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Singlet Oxygenation of cis *and* trans-*1, 4-polyisoprene and* cis-*2,6-dimethylocta-2,6-diene*

A. RICHARD ARNOLD*, ANDREW J. BOON**,
JOHN L. COURTNEIDGE*** AND PAUL S. FARLEY***

Mono- and bis-hydroperoxides have been isolated from the reaction between singlet oxygen and 2,6-dimethyl-2,6-octadiene and their ^1H NMR spectral parameters are given. This information is used to examine both new and previously published ^1H and ^{13}C NMR data for the products of the reactions between singlet oxygen and both natural rubber and Gutta Percha. The relevance of these results to chain mobility in polyisoprenes is discussed.

2,6-dimethylocta-2,6-diene (DMOD), despite certain shortcomings, has proved a popular model for investigations on the reactions of 1,4-polyisoprenes. This popularity derives, in part, from the ready synthesis of the two geometrical isomers[1] and the comparatively simple spectroscopic characterisation which the products of their reactions might afford.

Interest in the singlet oxygenation of natural rubber (NR) and other polymers and suitable polymer-models was largely prompted by the possible role of this process in light-induced surface deterioration of polymeric materials[2]. The facility with which the oxygen scavenging nature of this reaction occurs resulted in a suggested design for an NR-based packaging material suitable for oxygen-sensitive commodities[3].

Although the detailed chemistry of this reaction is subtly different from that expected in the autoxidation of NR, such studies provide very suitable reference data for assessing the generation, or otherwise, of NR-bound allylic hydroperoxide groups during the latter process. Considering the available literature on the reactions of NR and NR-specific models with singlet oxygen, we recognised the need for a re-investigation of these reactions. Accordingly, we report herein our results on studies of the reactions of singlet oxygen with NR (and the synthetic *cis*-1,4-polyisoprene, Cariflex-IR-305), *Gutta Percha* and *cis*-DMOD. *Cis*-DMOD being a methyl-terminated diene, permits relatively simple regio-chemical product assignments, and the NMR data for its adducts with singlet oxygen may be compared with those of both the hydroperoxidised polyisoprenes and mono-ene models which are discussed below.

EXPERIMENTAL

Materials and Methods

Cis-DMOD (1: prepared according to the method of Greenlee and Wiley[1]) was presented by Dr A.V. Chapman of the MRPRA laboratories. Other materials were commercially available and were used as received: particular attention was paid to the use of HPLC-grade solvents for chromatographic procedures.

*Malaysian Rubber Producers Research Association, Brickendonbury, Hertford SG13 8NL, United Kingdom
Present address London International Group, Research and Development, Unit 205, Cambridge Science Park, Milton Road, Cambridge CB4 4GZ, United Kingdom
**Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8NL, United Kingdom
Present address Coates Lorilleux International, Cray Avenue, St Mary Cray, Orpington, Kent, BR5, 3PP, United Kingdom
***Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8NL, United Kingdom

Thin-layer chromatography was performed using aluminium-backed, silica gel-coated plates (E. Merck, Darmstadt, Art. No. 5554). Peroxidic spots were located using ADADH (p-dimethylammonium-aniline dihydrochloride, Fluka)[4,5] spray, once the developed plate had been examined under short-wavelength ultra-violet illumination. More generally, phosphomolybdic acid and acidified vanillin sprays were used for spot location.

Flash chromatography was carried out using 230–400 mesh silica gel (Merck, Grade 60). In preliminary experiments, samples were separated by combinations of Normal Phase (Prep-Pak 500 Silica; 10% v/v diethyl ether in hexane) and Reverse Phase (Partisil 10 ODS 2, 45% v/v acetonitrile in water at 50°C) Medium and High Performance-Liquid Chromatography (a Walters Prep 500 and a locally configured instrument respectively).

^{1}H and ^{13}C NMR spectra were recorded using a General Electric QE-300 spectrometer located in the MRPRA laboratories and a Varian VXR-400 Spectrometer located in the Chemistry Department, University College London. Elemental analyses were performed using a Perkin Elmer PE240 instrument by Mr J.E. Davey in the MRPRA laboratories.

Procedures

Cis-*DMOD singlet oxygenation*. In preliminary experiments, solutions of the diene (typically *ca* 0.4*M*) in dechloromethane (DCM) or 5% vol. methanol in tetrachloromethane with added methylene blue as sensitiser were irradiated using an external array of 4 × 100 watt tungsten filament light bulbs. At appropriate times, the reaction solutions were concentrated by rotary evaporation and, guided by the results of TLC examination, separations were effected by combinations of Medium and High Performance-Liquid Chromatography.

