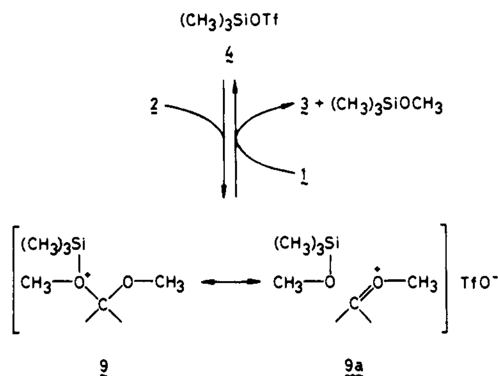
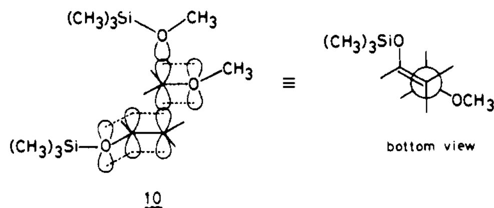
action creating new chiral centers, a high to moderate degree (depending on the systems) of stereoselectivity is obtained. Both (E)- and (Z)-enol silyl ethers give the erythro adducts selectively (entries 3–6 and 12–14), in sharp contrast to the stereoselection observed in ordinary aldol reaction.[3-5,6a]

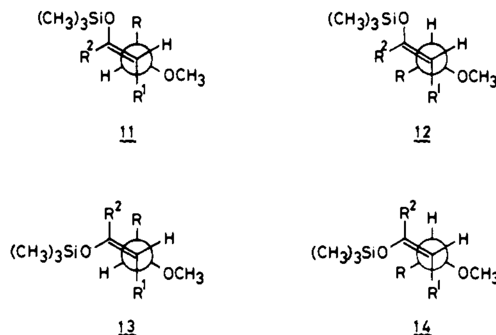
The use of trimethylsilyl moiety as both protecting group of enolates and initiator of the reaction allows this group serving as the chain carrier of the catalytic cycle involving supercationic species.[12] Electrophilic attack of the silyl triflate **4** on an oxygen atom of the acetal **2** generates the reactive oxonium intermediate **9**[13] that is in resonance with a methylcarboxonium ion/methoxytrimethylsilane contact pair, **9a.**[14]



Subsequent nucleophilic displacement by the enol silyl ether **1** gives rise to the condensation product **3** and methoxytrimethylsilane, accompanied by regeneration of the catalyst **4.**[15] The observed stereoselection is best accounted for in terms of the acyclic extended transition states of type **10** in which



electrostatic repulsion is minimized. In the reaction of enol silyl ethers possessing E configuration, the transition state **11** (R = phenyl or alkyl; R^1 and R^2 = alkyl) leading to the erythro isomer is sterically favored over the diastereomeric transition state **12** affording the threo adduct, in accord with the experimental findings (entries 3–6 and 13). In a like manner, the erythro transition state **13** (R = phenyl; R^1 = alkyl; R^2 = phenyl or alkyl) resulting from (Z)-enol silyl ethers is preferable to the alternative threo transition state **14** (entries 12 and 14).



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Supplementary Material Available: Spectral and analytical data for new compounds (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Trialkylsilyl Triflates. 5. Part 4: Murata, S.; Noyori, R. *Tetrahedron Lett.* **1980,** *21,* 767.

(2) Reviews: Nielsen, A. T.; Houlihan, W. J. *Org. React.* **1968,** *16,* 1. House, H. O. "Modern Synthetic Reactions", 2nd ed.; Benjamin: Menlo Park, 1972, pp 629–682.

