

# A $^{13}\text{C}$ NMR Study of Hydroxylated Natural Rubber

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## Synopsis

Two methods have been used to introduce hydroxyl groups into natural rubber. In the first method, epoxidized natural rubber was reduced with lithium aluminium hydride or aluminium hydride with the production of a tertiary alcohol. The  $^{13}\text{C}$  NMR spectrum of this product was assigned in terms of shift factors from model compounds and quantitative analysis of the spectra confirmed that the hydroxylation process of partially epoxidized rubber was a random process. At higher levels of epoxidation, evidence was obtained for the formation of larger rings from adjacent epoxy groups. The second method involved hydroboration of natural rubber followed by oxidation, which was expected to produce secondary alcohol groups, but gave a mixture of secondary and tertiary alcohol groups as shown by the  $^{13}\text{C}$  NMR spectrum. A reaction scheme was proposed to explain this result.

## INTRODUCTION

The long-term prospects and short-term problems of the natural rubber industry highlight the fact that producers of natural rubber need some protection against the worst effects of the vagaries of the world economy.<sup>1</sup> One means by which the value of natural rubber would be increased, would be by its chemical modification to produce a useful modified product as for example with epoxidized natural rubber.<sup>2-4</sup> The possibility of conferring thermoplastic properties on highly elastic systems by introducing specific chemical crosslinks has been explored<sup>5-7</sup> using the uncatalyzed exchange reaction of hydroxyl groups on  $\beta$ -keto esters or malonate esters. These crosslinks underwent rapid and reversible exchange at temperatures in the range 160° to 200°C, while being relatively stable to such exchange below 160°C. The rapid exchange at higher temperatures provided a mechanism for migration of the polymer chains relative to one another and allowed remolding of the material. In order to develop this exchange reaction, natural rubber was epoxidized and isomerized by treatment with aluminium isopropoxide to give the corresponding allylic alcohol.<sup>7</sup> But high temperature experiments indicated that the ester crosslinks were gradually replaced by permanent crosslinks, due to the allylic nature of the hydroxyl group.<sup>6</sup> In the present study, an attempt was made to incorporate a nonallylic hydroxyl group in natural rubber. Furthermore, since tertiary alcohols are sluggish in trans-

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esterification reactions,<sup>8</sup> particular attention was given to the preparation of secondary hydroxyl groups.

## EXPERIMENTAL

### Materials

All glassware was oven dried at 150°C before use and was assembled hot under a flow of nitrogen. Solid natural rubber was obtained from Sri Lanka and was purified according to the method of Hager et al.<sup>9</sup> Tetrahydrofuran (THF), diglyme, ethyl acetate, lithium aluminium hydride, aluminium chloride, sodium borohydride, boron trifluoride diethyl etherate, 30% hydrogen peroxide, sodium hydroxide, and sodium carbonate were analytical-grade reagents obtained from Aldrich Chemical Co. Anhydrous THF was prepared by treatment with excess lithium aluminium hydride and distillation. Spectral-grade deuterated chloroform, pyridine, and THF were used for NMR spectroscopy.

## METHODS

### NMR Spectroscopy

<sup>1</sup>H NMR spectra at 200 MHz and <sup>13</sup>C NMR spectra at 50.1 MHz were obtained using a JEOL FX 200 NMR spectrometer with an Oxford Instrument Co. magnet. For the <sup>13</sup>C NMR spectra, free induction decays were accumulated in 16 K data points, spectral width 15,000 Hz, 13 msec (45°) pulse width and 6 sec repetition time. Spectra were measured at 298 K and TMS was used as an internal standard. Spectral intensities were measured by cutting out and weighing each peak area. The modified<sup>10</sup> INEPT (insensitive nuclei enhancement by polarization transfer) pulse sequence of Morris and Freeman<sup>11</sup> was used to separate methyl, methylene, methine, and quaternary carbon atoms. Polymer was dissolved in CDCl<sub>3</sub> for lanthanide shift reagent (LSR) experiments.<sup>12</sup> Induced chemical shifts were obtained by the incremental addition of known amounts of solid Eu(fod)<sub>3</sub> to a 3% w/v solution of the polymer and a plot of induced shift versus the molar ratio of (LSR)/(hydroxyl group) was made. Tracing a particular signal back to the ordinate, allowed a check of the assignment from a knowledge of the chemical shift of the particular resonance in the absence of added LSR.

