Studies Relating to the Oxidative Degradation of Natural Rubber. The Autoxidation of 1-Methylcyclohexene: Primary Product Analysis, Allylic Hydroperoxide Isolation, and Regiochemistry of the Initial Events

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The autoxidation of 1-methylcyclohexene has been examined; the regiochemistry of the initial events has been defined by direct examination and isolation of the first-formed products and a synthetically useful method has been developed in which t-butyl hydroperoxide-loaded mixtures undergo rapid, low temperature autoxidation.

Study of the oxidative degradation of natural rubber (NR)[1] has formed the basis for understanding the autoxidation chemistry of diverse organic materials.[2] This understanding is based upon the now classical scheme of Bateman and Bolland[1] [equations (1)—(5)].

$$\begin{array}{lllr} \text{Initiator} & \rightarrow \text{X}\cdot & \text{Initiation} & (1) \\ \text{X}\cdot + \text{RH} & \rightarrow \text{R}\cdot + \text{XH} & \left.\right\} & (2) \\ \text{R}\cdot + \text{O}_2 & \rightarrow \text{ROO}\cdot & \text{Propagation} & (3) \\ \text{ROO}\cdot + \text{RH} & \rightarrow \text{ROOH} + \text{R}\cdot & & (4) \\ \text{R}\cdot, \text{ROO}\cdot & \rightarrow \text{Non-radical products} & \text{Termination} & (5) \end{array}$$

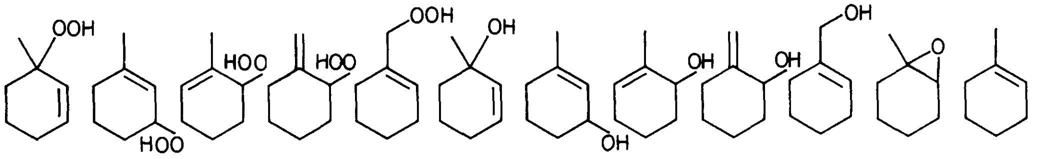
Notwithstanding the insights that this kinetic scheme affords, the detailed molecular events during autoxidation still provide a fruitful area of research.[2a,3] In particular, two aspects which still deserve attention include structural selectivity (regiochemistry, stereochemistry) and product diversity (polyperoxides *vs.* epoxides *vs.* allylic hydroperoxides, *etc.*) in such reactions.

Early workers considered the autoxidation of cyclohexene[4,5] and discovered that this reaction was a viable synthetic route to 3-hydroperoxy cyclohexene. Autoxidation is, however, often considered a poor synthetic procedure,[6] partly in view of the multiplicity of secondary products which arise during the comparatively forcing conditions which many of these reactions require.

In this communication, we report upon a synthetic procedure which allows the primary products of autoxidation to be cleanly isolated and, furthermore, gives insight into the regiochemistry and product distribution of trialkylalkene autoxidation.

Considering the classical scheme we reasoned that low temperature, rapid autoxidation could be facilitated in two ways. Firstly, if the propagation chain length could be

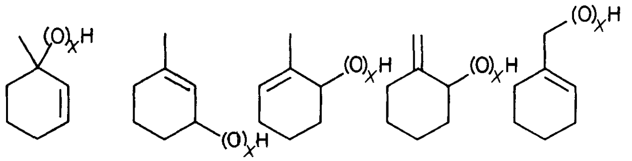
Table 1. Autoxidation of neat 1-methylcyclohexene over 27 h at 60 °C with ~30% conversion.



Integral[a]	128	108	127	12/2 =6	10/2 =5	36	30	29	3	<1	81	1113
% Peroxide[b]	34	29	34	2	1							
% Alcohol[c]						36	30	29	3	1		
% All products[d]	23	19	23	1	1	6	5	5	1	<1	15	

Product types mol % Peroxides : Alcohols : Epoxide
67 : 18 : 15

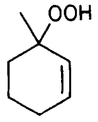
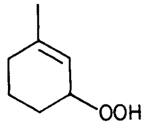
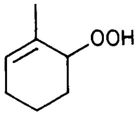
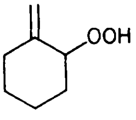
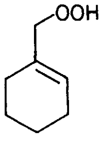
Oxygenation site



Selectivity[e]	mol %	35	29	33	2	1
		(33)	(29)	(37)	(-)	(1)

[a] ^{1}H N.m.r. integration for selected proton absorptions (400 MHz VXR400 spectrometer). [b] Mol% as proportion of total peroxides. [c] Mol% as proportion of total alcohols. [d] Mol% as proportion of total products. [e] Selectivity for oxygenation site: sum of alcohol and peroxide (x = 1, 2). Values in parentheses from Pritzkow *et al.*,[12] who report 73% total alcohol + peroxide, remainder being epoxide.