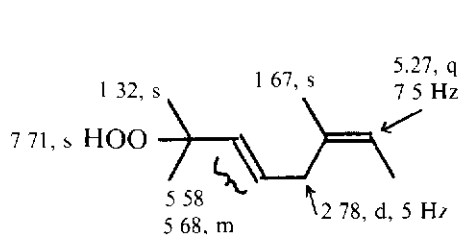
The larger part of the work reported here refers to material obtained in the following way. A solution containing *cis*-DMOD (3.17 g, 23 mmol), BHT (0.25 g, 1.1 mmol, Aldrich Chemical Company) and TPP (30 mg, 0.05 mmol, 99+% Aldrich) in dichloromethane (200 cm^3) was charged into an immersion-well photo-reactor (Pyrex glass), attached to an oxygen-filled water-adjusted gas burette. The solution, magnetically stirred at room temperature, was irradiated with the output from a 400W Thorn, high-pressure SON-T sodium lamp. The light was filtered through a running cold-water jacket placed between the lamp and the reaction solution and was reflected back onto the solution using an aluminium foil screen. Oxygen uptake was extremely rapid. Within 30 min, slightly less than 1*M* equivalent of oxygen had been absorbed to give an olive-green solution, which, upon rotary-evaporation (bath at room temperature; 25 mm Hg aspiration pressure) left a fairly viscous, red residue (6.90 g). A portion (1 cm^3, *ca* 1.5 g) of this residue was loaded onto a silica-gel filled flash-chromatography column (17 g, slurry packed with dichloromethane). This material was eluted using, initially, dichloromethane (200 cm^3) then stepped portions (100 cm^3) of methanol (1% vol. then 2% vol.) in dichloromethane. Fractions of the eluate (each 25 cm^3) were examined by TLC. *Fractions 3* and *4*, when combined and concentrated gave a reddish liquid (134 mg) containing the mono-hydroperoxides, while *Fractions 9–19* contained the bis-hydroperoxides as a green gum (676 mg). The contaminants in each material (judged by ^{1}H NMR spectroscopy to be TPP and BHT respectively) were removed by further chromatography of each material over a similar quantity of silica gel using dichloromethane eluant for the mono-hydroperoxides and, after an initial dichloromethane elution (100 cm^3), 2% vol. methanol in dichloromethane for the bis-hydroperoxides.

The mono-hydroperoxides (comprising three over-lapping spots, R_f (DCM) 0.36,

0.29 and 0.23) were collected, concentrated by rotary evaporation and finally dried by evacuation (room temperature, 0.05 mm Hg, 1 h) before prompt elemental analysis of the resultant slightly brown oil (106 mg). The data obtained corresponded to that expected for a mixture of DMOD-derived monohydroperoxides ($C_{calc} = 70.55\%$, $C_{found} = 71.0\%$; $H_{calc} = 10.66$, $H_{found} = 10.5\%$), while ^{1}H NMR spectroscopy showed this material to contain the compounds listed in *Table 1*. ^{1}H NMR data for reference compounds are given in *Table 2*.

The bis-hydroperoxides (showed by TLC to be somewhat unstable, despite expeditious handling) were collected in two portions. The less polar portion (gum, 197 mg, mainly R_f (DCM) = 0.15) and the more polar material (gum, 308 mg, R_f (DCM) = 0.13 – 0.15) were concentrated, freed from solvent traces and promptly analysed for elemental composition. For DMOD-derived bis-hydroperoxides calculated elemental values are C = 59.38% and H = 8.97%. For the less polar portion, values of 59.5% and 9.0% respectively

TABLE 1 ^{1}H NMR DATA FOR SOME SINGLET OXYGEN-DERIVED DMOD MONO-HYDROPEROXIDES[a]



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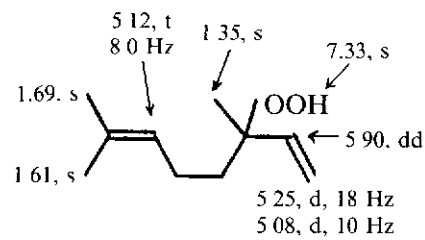

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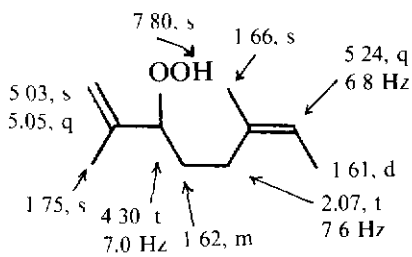

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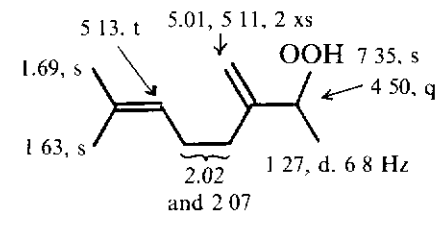
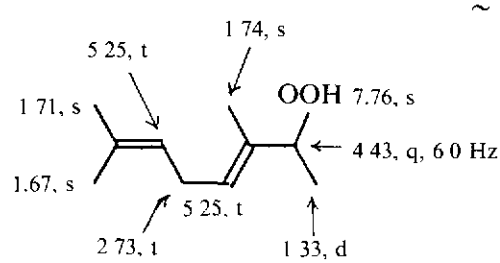


6[b]

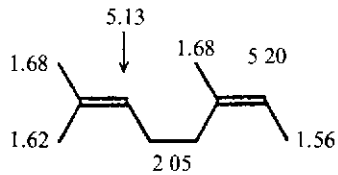


7[b]

[a]Chemical shifts quoted for deuteriochloroform solutions (δ; p.p.m., TMS reference)

[b]Tentative assignments for minor components

TABLE 2. ^{1}H NMR DATA FOR REFERENCE COMPOUNDS[a b]



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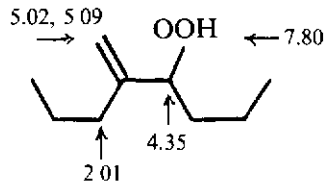

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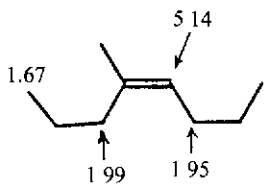

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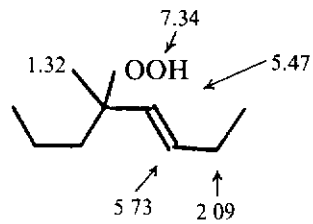

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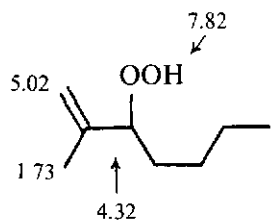