### Preparation of Lithium Aluminium Hydride and Aluminium Hydride Solutions

Excess lithium aluminium hydride was added to anhydrous THF and the mixture stirred for at least two hours under dry nitrogen. The resulting solution was filtered under a slight positive nitrogen pressure through a two-inch bed of lightly packed glass wool into a large flask and the solution kept in a closed bottle until it was used.

A solution of 0.52 g (0.004 mol) of aluminium chloride in 25 mL of anhydrous THF was added dropwise to 0.47 g (0.011 mol) of lithium aluminium hydride in THF. After stirring for 0.5 h, the solution was separated from the

precipitated lithium chloride by allowing it to flow into another reaction vessel via a stopcock plugged with glass wool.

### Reaction of Aluminium Hydride or Lithium Aluminium Hydride with Epoxidized Natural Rubber

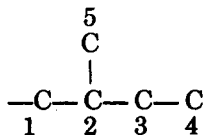
Epoxidized natural rubber<sup>4</sup> (0.75 g of 30% epoxidized or 0.33 g of 100% epoxidized natural rubber) in anhydrous THF was added dropwise to the aluminium hydride or lithium aluminium hydride solution prepared above. The reaction was continued for seven days at room temperature and the mixture hydrolyzed with ethyl acetate and 10% hydrochloric acid. The mixture was washed with distilled water and saturated aqueous sodium bicarbonate, after which the organic layer was separated and the solvent removed by distillation.

### Hydroboration of Natural Rubber Followed by Oxidation

Boron trifluoride diethyletherate (1 mL) in anhydrous diglyme (10 mL) was placed in a three-neck round-bottom flask fitted with a dry nitrogen-purging device and pressure-equalizing dropping funnel. A solution of 1 g of sodium borohydride in diglyme (25 mL) was added dropwise to this solution at 0°C. The diborane produced was passed by a slow flow of dry nitrogen into anhydrous THF (25 mL) and this solution was then added dropwise in a rubber solution at 0°C. The mixture was allowed to stand for 15 min at 0°C. The solution was immediately heated to 40°C and 10 mL of 30% aqueous sodium hydroxide added dropwise followed by 5 mL of 30% hydrogen peroxide. The mixture was allowed to stand for one hour at 40°C and the hydroborated rubber was then precipitated by pouring into excess water and filtered and dried at 34°C.

## RESULTS AND DISCUSSION

The unreacted isoprene units, isoprene units with a hydroxyl group in the tertiary position, and isoprene units with a hydroxyl group in a secondary position are denoted by C, H, and S, respectively. The triad sequences in partially modified rubbers are denoted using these symbols. For example, the possible triad sequences involving C and H are shown in Figure 1. The numbering of the carbon atoms of the center isoprene unit in these triads uses the system employed previously for partially epoxidized natural rubber.<sup>4</sup> For example C<sup>1</sup>HC denotes the C-1 carbon atom of the center unit in the triad CHC, and in general, the superscripts denote the corresponding carbons in the isoprene unit,



