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Formation of 2,4-Dimethyl-2-ethenylcyclohexene from Pyrolysis of Natural Rubber and Its Relevance to the Depolymerisation Mechanism of 1,4-Polyisoprenes

SIDEK BIN DULNGALI

An isoprene dimer formed from the pyrolysis of natural rubber has been found by proton nuclear magnetic resonance and infra-red studies to be 2,4-dimethyl-2-ethenylcyclohexene and not its 1,4-dimethyl isomer or a mixture of both. It is postulated that the isoprene dimer is formed from cyclisation of polyisopropenyl radical $\cdot CH_2\text{-}C(CH_3)=CH\text{-}CH_2\sim\sim$, *and not as a result of Diels-Alder dimerisation of isoprene, formed during pyrolysis, or of Diels-Alder reaction between isoprene and the isopropenyl pendant group of a 3,4-unit previously thought to be present in natural rubber.*

Pyrolysis or thermal degradation of natural rubber(NR) has been known to produce two main products namely isoprene and dipentene, an isoprene dimer[1]. A third product formed to about a tenth in amount of dipentene was also thought to be a dimer of isoprene[2]. This product appeared to have gas-liquid chromatography retention time identical to that of a product characteristically formed from the pyrolysis of polyisoprenes containing 3,4- isoprene units[3]. The product was postulated to be 1,4-dimethyl-4-ethenylcyclohexene (1,4-DMEC), its 2,4-dimethyl isomer (2,4-DMEC) or a mixture of both[2,4,5,6]. The exact structure of the product from NR, however, was not established. Some workers[4,5,6] have postulated the formation of 2,4-DMEC in the pyrolysis of NR as being the consequence of 3,4- unit structures they believed to be present in NR. A Diels-Alder reaction between free isoprene, one of the two major pyrolysis products of NR, and the pendant isopropenyl group of a 3,4- unit was assumed. It is now, however, established that NR does not contain either 3,4- or *trans*-1,4-structures within 0.1% limit of detection[7]. Hence, the above postulated mechanism would be unlikely. This paper deals with the unambiguous identification of the DMEC formed from the pyrolysis of NR and the relevance of its formation to the depolymerisation mechanism of 1,4-polyisoprenes. The new pyrolysis technique[8] has provided a means of producing the DMEC in a quantity which could be isolated pure.

EXPERIMENTAL

Preparation of Dimethylethenylcyclohexene from Natural Rubber Pyrolysate

Deproteinised NR samples (10 × 2.0 g rubber) were pyrolysed at 500°C employing induction heating as described elsewhere[8]. A total yield of 19.1 g (95.5%) pyrolysate was obtained as distillate. After the removal of isoprene by distillation, the pyrolysate was subjected to pot-to-pot distillation (22°C, 10^{-2} mm Hg). By gas-liquid chromatography the distillate was found to consist essentially of C_{10} hydrocarbons and below with the major components being dipentene (65%) and DMEC (8%). Pure samples of DMEC were obtained by preparative gas-liquid chromatography (SE 30 stationary phase at 175°C). The isolated sample was structurally characterised by spectroscopic methods.

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Preparation of Authentic Reference Samples of 1,4- and 2,4-Dimethyl-4-ethenylcyclohexenes

The samples were synthesised by the method of Hammond *et al*[9]. and obtained pure by preparative gas-liquid chromatography. The pure isomers gave proton nuclear magnetic resonance (^{1}H n.m.r.) and infra-red spectra as shown in *Figures 1 – 4.*

Gas-liquid Chromatography

Three stationary phases were employed, namely:

- 10% silicone gum rubber (SE 30)

