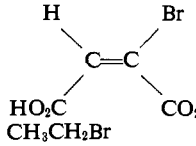
Table I. Esr Data for Various α-Chloro and α-Bromo Radicals Formed in Irradiated Solids

Host	Radical	Hyperfine tensor components, G ¹H	³⁵Cl or ⁸¹Br	g-Tensor components
$FCH(CONH_2)Cl$[a]	$F\dot{C}(CONH_2)Cl$		18, −3.2, −5.8	2.0021, 2.0069, 2.0076
$ClCH_2CO_2H$	$Cl\dot{C}HCO_2H$	−19, −13, −28	21, −3, −6[b]	2.002, 2.007, 2.009
CH_3Br (in CD_3OD)	$H_2\dot{C}Br$	−21	85	2.002
$BrCH_2CO_2H$	$Br\dot{C}HCO_2H$	−20, −15, −25	107, −48, −75	2.002, 2.016, 2.038
$BrCHMeCO_2H$	$Br\dot{C}MeCO_2H$	22	95	2.002
	$Br\dot{C}CO_2H(CH_2CO_2H)$	38 and <5 (2 H)	111, −50, −80[c]	2.002, 2.018, 2.032[d]
CH_3CH_2Br (in CD_3OD)	$Me\dot{C}HBr$	−22 (1 H), +22 (3 H)	85	2.002

[a] Reference 4. [b] $A_{iso} = +4$ G, $2B_{ax}(x) = +16$ G, $2B_{ax}(z) = -2$G [$a_{p_x}^2 = 16\%$, $a_{p_z}^2 = -2.0\%$]. [c] $A_{iso} = -6.3$ G, $2B_{ax}(x) = 107.3$ G, $2B_{ax}(z) = -20$ G [$a_{p_x}^2 \approx 19\%$, $a_{p_z}^2 \approx -3.5\%$]. [d] Orbital magnetism has not been allowed for in the calculations in footnote c, but this will not make an appreciable difference to these approximate results.

are nearly normal, but the A_y features are calculated to be a triplet, as shown, together with weak side lines which were not detected. The resulting interpretation, given in Figure 1, was confirmed by Q-band spectra and selected single-crystal studies and is probably fairly accurate.

We have analyzed these results using the signs indicated in Table I, since they give very reasonable results which compare well with those for the α-chloro radicals, whereas any other sign combination gave physically unreasonable results. The main cause of the marked deviation from axial symmetry in the hyperfine tensor components arises because the major spin density is on carbon and so there is a large spin polarization term which contributes negative spin density on bromine. We have, therefore, analyzed the data in terms of two axially symmetric tensors, one parallel to x [$2B_{ax}x$] (positive) and the other parallel to z [$2B_{ax}z$] (negative). The results were then converted into approximate orbital populations in the normal manner.[10] In Table I we list the results for the radical from α-bromomaleic acid since this had the most resolved spectrum.

Interestingly, delocalization appears to be slightly larger than that for chlorine which is in accord with the lower electronegativity of bromine. In both cases A_{iso} corresponds to extremely small s-orbital spin densities. This is because the negative contribution from spin on carbon almost exactly cancels the positive contribution from spin on halogen. We conclude that there is appreciable π bonding in agreement with the infrared studies.[6]

Finally, we should mention that the results for methyl and ethyl bromide were obtained using CD_3OD as solvent. This gave spectra of just the same form as that shown in Figure 1, whereas the spectra obtained from the pure compounds were quite different. These will be discussed in detail in our full report of this work. The esr spectra for ethyl bromide and α-bromopropionic acid also contained features characteristic of β-bromo radicals,[11] but these are sufficiently different to enable clear identification to be made for both species.

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Determination of the Composition and Sequence of a Glucan Containing Mixed Linkages by Carbon-13 Nuclear Magnetic Resonance

Sir:

Although carbon-13 nmr has been applied extensively to monosaccharides[1-3] and oligosaccharides,[3,4] its potential in determining polysaccharide structure has not been explored to any great extent. An investigation of amylose, a simple homopolymer, has been reported,[3] and more recently the ^{13}C spectrum of heparin, a heteropolymer, yielded information from which an alternating sequence of its two different component sugar residues was proposed.[5] We report here an investigation which demonstrates the remarkable resolution and scope of ^{13}C nmr for studies of polysaccharides. Multiplet resonances of conformational origin are present in the spectra.[6] Both the composition and sequence of a glucan (ex. *Tremella mesenterica*, NRRL Y-6158[7]) are obtainable from the ^{13}C nmr spectrum.