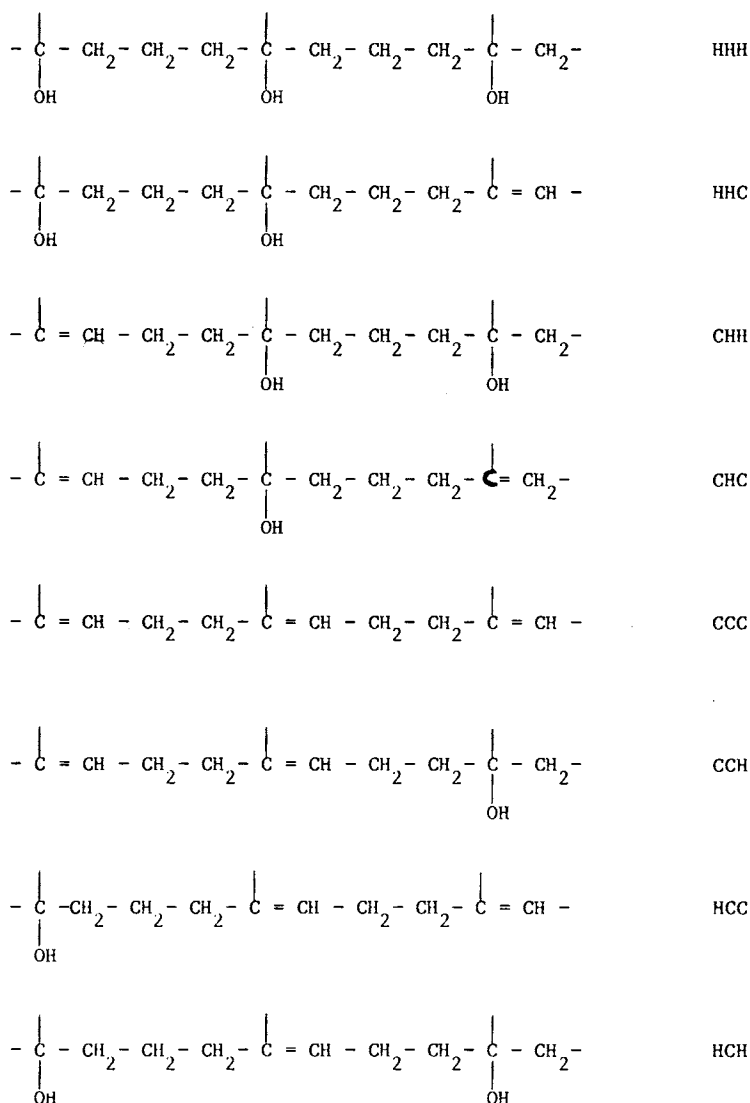


Fig. 1. Triad sequences involving unreacted isoprene units (C) and isoprene units with a hydroxyl group in the tertiary position (H).

### Hydroxylated Natural Rubber from Reduction of Epoxidized Rubber with Lithium Aluminium Hydride

Reduction of low molecular weight epoxides by lithium aluminium hydride involves an attack at the least substituted position, giving a product with the hydroxyl group on the more highly substituted carbon atom.<sup>13,14</sup> The interpretation of the <sup>13</sup>C NMR spectra of the product obtained after the 30% epoxidized natural rubber<sup>4</sup> was treated with lithium aluminium hydride (Fig. 2a) showed that in this instance, this was also the case. Resonance C<sub>4</sub> was assigned to a quaternary carbon atom by use of the INEPT pulse sequence (spectrum not shown). Reaction of the hydroxylated rubber with tri-

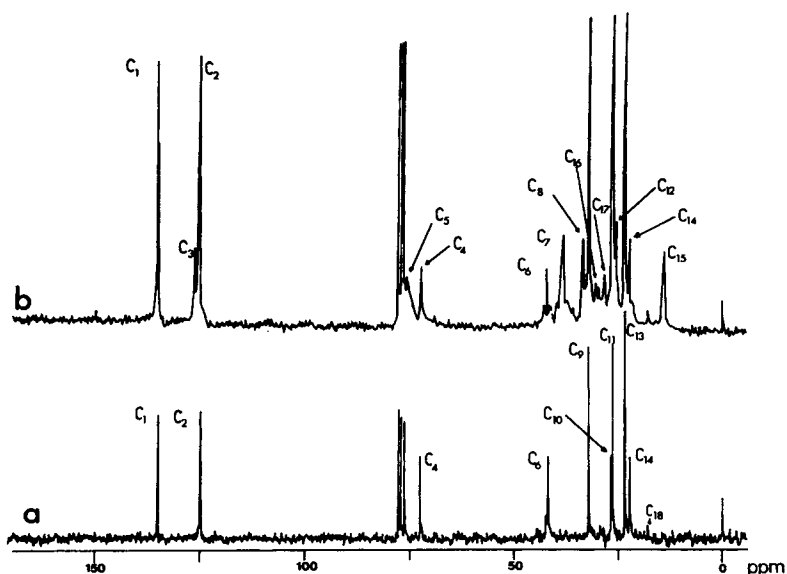


Fig. 2.  $^{13}\text{C}$  NMR spectra at 50.1 MHz in  $\text{CDCl}_3$  of hydroxylated natural rubber in  $\text{CDCl}_3$  obtained by (a) reduction of epoxidized natural rubber, (b) hydroboration and subsequent oxidation of natural rubber. The triplet resonance at 77 ppm is due to  $\text{CDCl}_3$ .

fluoroacetic anhydride caused trifluoroacetylation of hydroxyl groups and the  $\text{C}_4$  peak shifted downfield by 2.5 ppm. Since similar shifts had been observed for trifluoroacetylation of cyclohexanol derivatives,<sup>15</sup> this confirmed the assignment of the  $\text{C}_4$  resonance to a quaternary carbon atom bearing a hydroxyl group.