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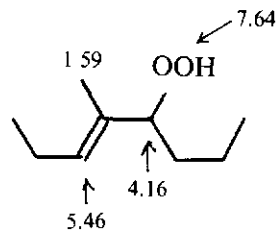

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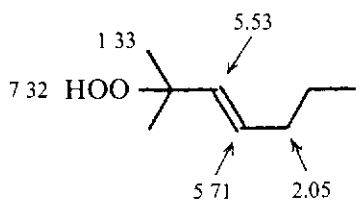

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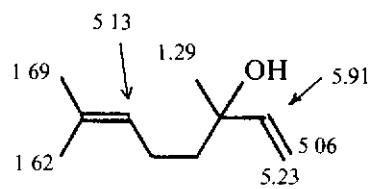
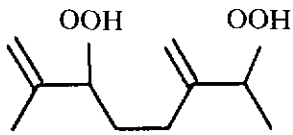


15

[a]Chemical shifts quoted for deuteriochloroform solutions (δ; p.p.m.; TMS reference)
[b]Compounds 1 (Reference 6); 9, 12-14 (Reference 7); 10, 11 (Reference 8); 15 (Commercial)

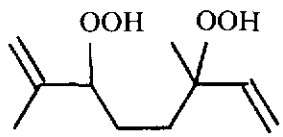
were found. For the more polar material, corresponding values of 60.8% and 9.3% were obtained. The ^{1}H NMR data for these materials are given in *Table 3*. The spectrum for the more polar portion contained significant absorptions (particularly in the

TABLE 3 ^{1}H NMR DATA FOR SOME SINGLET OXYGEN-DERIVED DMOD BIS-HYDROPEROXIDES[a]



16 (× 2)

4 × OO<u>H</u>	in range 8 1 – 8 7
2 × C = C<u>H</u>$_2$	one isomer 5 13 and 5 01 [2 × broad singlet (br s)]
	one isomer 5 01 (br s)
C<u>H</u> (OOH)	one isomer 4 52 multiplet (m)
	one isomer 4 40 (m)
Allylic C<u>H</u>$_2$	2 10 – 2 20
C<u>H</u>$_3$ – C = C	1 76, s
Homoallylic C<u>H</u>$_2$	1 5 – 1 7
C<u>H</u>$_3$ CH (OOH)	1 27 (one isomer), 1 26 (one isomer)
	[2 × doublet (d), J = 7 0 Hz]



17 (× 2)

4 × OO<u>H</u>	in range 8 1 – 8 6
C<u>H</u> = C<u>H</u>$_2$	5 88 (major isomer), 5 89 (minor isomer)
	each doublet of doublet (dd), J = 10 5 and 18 Hz
	5 22 (d, J = 10 5 Hz) and d5 24 (3, J = 18 Hz)
	both isomers superimposed
C = C<u>H</u>$_2$	5 01 (both isomers broad singlet)
C<u>H</u> (OOH)	4 32 (both isomers, distorted triplet, J ~ 6 5 Hz)
C<u>H</u>$_3$ – C = C	1 73 (both isomers, s)
C<u>H</u>$_3$ – C(OOH)	1 31 (both isomers, s)
2 × C<u>H</u>$_2$	1 5 – 1 7 and 1 2 – 1 3 (both isomers, multiplets)

[a]Chemical shifts quoted for deuteriochloroform solutions in units of parts per million (δ) from internal TMS

δ3.5 – 3.8 region) which could not satisfactorily be ascribed to the spectra of the predicted bis-hydroperoxides.

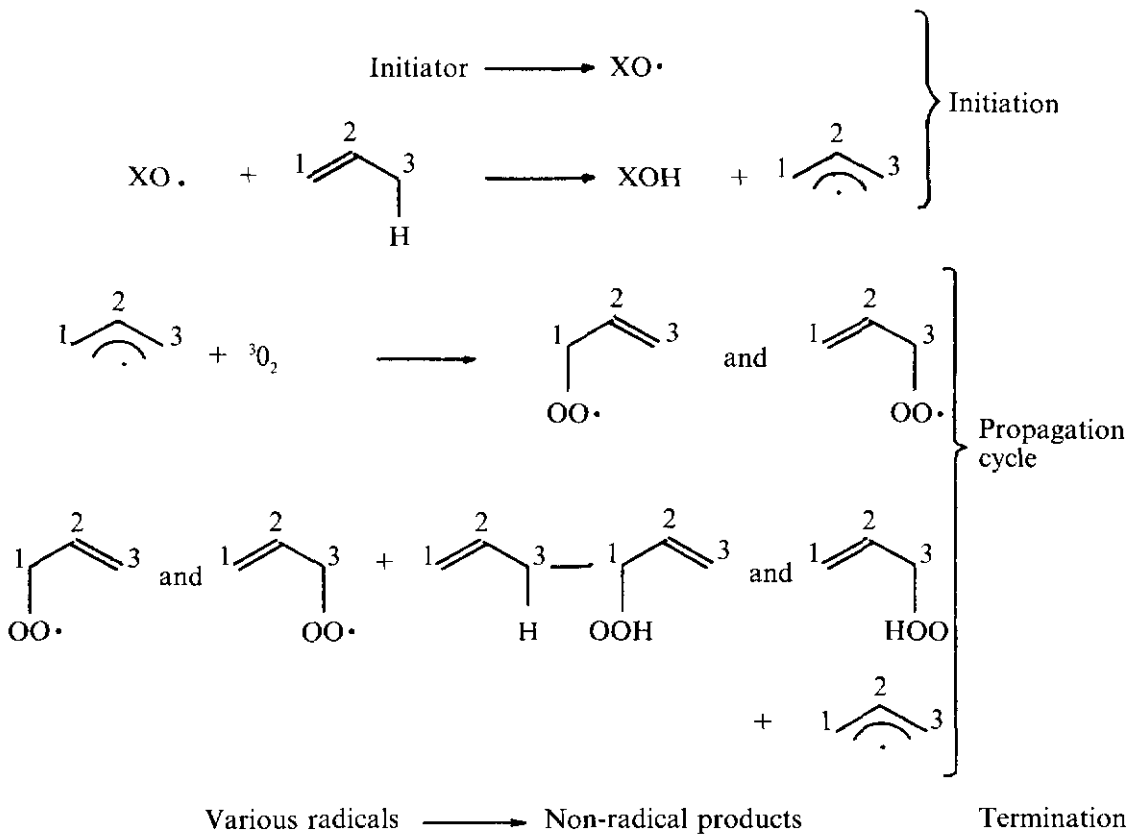
Polymer singlet oxygenation. Hydroperoxidised NR was prepared by dissolving DPNR (deproteinised NR 3 g) in dichloromethane (300 cm^3) which contained methylene blue (15 mg). After saturation with oxygen, and maintaining a flow of oxygen through the solution, the sample was illuminated using a 400W Thorn high-pressure SON-T sodium lamp. Withdrawn samples were monitored for hydroperoxide and carbonyl production, and after 45 min, the modified rubber was recovered by precipitation from a large excess of ethanol. Drying by evacuation at room temperature was followed by prompt spectroscopic analysis.