(3) (a) Li^+: Kleschick, W. A.; Buse, C. T.; Heathcock, C. H. *J. Am. Chem. Soc.* **1977,** *99,* 247. (b) Li^+: Dubois, J. E.; Fellmann, P. *Tetrahedron Lett.* **1975,** 1225. Buse, C. T.; Heathcock, C. H. *J. Am. Chem. Soc.* **1977,** *99,* 8109. Meyers, A. I.; Reider, P. J. *Ibid.* **1979,** *101,* 2501. Heathcock, C. H.; White, C. T. *Ibid.* **1979,** *101,* 7076. Heathcock, C. H.; Pirrung, M. C.; Buse, C. T.; Hagen, J. P.; Young, S. D.; Sohn, J. E. *Ibid.* **1979,** *101,* 7077. (c) Li^+, Mg^{2+}, Zn^{2+}: House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *Ibid.* **1973,** *95,* 3310.

(4) B^{3+}: Mukaiyama, T.; Inoue, T. *Chem. Lett.* **1976,** 559. Inoue, T.; Uchimaru, T.; Mukaiyama, T. *Ibid.* **1977,** 153. Fenzl, W.; Köster, R.; Zimmerman, H.-J. *Justus Liebigs Ann. Chem.* **1975,** 2201. Masamune, S.; Van Horn, D.; Brooks, D. W. *Tetrahedron Lett.* **1979,** 1665. Van Horn, D. E.; Masamune, S. *Ibid.* **1979,** 2229. Hirama, M.; Garvey, D. S.; Lu, L. D.-L.; Masamune, S. *Ibid.* **1979,** 3937. Evans, D. A.; Vogel, E.; Nelson, J. V. *J. Am. Chem. Soc.* **1979,** *101,* 6120. Inoue, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1980,** *53,* 174.

(5) Al^{3+}: Jeffery, E. A.; Meisters, A.; Mole, T. *J. Organomet. Chem.* **1974,** *74,* 373. Maruoka, K.; Hashimoto, S.; Kitagawa, Y.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1977,** *99,* 7705. Nozaki, H.; Oshima, K.; Takai, K.; Ozawa, S. *Chem. Lett.* **1979,** 379.

(6) Ti^{4+}: (a) Mukaiyama, T.; Narasaka, K.; Banno, K. *Chem. Lett.* **1973,** 1011. Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974,** *96,* 7503. (b) Chan, T. H.; Aida, T.; Lau, P. W. K.; Gorys, V.; Harpp, D. N. *Tetrahedron Lett.* **1979,** 4029.

(7) Quaternary ammonium enolates: Noyori, R.; Yokoyama, K.; Sakata, J.; Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1977,** *99,* 1265. See also ref 3a.

(8) Isomerically pure *erythro-* and *threo*-2-(hydroxyphenylmethyl)-1-cyclohexanone were obtained by chromatographic separation of the mixture obtained by reaction of cyclohexanone lithium enolate and benzaldehyde.[3c]

(9) For directed aldol and related reactions, see ref 6 and the following: Wittig, G.; Frommeld, H.-D. *Chem. Ber.* **1964,** *97,* 3548. Wittig, G.; Suchanek, P. *Tetrahedron, Suppl.* **1966,** No. 8, Part I, 347. Corey, E. J.; Enders, D. *Tetrahedron Lett.* **1976,** 3. Corey, E. J.; Enders, D.; Bock, M. G. *Ibid.* **1976,** 7.

(10) Reaction of a 1:1 mixture of **5** and its 2-methylated derivative with acetone dimethyl acetal (2 equiv) in the presence of **4** (5 mol %) produced only the adduct of **5** in 90% yield.

(11) Reaction of enol silyl ethers and acetals or carbonyl compounds using a stoichiometric amount of $TiCl_4$ is known (ref 6 and Mukaiyama, T.; Hayashi, M. *Chem. Lett.* **1974,** 15). Stereoselectivity of the $TiCl_4$-promoted reaction of acetals is lower than that of the present reaction. For instance, the reaction of 1-trimethylsiloxycyclohexene and isobutyraldehyde dimethyl acetal gave the erythro:threo ratio of 55:45.

(12) The cationic intermediates under such conditions have only negligible interactions with the counter anion (triflate) or solvents and, consequently, display strong electrophilic behavior. The silyl triflate **4,** though having a covalent Si–O bond, affords the lowest ^{29}Si NMR chemical shift among various trimethylsilyl derivatives: Marsmann, H. C.; Horn, H.-G. *Z. Naturforsch. B.* **1972,** *27,* 1448.