Resonances  $\text{C}_{10}$  and  $\text{C}_{13}$  were found to be methyl carbons by the INEPT experiment and were thus assigned to  $^5\text{H}$  and  $^5\text{C}$ , respectively. To facilitate assignment of the other peaks in this region, the  $^{13}\text{C}$  NMR chemical shifts of all the methylene carbon atoms in the possible triads were calculated using a method discussed previously.<sup>16-18</sup> The chemical shifts of the methylene carbon atoms of hydrogenated polyisoprene, the shift factors used to determine the effect of double bonds and the substitution factors used to determine the effect of quaternary hydroxyl substitution<sup>19</sup> are given in Table I. The chemical shifts of carbon atoms in C- and H-type residues were then calculated using the chemical shifts of hydrogenated polyisoprene and applying the relevant shift and substitution factors from Table I. These calculated values were then used to assign the resonances given in Table II.

Resonance  $\text{C}_{13}$  was assigned to  $\text{CC}^4\text{H}$  and  $\text{HC}^4\text{H}$  (with the calculated value of 24.16 ppm) in addition to its previous assignment of  $^5\text{C}$ . This was confirmed by the INEPT spectrum in which the  $\text{C}_{13}$  peak was smaller due to the overlap of a large methyl signal and a small (negative) methylene signal. This assignment was consistent with the separation of small peaks from signal  $\text{C}_{13}$  when trifluoroacetic anhydride was added. Similarly a peak separated from the  $\text{C}_9$  signal when trifluoroacetic anhydride was used. The two new peaks separated from  $\text{C}_{13}$  and  $\text{C}_9$  were designated  $\text{C}_{20}$  and  $\text{C}_{19}$ , respectively, and are given in Table II. The assignments in Table II were confirmed by lanthanide

TABLE I  
Chemical Shifts, Shift Factors, and Substitution Factors  
Used in  $^{13}\text{C}$  NMR Chemical Shift Calculations

Hydrogenated polyisoprene	Chemical shifts (ppm)
$\begin{array}{c} \text{}^d\text{CH}_3 \\   \\ -\text{C}-\text{C}-\text{C}-\text{C}- \\ \text{}^a \quad \text{}^e \quad \text{}^a \quad \text{}^b \end{array}$	$a = 37.47$ $b = 24.51$ $d = 19.83$ $e = 33.12$
Polyisoprene	Shift factors (ppm)
$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{C}=\text{CH}-\text{C}- \\ \text{}^x \quad \quad \quad \text{}^y \end{array}$	$X(\text{cis}) = -5.2$ $Y(\text{cis}) = +1.8$
Tertiary alcohol	Substitution factors (ppm)
$\begin{array}{c} \text{}^{\beta_2}\text{CH}_3 \\   \\ -\text{C}-\text{C}-\text{C}- \\   \quad   \quad   \\ \text{OH} \quad \text{}^{\beta_1} \quad \text{}^{\gamma} \end{array}$	${}^1\alpha_1 = +41.2$ ${}^1\beta_1 = +4.9$ ${}^1\beta_2 = +6.8$ ${}^1\gamma = -2.2$
Secondary alcohol	
$\begin{array}{c} \text{}^{\gamma_3} \text{CH}_3 \text{}^{\alpha} \text{}^{\beta_2} \text{}^{\gamma_2} \\   \\ -\text{C}-\text{C}-\text{C}-\text{C}- \\ \text{}^{\gamma_1} \text{}^{\beta_1} \quad   \\ \text{OH} \end{array}$	${}^2\alpha = +40.8$ ${}^2\beta_1 = +5.4$ ${}^2\beta_2 = +7.7$ ${}^2\gamma_1 = -3.4$ ${}^2\gamma_2 = -3.4$ ${}^2\gamma_3 = -2.2$

TABLE 2  
Assignments of the Methyl and Methylene Regions of the  $^{13}\text{C}$  NMR Spectrum of Hydroxylated Natural Rubber Obtained by Reduction of Epoxidized Rubber by Lithium Aluminium Hydride (Refer to Figure 2a)

Carbon atom	Chemical shifts (ppm)		Peak
	Calculated	Observed	
$\left. \begin{array}{l} \text{H}^1\text{HH}, \text{HH}^3\text{H}, \text{H}^1\text{HC} \\ \text{HH}^3\text{C}, \text{C}^1\text{HH}, \text{CH}^3\text{H} \\ \text{C}^1\text{HC}, \text{CH}^3\text{C} \end{array} \right\}$	42.37	41.31	$\text{C}_6$
$\text{HH}^4\text{H}, \text{CH}^4\text{H}$	20.11	19.00	$\text{C}_{18}$
$\text{HH}^4\text{C}, \text{CH}^4\text{C}$	22.31	22.30	$\text{C}_{14}$
$\text{C}^1\text{CC}, \text{C}^1\text{CH}$	32.23	32.23	$\text{C}_9$
$\text{H}^1\text{CC}, \text{H}^1\text{CH}$	32.23	32.23	$\text{C}_9(\text{C}_{19})$
$\text{CC}^4\text{C}, \text{HC}^4\text{C}$	26.36	26.36	$\text{C}_{11}$
$\text{CC}^4\text{H}, \text{HC}^4\text{H}$	24.16	23.40	$\text{C}_{13}(\text{C}_{20})$
${}^5\text{C}$	24.16	23.40	$\text{C}_{13}$
${}^5\text{H}$	26.90	26.90	$\text{C}_{10}$