Singlet oxygenated IR was prepared in the same way, using commercial Cariflex IR-305.

Gutta Percha was purified by dissolution in warm petroleum ether (bp 60°C–80°C) followed by filtration through lens tissue into cold methanol. The resultant, almost white material was found to be readily soluble in dichloromethane and was hydroperoxidised as described above for DPNR.

RESULTS AND DISCUSSION

A simplified free-radical initiated alkene autoxidation scheme is presented below *(Scheme 1)*.



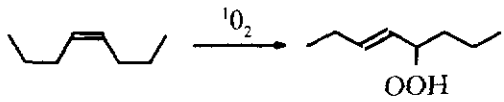
Scheme 1
Simplified free radical-mediated, alkene autoxidation reaction scheme.

Unlike the free-radical process, where even a symmetrically substituted alkene will usually give a mixture of allylic hydroperoxides, the reactions of singlet oxygen ($^1O_2$) with alkenes (an ene reaction in which an intra-molecular double-bond shift occurs[9]) can provide simpler products Some examples are given in *Equations 1*[10] *2*[11] and *3*[7]

Even though the singlet oxygen reaction offers this simplification for the preparation of DMOD mono-hydroperoxides, seven such isomers can be expected for each DMOD isomer For *cis*-DMOD (1), the possibilities are outlined in *Scheme 2*

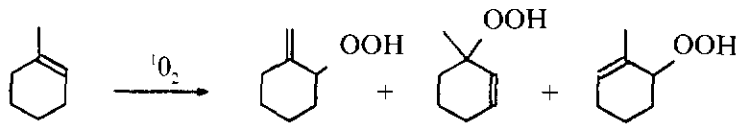
Despite the number of potential products, recent advances in separational and spectroscopic techniques place us in a position to characterise the products of this reaction and compare their spectral properties with the products of singlet oxygen-modified NR, Cariflex IR-305 (IR) and *Gutta Percha*

In considering the target reaction *(Scheme 2)*, it was anticipated that, at synthetically useful conversions, the onset of initial product conversion to more highly substituted co-products would become important All of the postulated DMOD mono-hydroperoxides 2–8 contain at least one tri-substituted double bond and each is anticipated to be about as reactive towards a singlet oxygen molecule as the double bonds in substrate 1 A complex mixture was therefore expected to result Taking diastereoisomers into account, attack at the unmodified double bonds in 2–7 would result in the formation of twenty-one bis-hydroperoxides and, with attack at the already modified double bond, a further seventeen possible bis-hydroperoxides



