30. *Radical Mechanisms in Saturated and Olefinic Systems. Part II. Disubstitutive Carbon–Carbon Cross-linking by* tert.-*Alkoxy-radicals in Isoprenic Olefins and Rubber.*

By E. H. Farmer and C. G. Moore.

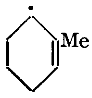
The high degree of dehydrogenation effected by *tert.*-butoxy-radicals at the α-methylenic groups of olefins enables these radicals to be used for the carbon-to-carbon cross-linking of unsaturated carbon chains, and especially of the polyisoprenic chains of natural rubber. Such cross-linking amounts to a vulcanisation process in which the connecting links between chain molecules are just C–C bonds, which may be expected to have appropriate attributes.

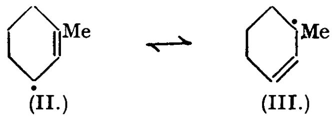
An examination has first been made of the cross-linking produced by *tert.*-butoxy-radicals (from di-*tert.*-butyl peroxide) at 140° between the short isoprenic chains in 1-methyl*cyclo*hexene, 4-methylhept-3-ene, 2 : 6-dimethylocta-2 : 6-diene, and digeranyl. Cross-linking proceeds efficiently in each case, and the points of union in these isoprene units which become directly joined are not confined to *original* α-methylenic carbon atoms. Where the reagent radicals are in considerable deficit (*e.g.*, one per two or three of the isoprene units present) those olefin molecules which are attacked become linked together mostly by single unions to form aggregates containing two, three, or four molecules; but in the tetraisoprenic olefins the extent to which more than one union is formed between some of the directly linked molecules becomes appreciable.

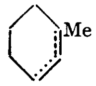
In natural rubber, cross-linking occurs smoothly and to nearly the full extent corresponding to the (in practice restricted) proportion of peroxidic reagent employed. Good vulcanisates can be so obtained in which the tensile strength is found to increase towards a maximum and then to decline rapidly as the degree of cross-linking steadily increases. Thus to obtain vulcanisates of the optimum physical characteristics the degree of cross-linking must be suitably chosen. The rôle of the peroxidic reagent is almost entirely non-additive and non-degradative.

The efficiency of *tert.*-butoxy-radicals in dehydrogenating olefinic and paraffinic hydrocarbons, thereby permitting the coupling of the resulting radicals, has been demonstrated in Part I (preceding paper). The process provides a ready means for cross-linking carbon chains by carbon-to-carbon bonds; moreover, by repetition of the process in long chains an increasing degree of cross-linking can be obtained. It is of considerable practical interest to observe the effect on the physical properties of long-chain hydrocarbons (and especially of polyisoprenic and polybutadienic rubbers) of increasing gradually the proportion of carbon–carbon cross-links per molecule for ultimate comparison with corresponding effects in the sulphur-bridge cross-linking of the same chains, which (so far as is known) is mainly of substitutive–additive type, the bridges containing 1—6 sulphur atoms. The present account deals principally with the cross-linking of natural rubber molecules by radicals, but briefly reports also a series of preliminary experiments carried out with short-chain olefins (" model " rubber molecules) containing 1—4 isoprene units. For comparison with rubber, it was desirable to have all the isoprene units of the model molecules of the unmodified " rubber-type," $-\overset{\alpha}{C}H_2-\overset{\beta}{C}Me=\overset{\gamma}{C}H-\overset{\delta}{C}H_2-$, which, because of the primary character of the methylic C–H bonds, would not be liable to undergo any very appreciable degree of attack at other than the two secondary α-methylene groups. But obviously this was only partly feasible, since all the terminal isoprene units of relatively short-chain polyisoprenes necessarily have their outermost α-methylene groups embodied in (primary) methyl groups, so making the comparison with rubber not quite exact in respect of the distribution of radical attack. It is particularly to be noted that the two isoprene units of the most readily available model molecule, dihydromyrcene (or, better, its synthetic counterpart, 2 : 6-dimethylocta-2 : 6-diene, which does not contain the occasional vinylic isoprene units, $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2$, to which naturally occurring terpenic chains are liable), each contain only one secondary α-methylene group, so that attack on the molecule by radicals, provided that not more than one radical per unit is employed, is likely to be almost wholly confined to the mid-chain pair of methylene groups. In order to ensure that every *tert.*-butoxy-radical may have a good chance of encountering an unattacked isoprene unit, the initial concentration of the former has been restricted to an average of one per two isoprene units in the case of monoisoprenes, and to one per three units in that of di- and tetra-isoprenes. Hence, the maximum average degree of cross-linking which can ensue falls far short of one cross-link emanating from every unit of every chain. The mono-olefins selected for examination are two disubstituted isoprenes, $\mathrm{R{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2R'}$, in the first of which the groups R and R′ are polarly equal (since they consist of the same system $\mathrm{{\cdot}CH_2{\cdot}CH_2{\cdot}}$), and in the second are polarly unequal, so that the distribution of negative activation [*] within the isoprenic system may be considered normal in the first and somewhat unbalanced in favour of C_δ in the second.