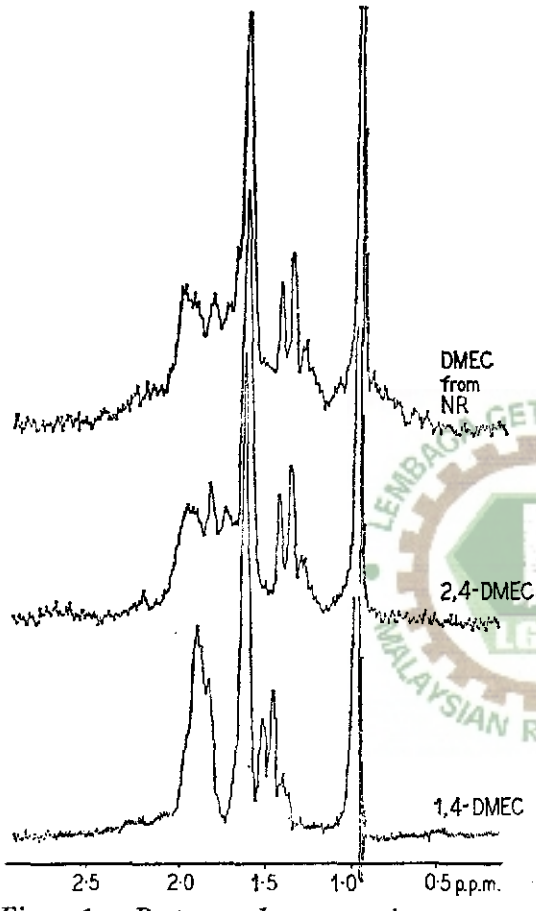

Figure 1. Proton nuclear magnetic resonance spectra (aliphatic region) of 1,4- and 2,4-dimethyl-4-ethenylcyclohexenes and the dimethylethenylcyclohexene isolated from pyrolysis of natural rubber.

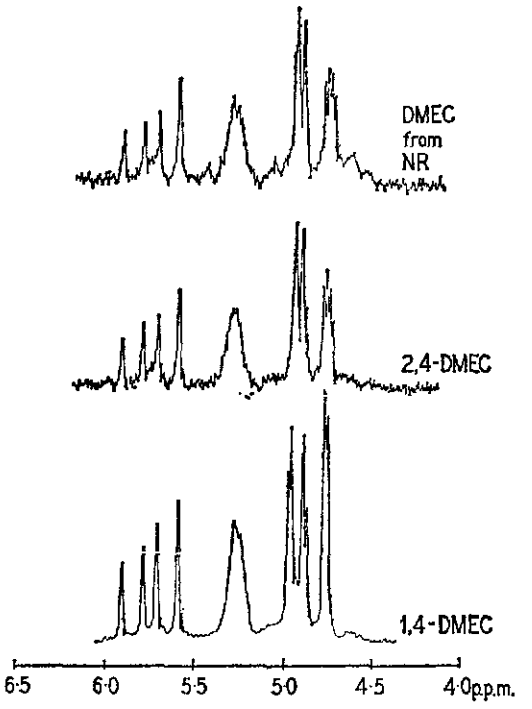

Figure 2. Proton nuclear magnetic resonance spectra (olefinic region) of 1,4- and 2,4-dimethyl-4-ethenylcyclohexenes and the dimethylethenylcyclohexene isolated from the pyrolysis of natural rubber.

- 5% poly (ethylene glycol) 4000 (PEG 4000)
- 8.5% *bis* [4-(hexyloxy)phenyl]diazene-l-oxide (a liquid crystal).

All stationary phases were coated on to Chromosorb G support.

Spectroscopic Analysis

Proton nuclear magnetic resonance spectra were recorded using a Perkin-Elmer R32 90 MHz spectrometer; tetramethylsilane was used as internal standard. Infra-red spectra were obtained using a Perkin-Elmer 157 spectrophotometer; samples were examined as thin films between sodium chloride cells.