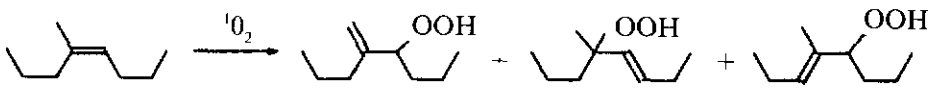
1

98% trans



2

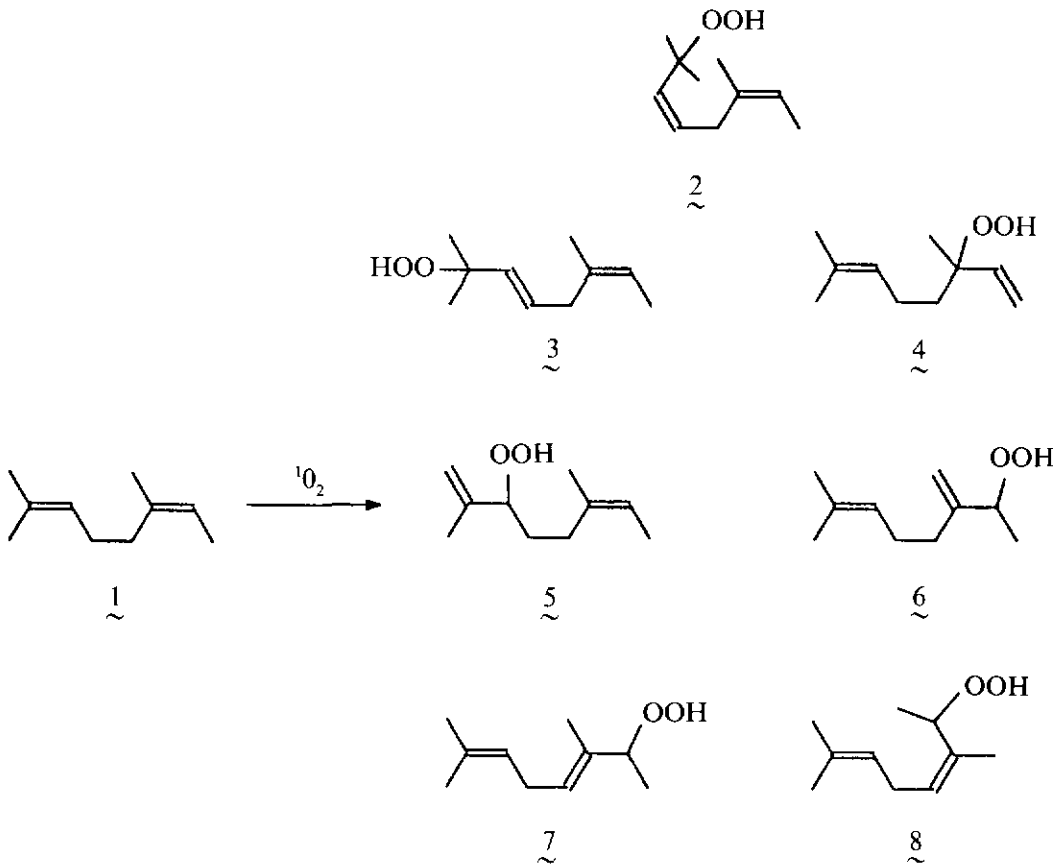
43% 41% 16%



3

23% 75% 3%[a]

[a]Isolated as other products



Scheme 2

Possible mono-hydroperoxides from the singlet oxygenation of *cis*-DMOD

It was anticipated that the chromatographic polarities of the mono- and bis-hydroperoxides (and indeed any more highly oxygenated products) would be significantly different and this expectation proved to be the key to the isolation of the simple mono-hydroperoxides

Thus, limited photo-oxygenation of *cis*-DMOD gave a mixture which could initially be separated by Flash Chromatography[12] into two fractions of different polarities The first fraction had thin-layer chromatographic polarity typical of mono-hydroperoxides and thus were considered to be a mixture of DMOD-derived mono-hydroperoxides this was shown to be the case by a satisfactory combustion analysis for this first fraction and by high field ^{1}H NMR spectroscopic analysis of the fraction as a whole, and of individual isomers subsequently separated therefrom

Our structural assignments for these mono-hydroperoxides *(Table 1)* are based on the predicted spectroscopic properties of structures 2–8 and spectroscopic data which we have collected *(Table 2)* for compounds, either commercially available or prepared during the course of related studies

The more polar materials were collected in two further fractions The first portion gave a combustion analysis consistent with

the presence of only bis-hydroperoxides and ^{1}H NMR analysis indicated that two pairs of diastereoisomers were present (16 × 2 and 17 × 2: *Table 3*).

Combustion analysis of the second portion was not consistent with the sole presence of bis-hydroperoxides (high values for both carbon and hydrogen were found) and ^{1}H NMR spectroscopic analysis suggested the presence perhaps of other bis-hydroperoxides, along with other, unidentified products.

Tanielian and Chaineaux[13] previously reported a study of the singlet oxygenation of *trans*-DMOD and (apparently) a mixture of the *cis*- and *trans*-isomer. Faced with the product complexity, they resorted to analysis of the whole product after reduction of the peroxides, followed by trimethylsilylation of the resultant alcohols. Assignment of isomers was based solely on the mass-spectral fragmentation patterns of the gas chromatographically-separated trimethylsilyl ethers. They claimed that, as the photo-oxygenation progressed, the initially-formed mono-hydroperoxides were converted, at about half the rate of the starting diene, into bis-hydroperoxides; and that, of the two dienes, the *trans*-isomer was slightly more reactive than the *cis*-isomer.

In view of the complication of competitive subsequent conversion of the first-formed mono-hydroperoxides, it is difficult for us to comment in detail on the isomeric distribution of the isolated mono-hydroperoxide mixture. Suffice to say that from our NMR analysis, the *tertiary* and *exo*-methylene isomers were preponderant. This is commensurate with isomer ratios found during the singlet oxygenations of many tri-substituted alkenes[14,15] and with the probable origins of the bis-hydroperoxides identified in our reaction (*Table 3*).

The singlet oxygenation of 1,4-polyisoprenes has been extensively studied and the principal findings have been reviewed by Golub[16], but the reviewed data was obtained before high field NMR spectrometers were widely available. We can now present detailed ^{1}H and ^{13}C NMR for singlet oxygenated NR (*cis*-1,4-polyisoprene) and *Gutta Percha* (*trans*-1,4-polyisoprene), prepared at low conversions, using the optimum photo-sensitiser (tetraphenylporphin: TPP) in the presence of a protective antioxidant (2,6-di-*t*-butyl-4-methylphenol: BHT)*: *Tables 4, 5* and *6*.

The micro-structural quantitations given in *Table 4* rely on 'trace and weigh' analysis of a comprehensive selection of the ^{1}H NMR absorptions shown in *Table 5* such that self-consistent sets of relative ratios were obtained. As an indication of the quality of spectra available by this technique, selected portions of the ^{1}H NMR spectrum of a NR singlet oxygenation product are reproduced in *Figure 1* (data for the vinylic methylene signals were best obtained from spectra of IR-derived material: the lower molecular weight of this polymer results in a narrower overlapping vinylic proton signal for the unmodified polymer segments).