The Cross-linking of 1-*Methyl*cyclo*hexene and of* 4-*Methylhept*-3-*ene.*—Dehydrogenation of the two secondary α-methylenic groups in 1-methyl*cyclo*hexene can give only the radical forms (I—III), since the amount of attack at the methyl group (as experience in such cases confirms)

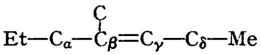

(I.)


(II.) (III.)


(IV.)

is likely to be negligible. Of these three, two are resonance forms of the mesomeric radical (IV). By the coupling of the three forms in pairs a maximum of six structurally different dimers becomes possible, and by the further coupling of the original and the new radical forms still larger numbers of isomeric trimers and isomeric higher polymers are likely to arise. In practice, fractions consisting of dimers ($C_{14}H_{22}, \overline{\lceil 2}$), trimers ($C_{21}H_{32}, \overline{\lceil 3}$), tetramers ($C_{28}H_{42}, \overline{\lceil 4}$), and higher polymers [†] were readily separated in relative proportions of about 5 : 2 : 1 : 2. The individual isomers constituting the dimer could not be separated by distillation, or by fractionation of their tetrahydrides or tetrabromides; and, in view of the rather complicated character of the degradative scission products to be expected, no detailed analysis of structural forms was attempted.

The polar inequality between the ethyl and methyl groups in 4-methylhept-3-ene may be expected to enhance slightly the negative activation at C_δ (V) relative to that in an ordinary rubber unit, in which the flanking alkenylmethyl groups, RR′, although different in size and detail, may be considered polarly equal. This should cause a somewhat increased degree of substitutivity at C_δ, and of course at the corresponding resonance position C_β. By treatment of the olefin with the peroxide, the usual mixture of dimers and higher polymers was obtained. The dimer fraction ($C_{16}H_{30}, \overline{\lceil 2}$) was composed of a mixture of hexadecadienes, which was shown by infra-red spectrographic examination to contain olefinic groupings of the type, $\mathrm{RR'C{:}CHR''}$, characterising the original olefin and its derived radicals (VI and VIII),[‡] as well as of a new type, $\mathrm{RCH{:}CHR}$, doubtless resulting from incorporation in the dimers of the resonance form (VII). The proportion of the new grouping, as deduced from the relevant extinction coefficient,



$$\mathrm{Et{-}C_\alpha{-}\overset{C}{\overset{|}{C_\beta}}{=}C_\gamma{-}C_\delta{-}Me}$$

(V.)