shift reagent experiments<sup>12</sup> illustrated in Figure 3. As expected, resonance  $\text{C}_6$ , which arises from the methylene carbon  $\beta$  to the OH group, showed the highest shift. Due to the very low intensity of the  $\text{C}_{18}$ , it was not possible to follow its movement.  $\text{C}_{14}$  and  $\text{C}_{20}$  had similar movements as both arise from a methylene carbon  $\gamma$  to one hydroxyl group.  $\text{C}_{19}$  which is due to a methylene

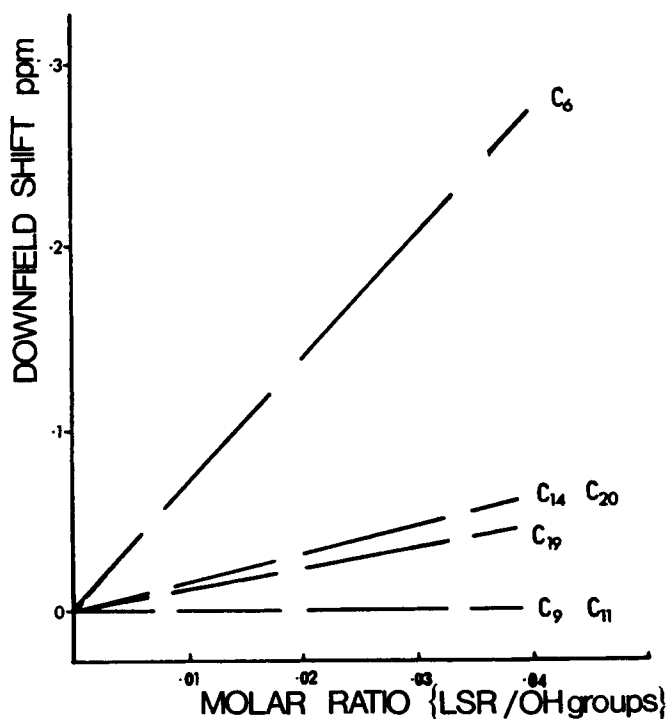


Fig. 3. Lanthanide shifts of some resonances given in Figure 2a and Table II.

carbon  $\delta$  to one hydroxyl group moved minimally, while C<sub>9</sub> and C<sub>11</sub> remained unchanged, as expected from their assignments (Table II). Resonances C<sub>1</sub> and C<sub>2</sub> were assigned to the C-2 and C-3 olefinic carbons of isoprene (C) residues<sup>4</sup> and they were insensitive to dyad or triad sequences, which was unexpected, since in epoxidized rubber they were sensitive to pentad sequences.<sup>4</sup> However, after trifluoroacetylation, the olefinic resonances showed splitting, and on addition of lanthanide shift reagents, also caused some separation of peaks. The C<sub>4</sub> resonance due to the quaternary carbon atom attached to the hydroxyl group was also insensitive to dyad or triad structure.

Because of the overlapping nature of the resonances, it was not possible to use them directly (as was done with epoxidized natural rubber<sup>4</sup>) to estimate the percentage of various triads. However, the separation of the C<sub>20</sub> and C<sub>13</sub> signals on addition of trifluoroacetic anhydride made it possible to use the peaks due to the C-4 carbon atom (C<sub>18</sub>, C<sub>14</sub>, C<sub>20</sub>, and C<sub>11</sub>) for quantitative analysis, see Table III. The percentage of the dyads in this product should be the same as that of the 30% epoxidized natural rubber from which it was produced and these values<sup>4,18</sup> are also given in Table III for comparison. The agreement between the two sets of results was reasonable except for HH where the difference was larger than expected (see also Table VI in Ref. 4), but probably not outside the limits of experimental error. A sample of 100% epoxidized natural rubber was reduced with lithium aluminium hydride and the  $^{13}\text{C}$  NMR spectrum showed the presence of five- and/or six-membered cyclic structures containing an oxygen atom.<sup>20</sup> The presence of two or more

