yield a satisfactory analysis for **4,** even though all standard methods indicated that this material was pure. However, we noted that the compound did not store well and that it decomposed fairly rapidly at room temperature.

(18) Irreversible anodic waves were found in all cases. A wide variation in conditions, involving both solvent changes and sweep rate changes, did not permit the observation of a corresponding cathodic wave. The values of the half-wave potentials were determined by subtraction of the solvent background and establishment of the base line followed by introduction of a line parallel to the base line through the peak of the current curve. A line midway between these two parallel lines was then drawn. The point at which this third line intersected the anodic wave was taken as the half-wave potential. Literature values for compounds of known half-wave potential were readily reproduced using this method.

Synthesis of α-(1→3)-Branched Dextrans by Copolymerization and α-D-Glucosidation

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Abstract: A family of stereoregular (1→6)-α-D-glucopyranans with randomly distributed 3-*O*-(α-D-glucopyranosyl) side chains has been synthesized as models of microbial dextrans, by the following series of reactions: 1,6-anhydro-2,4-di-*O*-benzyl-3-*O*-but-2-enyl-β-D-glucopyranose (DBCGL, M_1) has been copolymerized with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (TBGL, M_2) to give a series of polymers of very high molecular weight. Crotyl groups are removed quantitatively and side chains introduced by reaction of the hydroxylated polymers with 6-*O*-(*N*-phenylcarbamoyl)-2,3,4-tri-*O*-(*p*-methylbenzyl)-1-*O*-tosyl-D-glucopyranose. Decarbanilation and debenzylation gave a family of dextrans with different degrees of branching. The polymers have been characterized by viscosity, optical rotation, circular dichroism, molecular weight, and ^{1}H and ^{13}C NMR. Weight fractions and sequence length distributions of the branched unit have been calculated from copolymerization data. Comparisons of structure and ^{13}C NMR spectra are made with dextrans from various strains of *Leuconostoc mesenteroides*.

Introduction

Stereoregular homo- and heteropolysaccharides have been synthesized by cationic ring opening polymerization of 2,3,4-tri-O-substituted 1,6-anhydrosugars followed by removal of the substituents with sodium in liquid ammonia.[1] The resulting products have been used to investigate lectin–carbohydrate reactions[2,3] and as model compounds in the fields of allergy,[4,5] enzymology,[6] and immunology.[7,8]

The α-(1→6)-linked glucopyranan formed by polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (TBGL) corresponds to the backbone of most natural dextrans

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