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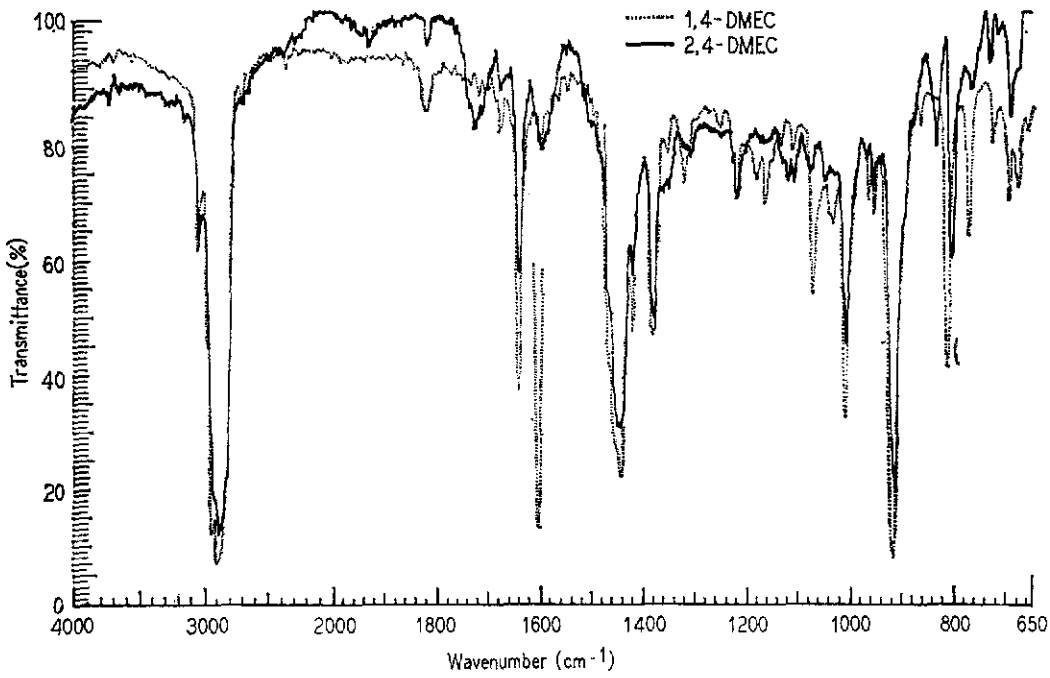


Figure 3. Infra-red spectra of 1,4- and 2,4-dimethyl-4-ethenylcyclohexenes.

RESULTS AND DISCUSSION

Structure of Dimethylethenylcyclohexene from Natural Rubber Pyrolysate

The synthesised reference samples of 1,4-DMEC and 2,4-DMEC were found to have identical gas-liquid chromatography retention times in the three stationary phases employed. The liquid crystal stationary phase which was claimed to be capable of separating the two positional isomers[5] was found not to be so even though similar gas-liquid chromatography conditions were employed including the use of Chromosorb W as support. It was however found possible to separate dipentene (1-methyl isomer) from its 2-methyl isomer (diprene).

Proton nuclear magnetic resonance and infra-red spectra of the reference samples of 1,4-DMEC and 2,4-DMEC *(Figures 1–3)* however showed some distinctive and distinguishable differences. Particular differences in the ^{1}H n.m.r. signals of the allylic methylene protons (*ca* 1.9 p.p.m.) and of the terminal vinylic protons (4.7 – 5.0 p.p.m.) are worth noting. *Table 1* summarises the structural assignments made for the synthesised reference samples of 1,4-DMEC and 2,4-DMEC. The infra-red spectra of the two isomers also showed minor differences *(Figure 3)*. Absorptions at 770 (medium), 1065 (medium) and 1320 (weak) cm^{-1} observable from 1,4-DMEC were not present in the spectrum of 2,4-DMEC, while absorptions at 830 (weak) and 1120 (weak) cm^{-1} observable from the 2,4-DMEC spectrum were not present in the 1,4-DMEC spectrum.

Analysis of DMEC isolated from the NR pyrolysate showed that the ^{1}H n.m.r. spectrum was identical to that of 2,4-DMEC *(Figures 1* and *2)*. Hence the second isoprene dimer formed in the pyrolysis of NR