TABLE III  
Percentage of Different Dyads in 30% Hydroxylated Natural Rubber from  $^{13}\text{C}$  NMR Spectrum and from 30% Epoxidized Natural Rubber<sup>4</sup>

Signal	Carbon atom	Dyad	% of Dyads from	
			Figure 2a <sup>a</sup>	30% epox. rubber <sup>4</sup>
C <sub>18</sub>	HH <sup>4</sup> H,CH <sup>4</sup> H	HH	9	4
C <sub>14</sub>	HH <sup>4</sup> C,CH <sup>4</sup> C	HC	21	23
C <sub>20</sub>	CC <sup>4</sup> H,HC <sup>4</sup> H	CH	21	23
C <sub>11</sub>	CC <sup>4</sup> C,HC <sup>4</sup> C	CC	49	50

<sup>a</sup> Modified by trifluoroacetylation which separated resonance C<sub>20</sub> from C<sub>13</sub>.

adjacent epoxy groups may initiate cyclization, which probably occurs through a carbanion produced by the attack of H<sup>-</sup>.

### Hydroxylated Natural Rubber Produced by Reduction of Epoxidized Rubber with Aluminium Hydride

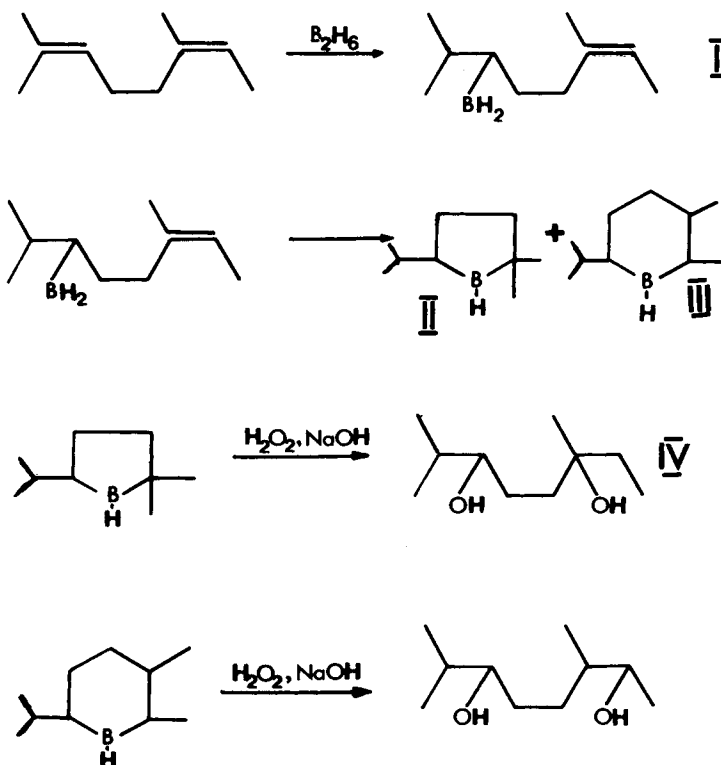
The reduction of epoxidized natural rubber with aluminium hydride was expected to give the polymeric secondary alcohol, that is, the anti-Markovnikov product was expected, since low molecular weight epoxides reacted in this manner.<sup>21,22</sup> Unfortunately, the  $^{13}\text{C}$  NMR spectrum of the product showed that it was identical with that obtained with lithium aluminium hydride reduction, that is, only the tertiary alcohol was obtained. When the aluminium hydride reduction was carried out with 100% epoxidized natural rubber, a product with large cyclic rings resulted. Further, some elimination reaction was observed as indicated by the presence of olefinic peaks in the product. This may be due to the presence of dichloroalane (AlHCl<sub>2</sub>), a biproduct formed in the LiAlH<sub>4</sub>-3AlCl<sub>3</sub> reaction mixture.<sup>23-25</sup>

### Hydroboration of Natural Rubber and Subsequent Oxidation

The hydroboration of alkyl-substituted olefins proceeds in an anti-Markovnikov manner with the boron being bonded to the least-substituted carbon atom.<sup>26</sup> Consequently, the hydroboration of such olefins, followed by oxidation of the resulting organoborane by hydrogen peroxide and sodium hydroxide, should provide a convenient procedure for the introduction of the hydroxyl group on the least-substituted carbon.<sup>27</sup> This reaction had been applied earlier<sup>28</sup> to diene polymers including polyisoprene and the resulting hydroxylated polymer had been characterized by infrared (IR) spectroscopy.