The micro-structural ratios (I–III) for both NR and *Gutta Percha* reported here are markedly different from those that have been given by previous workers. For *Gutta Percha* we are quite confident that our findings both of a near equality of micro-structures I and III and the fact that micro-structure II is not detectably formed are correct on the basis of published data by other workers for model *trans*-trisubstituted alkenes and for our own unpublished data for comparable systems: for NR, the micro-structural ratio I:III of 3.5:1 is the same as that which we find for the singlet oxygenation of cis-4-methyl-4-octene[7], although for other systems[14] containing more highly branched alkyl groups, this ratio approaches 8:1.

The proportion of products having micro-structure II is expected to vary with the

*Workers should be aware that BHT can act as a competitive substrate for singlet oxygen and the mono-hydroperoxide derived therefore can cause difficulties in product isolation[7]

TABLE 4 MICRO-STRUCTURE ISOMER RATIOS AFTER SINGLET OXYGENATION OF NR AND *GUTTA PERCHA*[a]

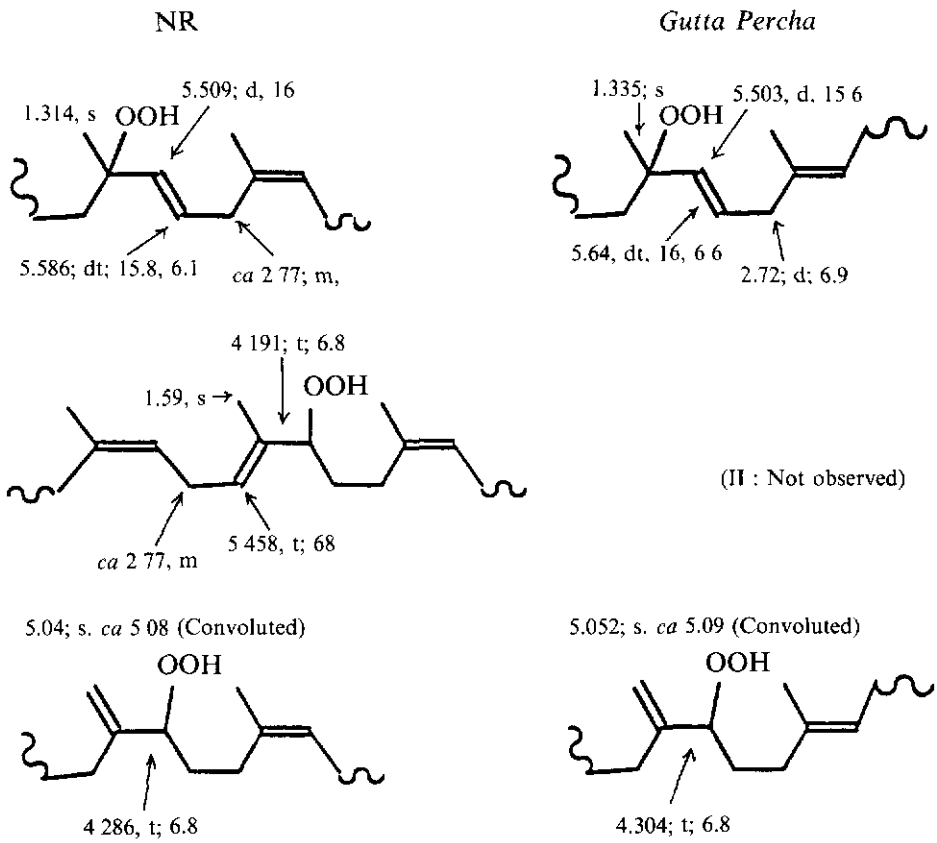
1,4-Polyisoprene configuration	OOH I	OOH II	OOH III	Reference
cis	58 7	21 8	19 5	This work
cis[b]	62 2	21 6	16.2	This work
cis[c]	64 4	18 5	17.1	This work
cis	47	47	6	16
trans	51 4		48 6	This work
trans	48	26	26	16

[a]Analysis by quantitative ^{1}H NMR (400 MHz, $CDCl_3$; TMS, *ca* 12 mol%) conversions

[b]Duplicate preparation

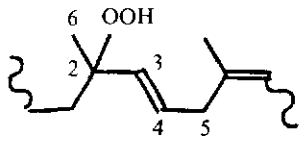
[c]Analysis as allylic alcohols after triphenylphosphine reduction

TABLE 5 CHARACTERISTIC ^{1}H NMR SIGNALS FOR MICRO-STRUCTURES I–III[a]

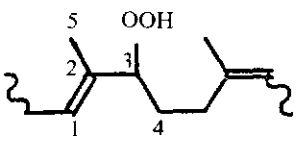


[a]δ (OOH): individual signals at variable shifts 7.2–7.8 in appropriate intensities for micro-structural ratios given in *Table 4*.

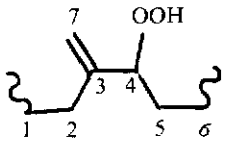
TABLE 6 CHARACTERISTIC ^{13}C NMR SIGNALS FOR MICRO-STRUCTURES I–III



	NR	*Gutta Percha*
C1	38 05	34 23
C2	84 31	84 42
C3	133 01	133 26
C4	129 58	130 68
C5	35 14	35 65
C6	21 55	21 19