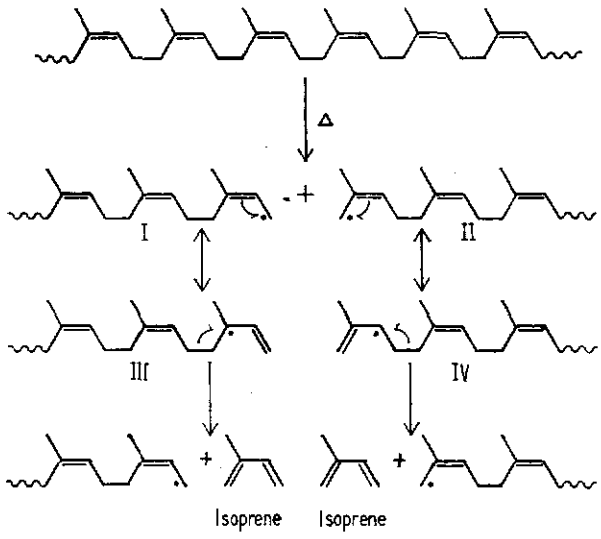


Figure 4. Formation of isoprene.

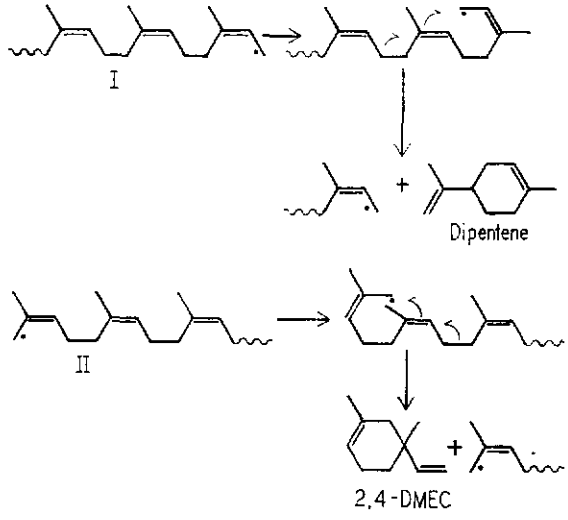


Figure 5. Formation of isoprene dimers.

was found to be 2,4-DMEC and not 1,4-DMEC.

Mechanism of Natural Rubber Depolymerisation

The mechanism of the anaerobic thermal degradation of NR was first postulated by Bolland and Orr[10]. They postulated that initial bond scission occurs at an isoprene link (*i.e.* the carbon-carbon single bond at the β position with respect to two double bonds) randomly along the rubber chain and hence leads to the formation of two allylic radicals, *I* and *II*, which are stabilised by resonance *(III* and *IV) (Figure 4)*. The formation of isoprene is by scission from the end of an already broken chain, a process now considered as the reverse of the 1,4-polymerisation step. Although the formation of isoprene from radical *I* only is described, the formation of isoprene from radical *II* is considered equally feasible. The isoprene formation is accompanied by the generation of further allylic radicals, thus providing a chain reaction for the 'unzipping' of isoprene.

The formation of dipentene was postulated by Bolland and Orr to occur by two possible reactions. One was by the radical chain ends acquiring a configuration so as to enable cyclisation to occur followed by bond scission of the penultimate isoprene

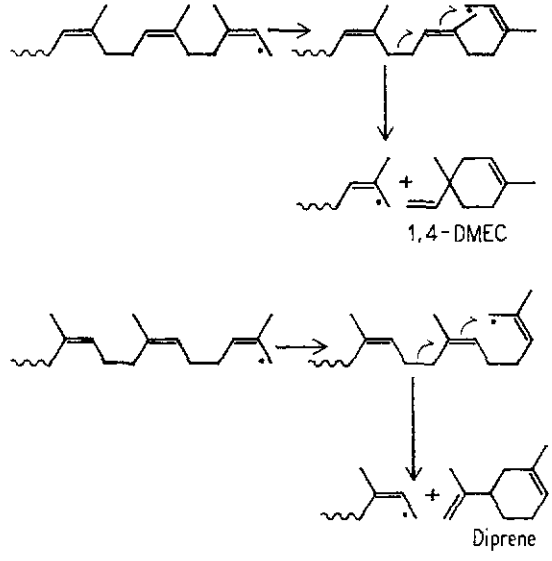
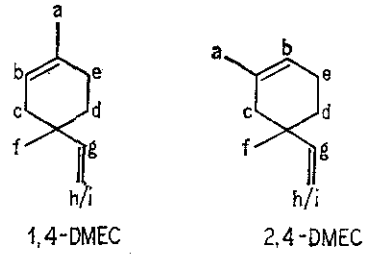


Figure 6. Formation of 1,4-dimethyl-4-ethenylcyclohexene and diprene.