The  $^{13}\text{C}$  NMR spectrum of the product obtained in the present work is illustrated in Figure 2b. The spectrum contains all the peaks (including C<sub>4</sub>) of Figure 2a. An INEPT NMR spectrum confirmed that C<sub>4</sub> is due to a quaternary carbon and C<sub>5</sub> is due to a methine carbon. Addition of trifluoroacetic anhydride confirmed that both these peaks are due to carbons atoms  $\alpha$  to hydroxyl groups. This confirmed the presence of both secondary and tertiary alcohol groups in the product, although only the secondary alcohol groups were expected. To account for the formation of tertiary alcohol groups, reaction Scheme I has been proposed. Thus once the diborane was added to an alkene





Scheme 1

group, the resulting monoalkyl borane (I) can then react with a second alkene moiety to give a dialkyl borane. This may either occur intermolecularly (not shown in Scheme I) or intramolecularly (shown in the second step of Scheme I) with a neighboring double bond. Intramolecular addition could give either a five-membered (II) or six-membered (III) cyclic dialkyl borane, depending on the direction of addition to the double bond. With cycloboranes the six-membered ring is less favorable than the five-membered ring.<sup>26</sup> Oxidation of five-membered dialkyl borane results in formation of a secondary alcohol group and an adjacent tertiary alcohol group (IV). According to this mechanism, the tertiary alcohol group could only be formed adjacent to a secondary alcohol group but two adjacent tertiary alcohol groups would not be possible.

The assignment of the remaining peaks was completed by considering triad sequences involving C, H, and S. Eight sequences involving S and C are possible. According to the mechanism shown in Scheme I, tertiary alcohol groups are possible only on the right side of a secondary alcohol group, so that only four arrangements are possible involving the H unit. From an INEPT spectrum it was found that in the upfield region of Figure 2b,  $\text{C}_{13}$  and  $\text{C}_{15}$  were due to methyl carbons,  $\text{C}_7$  to a methine carbon and the rest due to methylene carbons. To facilitate further assignments, the  $^{13}\text{C}$  NMR chemical shifts were calculated using shift factors and substitution effects of secondary alcohol groups<sup>18,29</sup> as given in Table I. The values so calculated are given in Table IV. For the most part, the calculated and observed chemical shift values

TABLE IV  
Assignment of the Upfield Region of the  $^{13}\text{C}$  NMR Spectrum (Figure 2b) of Hydroxylated  
Natural Rubber Obtained by Hydroboration and Subsequent Oxidation

Carbon atom	Chemical shifts (ppm)		Peak
	Calculated	Observed	
$^5\text{S}$	17.90	14.22	$\text{C}_{15}$
$\text{C}^1\text{SC}, \text{C}^1\text{SS}, \text{C}^1\text{SH}$	34.07	33.60	$\text{C}_8$
$\text{C}^2\text{SC}, \text{S}^2\text{SC}, \text{C}^2\text{SS}$	38.80	38.57	$\text{C}_7$
$\text{S}^2\text{SS}, \text{C}^2\text{SH}, \text{S}^2\text{SH}$			
$\text{S}^1\text{HC}, \text{S}^1\text{HS}$			
$\text{CS}^4\text{C}, \text{C}^1\text{CS}, \text{SS}^4\text{C}$	32.23	32.23	$\text{C}_9$
$\text{CS}^4\text{S}, \text{SS}^4\text{S}$	28.83	28.41	$\text{C}_{17}$
$\text{S}^1\text{CC}, \text{S}^1\text{CS}$			
$\text{CC}^4\text{S}, \text{SC}^4\text{S}$	26.36	25.90	$\text{C}_{12}$
$\text{CC}^4\text{C}, \text{SC}^4\text{C}$	26.36	26.36	$\text{C}_{11}$
$\text{S}^1\text{SC}, \text{S}^1\text{SS}, \text{S}^1\text{SH}$	30.67	30.42	
$\text{CS}^4\text{H}, \text{SS}^4\text{H}$	30.01	29.72	$\text{C}_{16}$
$\text{SH}^3\text{C}, \text{SH}^3\text{S}$	42.37	41.31	$\text{C}_6$
$\text{SH}^4\text{C}, \text{SH}^4\text{S}$	22.31	22.33	$\text{C}_{14}$