(13) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1979,** *101,* 2738.

(14) In view of the lack of reactivity of carbonyl compounds, free methylcarboxonium ions are unlikely to be involved as the reactive species.

(15) Reaction of acetals and alkenyl alkyl ethers promoted by BF_3 may be mechanistically related: Isler, O.; Lindlar, H.; Montavon, M.; Ruegg, R.; Zeller, P. *Helv. Chim. Acta* **1956,** *39,* 249.

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^{13}C NMR Spectra of Cellulose Polymorphs

Sir:

We report high resolution ^{13}C NMR spectra of the two major crystalline polymorphs of cellulose and an amorphous sample, recorded using the cross polarization/magic angle spinning (CP/MAS) technique. The spectra provide important new evidence concerning the basic structure of cellulose; they demonstrate nonequivalence of adjacent anhydroglucose units and are consistent with conformational differences between the polymorphs.

Cellulose, which is the primary constituent of plant cell walls, is the β-1,4 polymer of anhydroglucose. Its two most common polymorphs, celluloses I and II, are usually identified with the native and the mercerized or regenerated forms, re-

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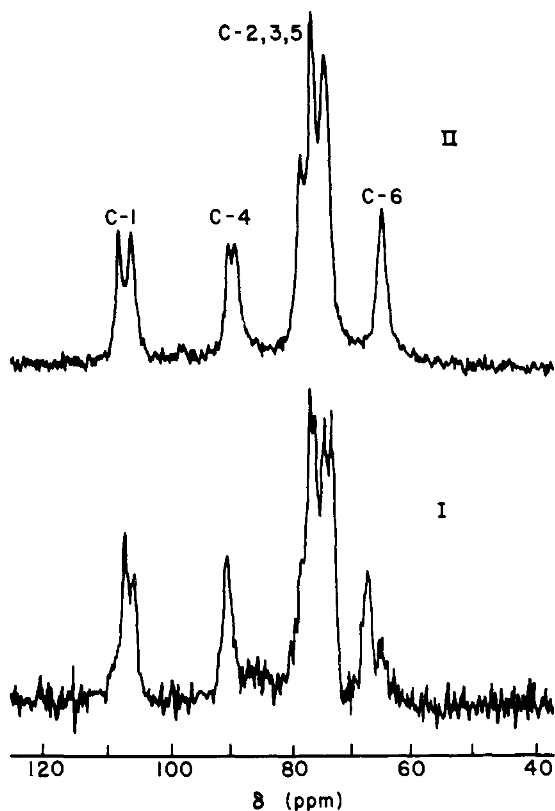

Figure 1. CP/MAS ^{13}C NMR spectra of highly crystalline cellulose I and II. Chemical shifts are shown in parts per million (to lower shielding) relative to Me_4Si. Assignments of the C-1, C-4, and C-6 regions are based on analogies with pertinent liquid-state spectra. I: 13 000 3-s repetitions, 1-ms contact time, 127-ms 11-G ^1H decoupling, 0.35-cm^3 sample, 2.2-KHz spinning. II: 12 342 3-s repetitions, 1-ms contact time, 127-ms 11-G ^1H decoupling, 0.7-cm^3 sample, 2.2-KHz spinning.