Chemical evidence has indicated that the glucan contains two types of linkage, 1 → 4-α and 1 → 6-α, in an approximate ratio of 2:1.[7] Thus, one might expect different ^{13}C resonance frequencies for the various anomeric, four, and six carbon atoms, depending on whether or how they are linked. Examination of the

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(6) The words "multiplet" and "doublet" used in the text do not imply coupling between the ^{13}C nuclei or with any other nucleus. They are used to indicate the appearance of more than one resonance where only one might be expected.
(7) C. G. Fraser and H. J. Jennings, *Can. J. Chem.*, **49**, 1804 (1971).

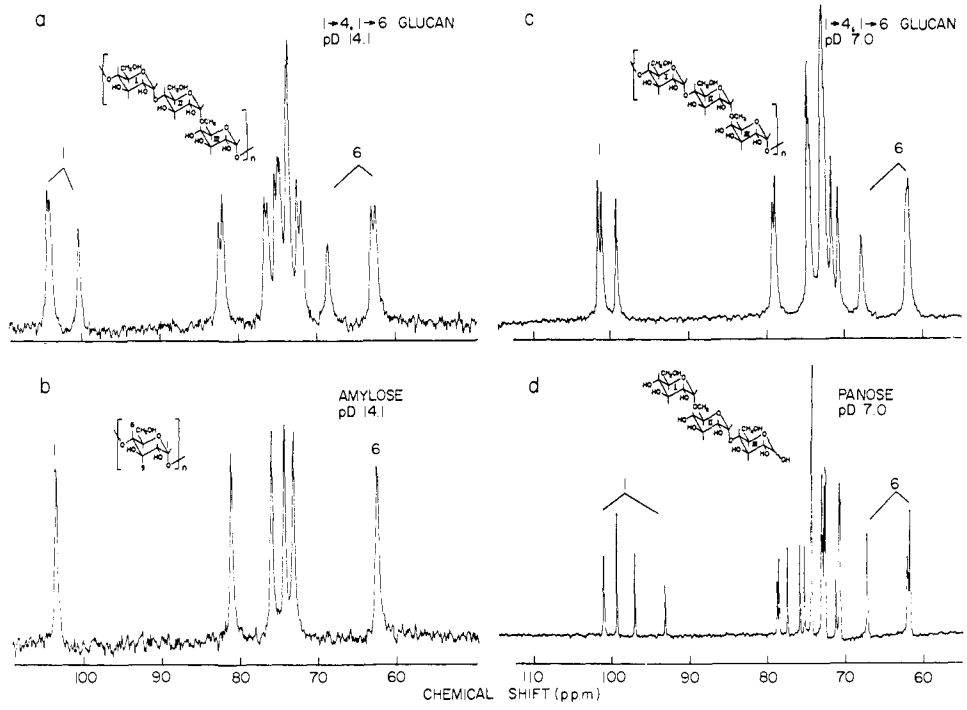

Figure 1. Carbon-13 nmr spectra (25.16 MHz) obtained on a Varian XL-100 spectrometer, Fourier transform mode with complete proton decoupling, 37°, of (a) glucan in deuterium oxide, 100 mg/ml, pD 14.1, sweep width 5.0 kHz, 138,000 acquisitions; (b) amylose in deuterium oxide, 100 mg/ml, pD 14.1, sweep width 5.0 kHz, 149,000 acquisitions; (c) glucan in deuterium oxide, 100 mg/ml, pD 7.0, sweep width 2.5 kHz, 48,000 acquisitions; (d) panose in deuterium oxide, 50 mg/ml, pD 7.0, sweep width 2.5 kHz, 44,500 acquisitions.