Table 2. t-Butyl hydroperoxide-loaded autoxidation of 1-methylcyclohexene.

θ / °C	t/h	% Conversion	Sample storage[a]					
30	24	40	A	36	37	24	1.5	1.5
40	5	30	A	33	40	25	1	1
			B	31	37	26	3	3
50	4	30	A	31	40	26	1.5	1.5
			B	33	39	24	2	2

[a] Approximate conversion based on oxygen uptake. [b] A = oxidate stored as frozen benzene solution prior to n.m.r. sample preparation, B = concentrated oxidate stored in deep freeze prior to n.m.r. sample preparation.

increased, a reduced number of termination events would, hopefully, lead to fewer secondary products. Secondly, if an added hydroperoxide were to be included, then an additional equilibrium, equation (6), could be added to the propagation cycle which might prevent the intermediate product peroxyl radical(s) undergoing further reactions such as Brill–Schenck rearrangements[7] or addition reactions.[8]

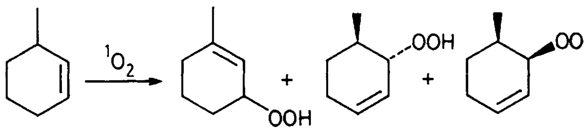
$$\mathrm{ROO\cdot + R'OOH \rightleftharpoons ROOH + R'OO\cdot} \qquad (6)$$

We decided that the inclusion of t-butyl hydroperoxide in the autoxidation medium would achieve these objectives: its chain-carrying t-alkyl peroxyl radicals undergo a reduced rate of self reaction in the termination steps[9] and it is conveniently evaporated from the reaction mixture at the end of the oxidation. Indeed, Ingold, Howard, and co-workers have employed t-butyl hydroperoxide in kinetic studies as a chain-carrying peroxyl radical,[10] implicating equation (6) as a viable equilibrium.

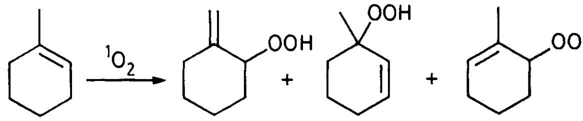
As substrate, we chose to examine the autoxidation of 1-methylcyclohexene: it is a representative trialkylalkene (*cf.* the repeat structure of NR) and, like cyclohexene, it can avail itself of the advantageous entropic factors suggested in other hydrogen atom abstraction reactions[11] of cyclic alkenes.

The autoxidation of this alkene has been studied before; Pritzkow and co-workers examined the behaviour of the neat hydrocarbon[12] and examined the oxidate by g.l.c. and product isolation, after reduction of the peroxidic components by sodium sulphite or lithium aluminium hydride. Herein we report studies of this oxidate along with oxidates derived from our t-butyl hydroperoxide-loaded procedure as intact product mixtures and make our product assignments on the basis of isolated allylic hydroperoxides, allylic alcohols, and epoxide.

In Table 1 we give the product distribution for an uninitiated, neat hydrocarbon autoxidation (2.705 g, Aldrich Chemical Co., 95%, remainder methylenecyclohexane, distilled prior to use from lithium aluminium hydride under nitrogen). The alkene was kept under pure oxygen at 1 atm, unstirred, at 59.8 °C. Over 28 h it absorbed 210 cm^3 of oxygen, equivalent to 31 mol% oxidation. The molar integral ratio (400 MHz ^{1}H n.m.r. spectroscopy) of collected products to residual alkene {(peroxides + alcohols + epoxides) : alkene} indicates 30 mol% oxidation. The spectroscopic assignments are based upon literature data for the allylic alcohols and epoxide along with our data for individually isolated allylic hydroperoxides.



(7)



(8)

Reagents and conditions: tetraphenylporphine (TPP)/$h\nu$, 2,6-di-t-butyl-4-methylphenol (BHT) in CH_2Cl_2.

In Table 2, we present product distributions for t-butyl hydroperoxide-loaded autoxidations (1 M Bu^{t}OOH, 0.1 M substrate, 10 mol% di-t-butyl peroxyoxalate as initiator† in benzene). In all cases, after rotary evaporation of the solvent and the bulk of the t-butyl hydroperoxide at cold water temperature ($p \approx 25$ mmHg), analysis (400 MHz ^{1}H n.m.r. spectroscopy) revealed the overwhelming presence of allylic hydroperoxides.‡ Direct flash chromatography§ of these oxidates afforded samples of the individual allylic hydroperoxides. The tertiary allylic hydroperoxide co-chromatographed