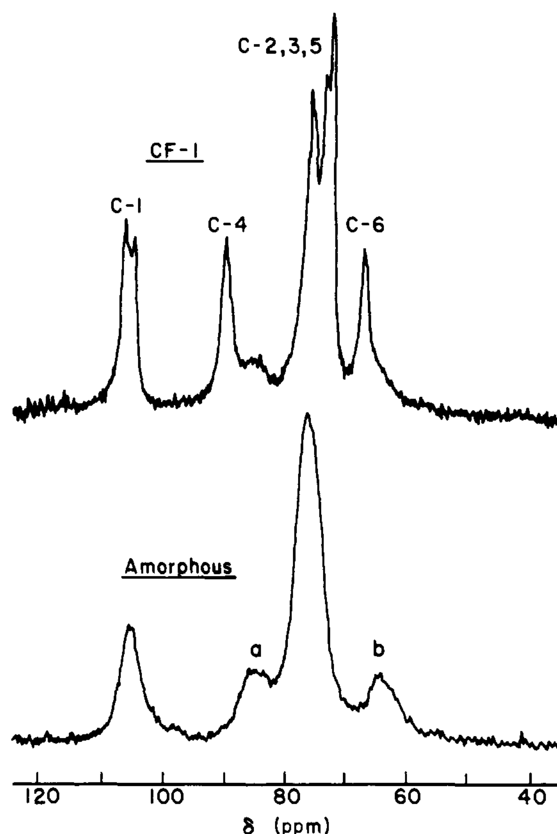

Figure 2. CP/MAS ^{13}C NMR spectra of native I (Whatman CF-1) and amorphous celluloses. Chemical shifts are in parts per million (to lower shielding) relative to Me_4Si. CF-1: 12 000 3-s repetitions, 1-ms contact time, 127-ms 11-G ^1H decoupling, 0.7-cm^3 sample, 2.2-KHz spinning. Amorphous: 8116 4-s repetitions, 1-ms contact time, 127-ms 11-G ^1H decoupling, 0.7-cm^3 sample, 2.2-KHz spinning.

spectively.[1-3] Analyses of their vibrational spectra have led to the conclusions that these two crystalline polymorphs represent different conformations of the extended molecular chains.[4,5] In addition, one of us has reported evidence indicating nonequivalence of alternate glycosidic linkages along the molecular chains and suggesting that the dimeric anhydrocellobiose must be viewed as the basic repeat unit in the crystalline structure.[6] X-ray and electron diffractometric studies have led to a number of different structures over the years.[1-3] An essential element in the interpretation of diffractometric data on any polymer is the assumed monomeric structure and its symmetry.[7] In studies of cellulose the anhydroglucose unit has usually been taken as the basic repeat unit. The problem has been complicated by the appearance of weak reflections which are not consistent with the symmetry ascribed to cellulose. Thus the refined structures vary according to whether or not the disallowed reflections are assumed negligible.[8-11] Development of the CP/MAS technique[12,13] and its application in investigations of complex natural products suggested that the ^{13}C NMR spectra of the celluloses could contribute to resolution of the questions concerning their structures.

We report on four samples of cellulose. Two were special samples of the highly crystalline polymorphic forms I and II previously characterized by X-ray diffractometry and Raman spectroscopy;[5] their preparations involved regeneration from phosphoric acid at different temperatures and in different media.[15,16] The third sample was Whatman CF-1 powder, a highly crystalline cellulose I identified by fiber microscopy as fragments of acid-hydrolyzed cotton linters. The final sample was a completely amorphous cellulose prepared by regeneration from the dimethyl sulfoxide–paraformaldehyde solvent system under anhydrous conditions. The ^{13}C NMR spectra were recorded using a modified JEOL FX-60Q system described elsewhere.[14]

The spectra are shown in Figures 1 and 2; partial assignments are noted on the basis of comparisons with solutions of the cello oligosaccharides and a low DP cellulose.[17] The most significant features in the spectra of the highly crystalline forms are those corresponding to carbons 1 and 4, which anchor the glycosidic linkages between the anhydroglucose units. The C-1 resonances for both forms and the C-4 resonance of II show very definate splittings, in each case into two lines of approximately equal intensities. These splittings provide direct evidence for the presence of two types of glycosidic linkages. Since the basic repeat distance along the chain direction is 10.3 Å, or the length of an anhydrocellobiose unit, the most plausible interpretation is an alternation of nonequivalent glycosidic linkages along the chains. The differences between other features in the spectra of celluloses I and II are also consistent with differences between chain conformations proposed on the basis of Raman spectral studies.[5,6]

The CP/MAS ^{13}C NMR spectrum of the amorphous sample, and, hence, its structure, is clearly quite distinct from those of the I and II polymorphs. Indeed, the spectrum parallels mostly that of the low DP cellulose in solution in dimethyl sulfoxide[17] if allowance is made for a solvent shift. Broad, high shielding shoulders appear in the C-4 and C-6 regions of some samples of polymorphs I and II; these correspond to peaks a and b in the spectrum of the amorphous cellulose.