	NR
C1	133 49
C2	134 98
C3	91 55
C4	23 26
C5	Convoluted



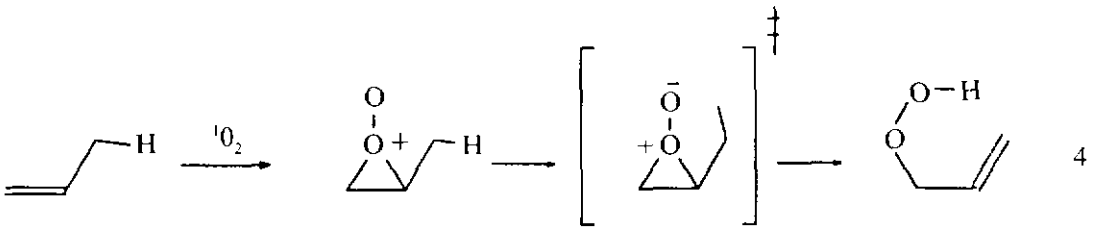
	NR	*Gutta Percha*
C1	30 32	29 73
C2	29 45	29 47
C3	147 56	147 44
C4	89 27	89 11
C5	32 09	30 99
C6	Convoluted	29 45
C7	113 00	113 28

extent of reaction but, again taking into account the literature data[14] for comparable systems, a percentage for micro-structure II of about 20% seems not unreasonable Indeed, the data reported here is consistent with the generalisation that singlet oxygen preferentially reacts by abstraction from the most highly-substituted side of a tri-substituted alkene[15-17]

This regio-selectivity in alkene singlet oxygenation has been discussed in terms of the ease with which the transferred hydrogen atom may be rotated towards the abstracting oxygen atom in a perepoxide inter-mediate *(Equation 4)*

Since the activation energy for the reaction is small, it has been argued that the differences between the rotational barriers present in unsymmetrically substituted alkenes govern the regio-selectivity of the reaction and, although a contrary view has recently been expressed[18], theoretical calculations have been advanced to support this contention[19]

Using this argument, the similarity between the micro-structural ratios I III for the models and the polymers suggests a similarity in the barriers to rotation for both cases in solution It remains to be seen, however whether this similarity will also



4

Perepoxide intermediate

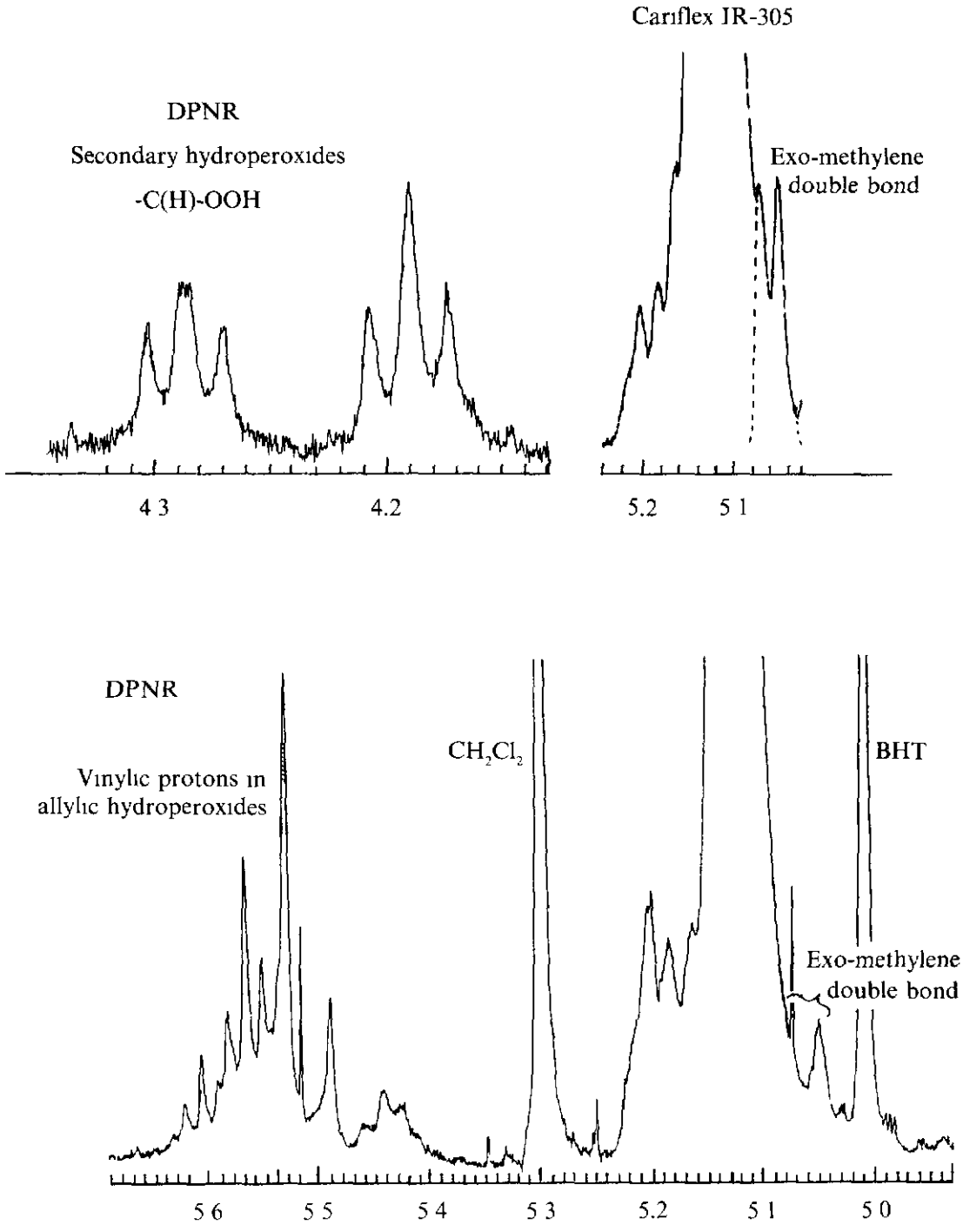


Figure 1 Representative portions of ^1H NMR spectra of singles oxygenated cis-1,4-polyisoprenes

prove to be the situation for local chain mobility in the bulk polymers.