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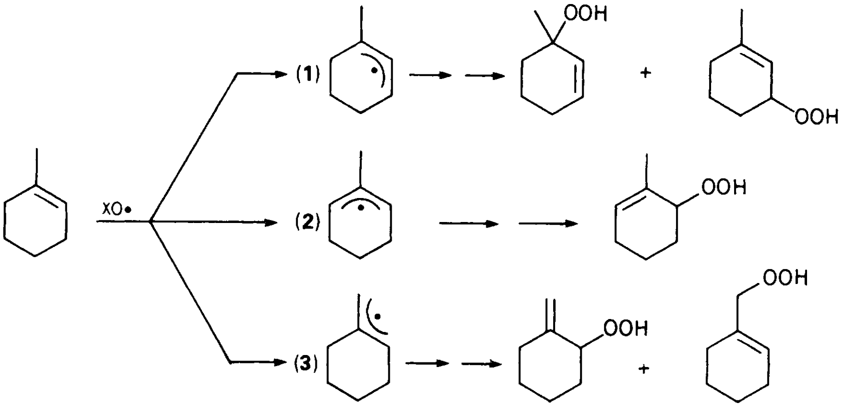
† *Hazard note*: this is an extremely friction sensitive material. In a preparation following, on the published scale, the procedure described by Bartlett and Pincock (*J. Am. Chem. Soc.*, 1960, **82**, 1762), we experienced an explosion caused by shaking of the solvent-wetted material upon transfer from one vessel to another.

‡ The spectra from the reaction products of reaction at 40 and 50 °C revealed the presence of trace amounts of epoxide; allylic alcohols if present at all were below the level of detection.

§ The separations were achieved by normal-phase flash chromatography using dichloromethane on Merck 9385 silica (or Aldrich equivalent); we find that, in certain instances, enhanced resolution can be achieved by operating the chromatography at sub-ambient temperatures (−10 to −20 °C). The structural assignments for the hydroperoxides rely upon 400 MHz ^{1}H n.m.r. spectra and correlation, after triphenyl phosphine reduction, with published data for known allylic alcohols.



Scheme 1. X = H, (allylic), (allyloxy).

with its allylically-related secondary isomer. In order to obtain a clean sample of the secondary isomer we resorted to separation of the product mixture from the photo-assisted singlet oxygenation of 3-methylcyclohexene, equation (7), and for the tertiary isomer to separation of the products of the equivalent reaction of 1-methylcyclohexene, equation (8).

The primary allylic hydroperoxide (present in only trace amounts in the autoxidation mixtures) was more readily available from the singlet oxygenation of methylenecyclohexane[13] or, better, from silver trifluoroacetate-assisted perhydrolysis[14] of the mixture of allylic chlorides derived from t-butyl hypochlorite chlorination[11] of 1-methylcyclohexene.

Apart from the synthetic utility of the t-butyl hydroperoxide-loaded autoxidations, some mechanistic questions may be addressed. First we consider the regiochemistry of allylic hydroperoxide formation. The selectivity of hydrogen atom abstraction in both autoxidation procedures accords qualitatively with predictions based on Bolland's rules,[15] the ratio per hydrogen atom (CH_2 *trans* to Me) : (CH_2 *gem* to Me) : (Me) being 3 : 1 : <0.1. This ratio varies with the nature of the autoxidation medium but seems essentially invariant over the temperature range of the experiments considered. Abstraction at the methylene *trans* to the methyl group gives what is probably the more stable allylic radical (1,1,3-alkylated), and reaction at this position is sterically least congested (Scheme 1).

In the t-butyl hydroperoxide-loaded experiments, reaction to give radical (**2**) seems slightly disfavoured over that to give radical (**1**), in comparison with the neat hydrocarbon autoxidation. This may be related to the different steric and/or electronic requirements of the chain-carrying radicals in each case (t-butylperoxyl in the former and a mixture of hydroxyl and allylic alkoxyl radicals in the latter).

Judged at face value, the data suggest that oxygen molecule attachment to the first-formed allylic radicals shows little discrimination for either end of each radical. It may be that Brill–Schenck equilibration between allylic peroxyl radicals plays a part in determining the final hydroperoxide product ratios; we will report soon upon the reactions of the individual allylic hydroperoxides under free radical conditions.

Secondly, we may consider the origin of the epoxide in the neat hydrocarbon case. The source(s) of epoxides in autoxidation product mixtures have been a matter for debate over the past thirty years.[2b,3,16] We will address this question in detail in later papers; however we note that in the case of neat hydrocarbon, a concordance between the overall yields of allylic alcohols and of epoxides is seen (mol ratio allylic hydroperoxides : allylic alcohols : epoxides = 4.5 : 1.2 : 1), and that the isomer ratio for the allylic alcohols reflects rather closely that of the allylic hydroperoxides.

We thank Mr. P. S. Farley of Malaysian Rubber Producers' Research Association (M.R.P.R.A.) for recording of the 400 MHz ^1H n.m.r. spectroscopic data and the Board of M.R.P.R.A. for permission to publish this work.

Received, 20th April 1989; Com. 9/01667H

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