The results outlined above concerning polymorphs I and II, when taken together with the vibrational spectra and the dimensions of the unit cells, suggest that adjacent anhydroglucose units are not equivalent, and that models of the structure of cellulose need to be constructed using anhydrocellobiose as the basic repeat unit.

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References and Notes

(1) Jones, D. W. In "Cellulose and Cellulose Derivatives", Bikales, N. M., Segal, L., Eds.; Wiley-Interscience, New York, 1971; Part IV, p 117.
(2) Ellefsen, O.; Tonnesen, B. A. Reference 1, p 151.
(3) Tonnesen, B. A.; Ellefsen, O. Reference 1, p 265.
(4) Atalla, R. H.; Dimick, B. E. *Carbohydr. Res.* **1975**, *39*, C1.
(5) Atalla, R. H. *Proc. Cellulose Conf., 8th, 1976, Appl. Polym. Symp.* **1976**, No. 28, 659.
(6) Atalla, R. H. *ACS Adv. Chem. Ser.* **1979**, No. 181, 55.
(7) Kakudo, M.; Nobutami, K. "X-ray Diffraction by Polymers"; Elsevier: New York, 1972; p 285.
(8) Petitpas, T.; Oberlin, M.; Mering, J. *J. Polymer Sci. S* **1963**, *2*, 423.
(9) Norman, M. *Text. Res. J.* **1963**, *33*, 711.
(10) Gardner, K. H.; Blackwell, J. *Biopolymers* **1974**, *13*, 1975.
(11) Sarko, A.; Muggli, R. *Macromolecules* **1974**, *7*, 486.
(12) Schaefer, J.; Stejskael, E. O. *Top. Carbon-13 NMR Spectrosc.* **1979**, *3*.
(13) Miknis, F. P.; Bartuska, V. J.; Maciel, G. E. *Am. Lab.*, in press.
(14) Maciel, G. E.; Bartuska, V. J.; Miknis, F. P. *Fuel*, in press.
(15) Atalla, R. H.; Nagel, S. C. *Science* **1974**, *185*, 522.
(16) Atalla, R. H.; Dimick, B. E.; Nagel, S. C. *ACS Symp. Ser.* **1977**, No. 48, 30.
(17) Gast, J. C.; Atalla, R. H.; McKelvey, R. D. *Carbohydr. Res.*, in press.

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High Resolution, Magic Angle Sample Spinning ^{13}C NMR of Solid Cellulose I[1]

Sir:

Recent developments in ^{13}C NMR in solids have made it possible to obtain spectra with lines narrow enough to distinguish resonances due to individual carbons in polymers.[2] We have combined the techniques of cross polarization, high power decoupling,[3] and magic angle sample spinning[4] to study a variety of solid samples. This report is a preliminary account of studies aimed at characterizing several preparations of cellulose.

We have measured the ^{13}C NMR spectra of glucose and cellobiose in the solid state and compared the spectra to peak assignments of the solution NMR spectra of the same compounds.[5] By analogy, it is relatively easy to identify the peaks in the solid-state spectrum of cellulose which correspond to carbons 1, 4, and 6. Figure 1 shows the structure of cellulose and the cross polarization/magic angle sample spinning (CP/MASS) spectrum of a sample of microcrystalline cellulose with the assigned peaks marked. This spectrum is virtually identical with other spectra obtained from native celluloses in our laboratory. This spectrum is also the same as the spectrum of Whatman CF-1 reported by Atalla et al.[1] It is significant that the peaks in the ^{13}C CP MASS spectra of glucose and of cellobiose do not have exactly the same chemical shifts relative to Me_4Si as the solution spectra of the same compounds. The differences in shifts might be attributed to packing effects in the solid or, more likely, to hydrogen bonding in the solid which is liable to be quite different from that in solution.