TABLE 1. PROTON NUCLEAR MAGNETIC RESONANCE SIGNALS OF 1,4- AND 2,4- DIMETHYL-4-ETHENYLCYCLOHEXENES

Proton assignment	Chemical shift[a] (p.p.m.)		Proton integral
	1,4-DMEC	2,4-DMEC	
g	5.87/5.76 5.67/5.56	5.86/5.75 5.66/5.55	1
b	5.25	5.23	1
h/i	4.94/4.93 4.86/4.85 4.74/4.73	4.88 4.84 4.72 (m)	2
c/e	1.87 (m)	1.96 (m) 1.8 (m)	9
a	1.62 (s)	1.62 (s)	
d	1.44 (t)	1.36 (t)	
f	0.97 (s)	0.97 (s)	3

[a]CCl_4 as solvent and tetramethylsilane as internal standard at 0.00 p.p.m.
(s) = singlet (t) = triplet (m) = multiplet

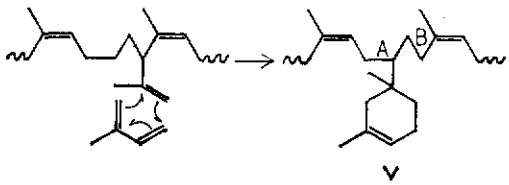


link *(Figure 5)*. They also postulated the possible formation of dipentene by the well-known Diels-Alder dimerisation of isoprene. This latter mechanism was however considered unlikely unless isoprene was not removed from the reaction system[11].

In the mechanism proposed by Bolland and Orr, the cyclisation of free radical *I* to form dipentene only was considered. By a similar mechanism, radical *II* on cyclisation and simultaneous scission at the penultimate isoprene link is expected to form 2,4-DMEC. However, 2,4-DMEC is only produced in about one-tenth of the amount of dipentene. This can be explained in at least two ways. One is probably due to the steric hindrance of the 6-methyl group in the cyclisation step. In the formation of dipentene from radical *I* no such steric hindrance is present. The other reason is probably due to the relative stability of radicals *I* and *II*. Whereas radical *I* resonates to a tertiary radical *III*, radical *II* resonates to a less stable, secondary radical *IV*.

The postulation by several workers[4,5,6] that 2,4-DMEC is formed from the pyrolysis of NR by the Diels-Alder reaction between isoprene and the 3,4- unit structure thought

to be present in NR and by the subsequent scissions at both bonds A and B *(V)* which are each in a β position to an olefinic double bond, is considered unlikely for several reasons. Firstly, such Diels-Alder reaction should also form 1,4-DMEC. Secondly, a yield of 2,4-DMEC normally at 2 weight percent from an assumed 2 percent 3,4-structure content of the rubber is quite improbable when the proposed mechanism requires both bond scission at both A and B. Finally, the Diels-Alder reaction could not possibly occur if the isoprene is removed



immediately from the reaction system. In any case it is now established that NR does not contain either 3,4- or *trans*-1,4- structures within 0.1% limit of detection by high resolution ^{13}C nuclear magnetic resonance spectroscopy[7]. Hence in the thermal depolymerisation of NR, the second isoprene dimer 2,4-DMEC is probably formed by the cyclisation of radical *II* with bond scission at the penultimate isoprene link.

From the above postulated mechanisms for the formation of isoprene dimers from 1,4-polyisoprenes, dipentene and 2,4-DMEC appear to be the consequence of head-to-tail isoprene sequence only. The presence of head-to-head and tail-to-tail isoprene sequences would lead to the formation of 1,4-DMEC and diprene respectively *(Figure 6)*. The absence of any detectable amounts of 1,4-DMEC or diprene in NR pyrolysate provided further evidence that NR is essentially 100% head-to-tail *cis*-1,4-polyisoprenes.

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