show good agreement except for a few cases where further explanation is required. For example,  $\text{CC}^4\text{S}/\text{SC}^4\text{S}$  gave the same calculated value (i.e., 26.36 ppm) as  $\text{CC}^4\text{C}/\text{SC}^4\text{C}$  (assigned to  $\text{C}_{11}$  at 26.36 ppm). But there was an unmatched peak at 25.9 ppm ( $\text{C}_{12}$ , Fig. 2b).  $\text{CC}^4\text{S}/\text{SC}^4\text{S}$  is one C—C bond away from a double bond and three C—C bonds away from an alcohol group while  $\text{CC}^4\text{C}/\text{SC}^4\text{C}$  is one C—C bond away from a double bond and two C—C bonds away from another double bond. Thus, a comparison should be made between a carbon atom which is three C—C bonds away from a secondary alcohol group (23.00 ppm in 5-nonyl alcohol) and a carbon atom which is two C—C bonds away from a double bond (23.44 ppm in non-4-ene). Therefore, it was reasonable to expect that  $\text{CC}^4\text{S}/\text{SC}^4\text{S}$  would be slightly (0.4 ppm) upfield from  $\text{CC}^4\text{C}/\text{SC}^4\text{C}$ . Thus,  $\text{CC}^4\text{C}/\text{SC}^4\text{C}$  was assigned to  $\text{C}_{12}$ , which is about 0.4 ppm upfield from  $\text{C}_{11}$ . Furthermore, the peaks due to methylene carbons  $\text{S}^1\text{HC}/\text{S}^1\text{HS}$  (calculated value 38.97 ppm) could be expected to be hidden under the methine peak  $\text{C}_7$ . The reason for the poor agreement between the observed and calculated chemical shifts of resonance  $\text{C}_{15}$ , assigned to methyl carbon  $^5\text{S}$  by an INEPT spectrum is not known.

The assignments shown in Table IV were confirmed by an LSR experiment illustrated in Figure 4.  $\text{C}_7$  which is due to a methine carbon only one C—C removed from a hydroxyl group had the largest shift. This was followed by the peaks  $\text{C}_8$  and  $\text{C}_{17}$  which are due to methylene carbons that are two C—C bonds removed from a hydroxyl group.  $\text{C}_{12}$ , which is due to a methylene carbon three C—C bonds removed from a hydroxyl group, exhibited the smallest shift. The fact that  $\text{C}_9$  did not move probably indicates that  $\text{CS}^4\text{C}$ ,  $\text{SS}^4\text{C}$ ,  $\text{CS}^4\text{S}$ , and  $\text{SS}^4\text{S}$ , which are only one C—C bond from a hydroxyl group, do not contribute appreciably to resonance  $\text{C}_9$ .  $\text{C}_6$  had a lanthanide shift similar to that of  $\text{C}_7$ . The intensity of  $\text{C}_{16}$  was so low that its movement could not be followed. However, the assignments could not be used for quantitative analysis due to overlapping of the signals, as evident from Table IV. The

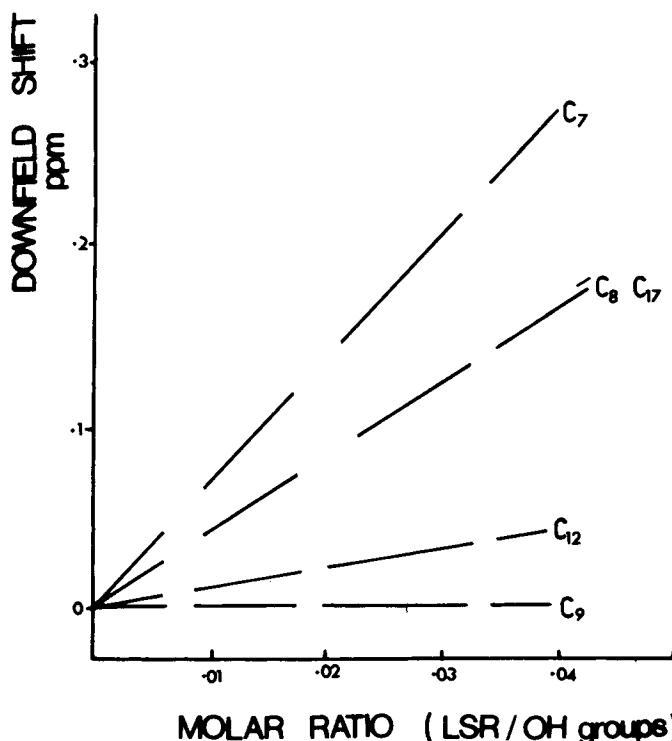


Fig. 4. Lanthanide shifts of some resonances given in Figure 2b and Table IV.

absence of the  $\text{C}_{18}$  resonance (due to adjacent tertiary alcohol groups) in Figure 2b is consistent with Scheme I for the production of tertiary alcohol groups adjacent to secondary alcohol groups. The assignments in Table IV are also consistent with Scheme I.

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