CONCLUSIONS

The singlet oxygenation of *cis*-DMOD can be carried out to provide isolated mono- and bis-hydroperoxides, NMR data for detailed analysis to be made for the corresponding 1,4-polyisoprene reactions. The similarity between the micro-structural ratios for the models and the polymers in solution suggests a similarity in the bond rotational freedom in both cases and this method of polymer conformational analysis is proposed as an approach for exploring local chain mobility in bulk polymers.

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REFERENCES

1. GRFFNLFF, K W AND WILEY, V G (1962) Geometry of Olefins and Diolefins, I *J Org Chem*, **27**, 2304

2 RABEK, J F. (1985) *Singlet O_2, (Frimer, A A, ed)*, Vol IV, Chap 1 Boca Raton, Florida CRC Press, Inc

3 ROONEY, M L (1982) Oxygen Scavenging a Novel Use of Rubber Photo-oxidation *Chem Ind*, 197

4. BUZLANOVA, M.M., STEPHANOVSKAYA, V.F., NESTEROV, A.F AND ANTONOVSKII, L V. (1966) Thin Layer Chromatography of Cyclic Ketone Peroxides, *J. Analyt. Chem. USSR* **21**, 454.

5 BUZLANOVA, M.M, STEPHANOVSKAYA, V F AND ANTONOVSKII. L.V (1966) Thin Layer Chromatography of Organic Peroxides *J Analyt Chem USSR*, **21**, 1324

6 McQUILLAN, F J AND PARKER, D G (1975) Complexing of Terpenes with Transition Metals Part V Reactions of 3,7-Dimethylocta-1,6-diene and of 7-Methoxy-3,7-dimethyloct-1-ene with Rhodium (III) and Thallium (III), *J. Chem, Soc, Perkin Trans, I*, 2092

7 (a) COURTNEIDGE, J.L., BUSH, M AND LOH, L-S. (1992). Initiated *tert*-Butyl Hydroperoxide-loaded Low-temperature Autoxidation of Alkenes: Alternative Hydroperoxide Syntheses and the Preparation of a Complete Set of Reference Materials *J. Chem. Soc. Perkin Trans.*, 1, 1539, (b) COURTNEIDGE, J.L. AND BUSH, M. Initiated *tert*-Butyl Hydroperioxide-loaded, Low-temperature Autoxidation of Alkenes: A Chemioselective Synthesis of Allylic Hydroperoxides, allowing Analysis of the Regioselectivity of Hydrogen Atom Abstraction from Some Unsymmetrically Substituted Substrates, *Ibid.*, 1531.

8 COURTNEIDGE, J.L. AND LOH, L-S. unpublished Data.

9 (a) ORFANOPOULOS, M. STRATAKIS, M AND ELMES, Y. (1989) Tet, Lett., 30, 4875, (b) TANIELIAN, C. AND MECHIN, R (1988) *J. Phys Chem.*, 92, 265; (c) DAVIES, A.G. AND SCHIESSER, C.H. (1989) *Ibid*, 30, 7099; (d) IDEM, (1991) *Tetrahedron*, **47**, 1707.

10 COURTNEIDGE, J.L., BUSH, M. AND LOH, L-S. (1992) 5-Endo Ring Closures of some Allylic Hydroperoxides: Useful Routes to 1,2-Dioxolanes Involving Strongly Stereoselective Free Radical and Polar Reactions, *Tetrahedron*

11. JEFFORD, C W AND RIMBAULT, C.G (1981) Syn Regio-selectivity of the Hydroperoxidation of cyclo Alkenes with Singlet Oxygen, *Tet. Lett.*, **22**, 91

12 STILL, W.C., KAHN, M AND MITRA, A (1978) Rapid Chromatographic Technique for Preparative Separations with Moderate Resolution, *J. Ong, Chem.*, **43**, 2923.

13. TANIELIAN, C. AND CHAINEAUX, J. (1978) Singlet Oxygen Reactions with Model Co.-pounds of *cis* and *trans* Polyisoprenes containing Two Units *J Photochem.*, **9**, 19

14 SCHULTE-ELTE, K H , MULLER B L AND RAUTENSTRAUCH V (1978) Preference for Syn Ene Additions of ^1O to Trisubstituted Acyclic Olefins, *Helv Chim Acta* **61,** 2777

15 ORFANOPOULOS, M BELLARMINE GRADINA, SR M AND STEPHENSON, L M (1979) Site Specificity in the Singlet Oxygen-trisubstituted Olefin Reaction *J Am Chem Soc* **101,** 275

16 GOLUB, M A (1980) Photosensitized Oxidation of Unsaturated Polymers *Pure Appl Chem* **52,** 305

17 SCHULTE-ELTE, K H AND RAUTENSTRAUCH V (1980) Preference for the Syn Ene Additions of ^1O to 1-Methylcycloalkenes, Correlation with Ground-State Geometry *J Am Chem Soc* , **102,** 1738

18 ORFANOPOULOS M , STRATAKIS, M , ELEMES, Y AND JENSEN F (1991) Do Rotational Barriers Dictate the Regioselectivity in the Ene Reactions of Singlet Oxygen and Triazolinedione with Alkenes? *J Am Chem Soc* , **103,** 949

19 HOUK, K N WILLIAMS JR , J C , MITCHELL, P A AND YAMAGUCHI, K (1981) Conformational Control of Reactivity and Regioselectivity in Singlet Oxygen Ene Reactions Relationship to the Rotational Barriers of Acyclic Alkylethylenes, *J Am Chem Soc* , **103,** 949