Table I. Carbon-13 Chemical Shifts[a] of the C-1 and C-6 Resonances of the Glucan and Related Sugars

Compd in D_2O	Anomeric carbons (glycosidic)			Anomeric carbons (reducing) β	Anomeric carbons (reducing) α	Exocyclic carbons		
Glucan	101.6	101.0	99.2			67.8	62.0	61.8
Panose		101.0	99.3	97.0	93.1	67.2	62.0	61.7
							61.9[b]	
Isomaltose			99.3	97.3	93.4	67.1	63.8	61.8
Maltose		100.8		97.1	93.1		62.0	61.7
							61.8[b]	
Glucose				97.4	93.5		62.3	62.2
Maltitol	101.7					64.0	63.5	61.6
Isomaltitol			99.5			63.8		61.9
Glucan (pD 14.1)	103.6	103.5	99.7			67.8	62.3	61.8
Amylose (pD 14.1)		102.9						62.0

[a] In ppm from external tetramethylsilane. [b] Multiplet of C-6 of glucose at reducing end due to anomerization.

^{13}C spectra, Figure 1a and 1c, of the glucan in deuterium oxide reveals multiplets at the positions expected[2] for the resonances of C-1 and -6. The assignments of these glucan resonances have been made by obtaining the ^{13}C nmr spectra of a series of related disaccharides (maltose, 4-*O*-α-D-glucopyranosyl-D-glucose; isomaltose, 6-*O*-α-glucopyranosyl-D-glucose; maltitol, 4-*O*-α-D-glucopyranosyl-D-glucitol; isomaltitol, 6-*O*-α-D-glucopyranosyl-D-glucitol), a trisaccharide (panose, *O*-α-D-glucopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→4)-D-glucose), and a homoglucan (amylose, 1 → 4 linked). The ^{13}C chemical shifts are presented in Table I and some nmr spectra in Figure 1. A complete assignment of the remaining resonances of the glucan is under study using other model compounds and specifically deuterated compounds.

The resonances due to anomeric carbons in the glucan (Figure 1a,c) were assigned by virtue of their position to low field.[2] The lowest field group is a doublet due to conformational effects (*vide infra*). It is assigned to the anomeric carbons involved in 1 → 4 linkages (rings I and III, Figure 1a) by comparison with the data for amylose (Figure 1b), panose (Figure 1d), maltose, and maltitol (Table I). The resonance at 99.2 ppm is assigned to the anomeric carbons involved in a 1 → 6 linkage (ring II, Figure 1a) by comparison with the data for panose (Figure 1d), isomaltose, and isomaltitol (Table I). Under conditions where the instrument cycle time (spectrum acquisition time plus delay before next pulse) was much greater than the longitudinal relaxation time of the anomeric carbon atoms, the relative areas of the group centered at 101.3 ppm and the line at 99.2 are 2.2:1.0. This is in agreement with the ratio of 1 → 4 to 1 → 6 linkages obtained by chemical means.

The resonances due to C-6 of the glucan were assigned by consideration of their high-field position,[2] by determining the spectra without proton decoupling, and by comparison with the spectra of glucose, the di-

saccharides, and panose. In this case the resonance attributable to the unlinked C-6's is a multiplet (62.0 and 61.8 ppm) due to conformational effects (*vide infra*). Comparison of the areas of the resonances due to linked and unlinked C-6's is not nearly as accurate an estimate of the relative amounts of the two linkages because the relaxation mechanisms and nuclear Overhauser enhancements of the two types of C-6 need not be identical. However, the areas do indicate that the 1 → 4 linkage is roughly twice as frequent as the 1 → 6 linkage.

The C-6 resonances of glucose, the terminal reducing glucose unit of maltose, and ring III of panose are doublets (Table I). The relative intensities of the two lines are similar to those of the anomeric carbon atoms of the reducing glucose moieties, indicating that C-6 is sensitive to the presence of α and β anomers at C-1. Thus, it is not unreasonable to suggest that in the glucan, where anomeric purity has been established by chemical methods, the C-6 resonances are sensitive to the nature of the linkage between C-1 of the same glucose unit and the neighboring unit. Thus, approximately equal frequencies of 1 → 4 and 1 → 6 linkages are seen by the C-6's of glucose residues linked at C-4 in the glucan. The only sequence consistent with these data is that shown in Figure 1a.