The chemical similarity of carbons 2, 3, and 5 make it reasonable that their resonance peaks should overlap, but, as yet, it has not been possible to make further assignments in this region. Integration of the peaks in Figure 1 gives a ratio of

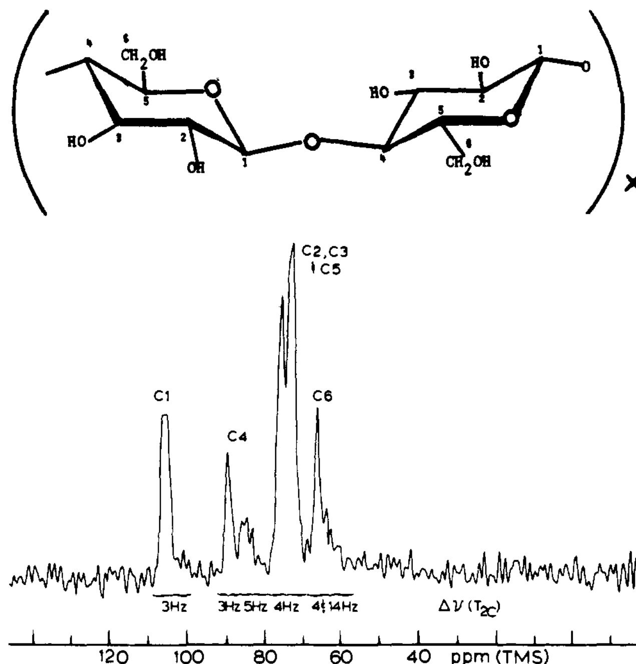

Figure 1. The CP/MASS spectrum of a dried sample of microcrystalline cellulose I. The chemical formula for cellulose is shown above. The transverse relaxation times, T_{2C}, are shown at the bottom of the figure with the regions of the spectrum to which they correspond. This spectrum is the result of 7000 scans with 1024 data points per scan at a dwell time of 50 μs per point. The external applied field was 1.4 T. The ^{13}C and ^{1}H radio frequency fields were matched at 57 kHz. The time between successive scans was 3.6 s and the spinning frequency was 2100 Hz.

1:1:3:1 but, to obtain this ratio, the C-4 resonance was assumed to include both the broad peak located between 81 and 88 ppm and the sharper peak centered at 90 ppm; similarly, the C-6 resonance included the high-field tail.

Two explanations for the broad resonance centered at 85 ppm and the upfield shoulder on C-6 were investigated. The first was that hydration of the cellulose resulted in shifts in C-4 and C-6 resonances due to hydrogen bonding with water molecules. A sample of microcrystalline cellulose[6] was carefully dried by heating to 140 °C for ~40 h under vacuum, followed by careful loading into a rotor which was sealed to prevent atmospheric water from hydrating the sample. The CP MASS spectrum of the dried sample was indistinguishable from that of a hydrated sample. Thus we have concluded that the spectral features are not due to hydration of the cellulose.

The second explanation for the broad resonances is an analogy to polyethylene where we have observed a single sharp resonance with a broad shoulder which could be attributed to noncrystalline carbons.[7] Relaxation time measurements have been used to establish that the noncrystalline regions of polyethylene exhibit much greater mobility than the crystalline regions.[8] We have investigated both the longitudinal, T_{1C}, and transverse, T_{2C}, relaxation times for the peaks observed in the ^{13}C spectrum of the carefully dried sample of cellulose I. Saturation recovery experiments were employed to get a qualitative idea of the longitudinal relaxation times, T_{1C}.[9] The long T_1 values observed in solid ^{13}C NMR in general cause T_{1C} measurements to suffer from poor signal to noise. As a result it was not possible to obtain quantitative values for the T_{1C} values, but several qualitative observations were made. The overall relaxation time for recovery of longitudinal magnetization is tens of seconds. Within the accuracy of the data, all peaks in the observed spectrum relax with the same time constant with the exception of the upfield shoulder on C-6. This shoulder has a somewhat shorter value of T_{1C}, indicating increased molecular mobility.

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