Similarly, the anomeric resonances of the glucan C-1's involved in 1 → 4 linkages have a multiplet structure. This suggests that, in like fashion to the C-6's, they are sensitive to the nature of the linkage at the C-4 or C-6 position of the same glucose unit. Since the C-1's involved in 1 → 4 links experience approximately equal frequencies of 1 → 4 and 1 → 6 linkages, the polysaccharide sequence must be that represented in Figure 1a.

A further confirmation of the sensitivity of the C-6 resonances to the nature of the linkage at C-1 of the same glucose unit comes from the spectrum of panose (Figure 1d), where there are four C-6 resonances. The resonance at 67.2 ppm is clearly that due to C-6 of ring II. The remaining three resonances are due to the C-6's of rings I and III, which are both primary, but have different frequencies due to the involvement of ring I in a 1 → 6 linkage and the influence on the C-6 of ring III by the α and β anomers at C-1.

Thus, the chemical shifts experienced by carbons 1 and 6, depending on how or whether they are linked, and their long-range conformational sensitivity, have enabled us to determine the composition and sequence of a homopolymer with mixed linkages. This technique provides a very powerful means of structural analysis for carbohydrates.

(8) Issued as N.R.C.C. Publication No. 13030.

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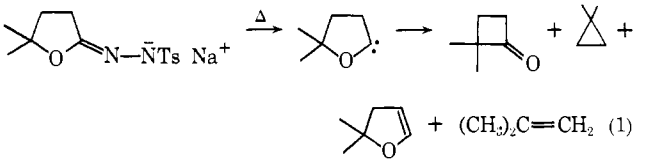
Stereochemical Consequences in the Pyrolysis of Lactone Tosylhydrazone Salts

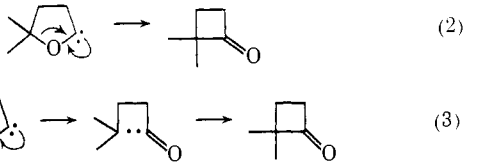
Sir:

Recently we described the pyrolytic decomposition of several lactone tosylhydrazone salts and suggested that the various observed products arose through rearrangement or fragmentation of intermediate oxycarbenes.[1,2] The species related to isocaprolactone, for example, gave the results shown in eq 1. A point



(1)

specifically left open was the pathway from oxycarbene to ring-contracted ketone, for which the two simplest possibilities are a concerted alkyl shift from oxygen to carbon (eq 2) and an open alkyl acyl biradical intermediate (eq 3). This question has significance beyond the

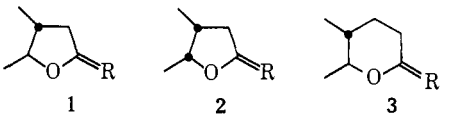


(2)

(3)

immediate mechanistic problem, since closely related reactions are involved in the photolysis[3-5] of both cyclobutanones and certain other cyclic ketones, as well as in the thermolysis[6] of cyclobutanones. Furthermore, the ring contraction proceeds in synthetically attractive yields in some cases,[1,2] and the mechanistic question then takes on importance for preparative chemistry.

We have now prepared and pyrolyzed tosylhydrazone salts related to the three lactones **1a–3a** in order to assess the stereochemical consequences of this decomposition. The lactones were prepared by known methods[7] and then converted to tosylhydrazones **1b–3b**[8] *via* the ortholactones **1c–3c** following a procedure previously described.[1] Hydrolysis of **1b–3b** in aqueous acid furnished **1a–3a**, respectively, and confirmed that no



1 2 3

a, R = O
b, R = NNHTs
c, R = $(OC_2H_5)_2$
d, R = $N\bar{N}TsNa^+$

loss of stereochemistry had occurred in these transformations. The derived dry sodium salts **1d–3d** were then thermally decomposed at 310° (0.1 Torr), and the products were analyzed, all according to methods employed earlier.[2] Structures were assigned to the enol ethers on the basis of spectroscopic properties and

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