$$\underset{\text{(VI.)}}{\mathrm{Et{-}CH_2{-}CMe{=}CH{-}\underset{\cdot}{C}H{-}Me}} \longleftrightarrow \underset{\text{(VII.)}}{\mathrm{Et{-}CH_2{-}\underset{\cdot}{C}Me{-}CH{=}CH{-}Me}}$$

$$\underset{\text{(VIII.)}}{\mathrm{Et{-}\underset{\cdot}{C}H{-}CMe{=}CH{-}CH_2{-}Me}}$$

was computed to be *ca.* 15%, which value is at least equal to that found for comparable (resonance-sited) C_β-substitution in 2-methylbut-2-ene (Part III). It was of interest that the recovered monomeric olefin gave evidence of containing traces of unsaturation of the type $\mathrm{{\cdot}CH{:}CH{\cdot}}$, which must be attributed to hydrogen-transfer reactions having occurred, *inter alia*, between the tertiary methylheptenyl radicals (VII) and the original olefin molecules :

$$\mathrm{CH_2Et{-}\underset{\cdot}{C}Me{-}CH{=}CHMe + CH_2Et{-}CMe{=}CH{-}CH_2Me \longrightarrow CH_2Et{-}CHMe{-}CH{=}CHMe + CH_2Et{-}CMe{=}CH{-}\underset{\cdot}{C}HMe}$$

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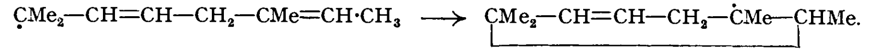
[*] The method of degradative analysis adopted elsewhere (Parts V and VII) is unsuitable for examining in detail the effect of altering the negativisation balance in favour of C_α or C_δ by using in turn different electron-donating substituents R and R′. Doubtless, study of the rates of substitutive (radical) reaction in the differently substituted olefinic chains, as in maleinisation, oxidation, and sulphuration, would be more effective.

[†] Actually all dehydropolymers (see preceding paper).

[‡] A proportion of the dimer molecules contained, as expected, groupings of the type $\mathrm{CH_2{:}CRR'}$, since the olefin sample employed was prepared by dehydration of $\mathrm{CHMePr_2{\cdot}OH}$, and so contained a little of the difficulty removable vinylic isomer, $\mathrm{CH_2{:}CPr_2}$.

The Cross-linking of 2 : 6-*Dimethylocta*-2 : 6-*diene and of Digeranyl.*—The dimers, trimers, etc., obtained from the first (di-isoprenic) olefin could not be satisfactorily separated by distillation owing to their high boiling point: hence, the presence of more than one cross-link connecting a pair of molecules could not easily be ascertained. The polymer mixture, when freed from unchanged monomer, proved to contain olefinic groupings of the original type, $RR'C{:}CHR''$, as well as quite an appreciable proportion of the type $R{\cdot}CH{:}CHR'$, and even some of the type $RR'C{:}CH_2$. This result was to be expected, but the additional observation that the polymer mixture showed only 82% of the original olefinic unsaturation had not been foreseen. The loss of unsaturation could only have been due to partial cyclisation, and the appearance of the latter in this example must apparently be deemed to result from the carbon chain now being of suitable length, unsaturation-pattern, and negative activation at one end of the double bond for intramolecular radical–double bond additions to succeed; *e.g.*,



$$\underset{\bullet}{C}Me_2{-}CH{=}CH{-}CH_2{-}CMe{=}CH{\cdot}CH_3 \longrightarrow CMe_2{-}CH{=}CH{-}CH_2{-}\dot{C}Me{-}CHMe.$$

The second (tetra-isoprenic) olefin $H[CH_2{\cdot}CMe{:}CH{\cdot}CH_2]_2{\cdot}[CH_2{\cdot}CH{:}CMe{\cdot}CH_2]_2H$ contained, in the main, two ordinary isoprenic units (these being arranged in tail-to-tail fashion);* and two possessing only one secondary α-methylene group each. In spite of the above-mentioned deficiency of reagent employed (one *tert.*-butoxy-radical per three units), one-fifth of the olefin molecules taken remained unlinked, so that (on average) only about 0·8 cross-link per digeranyl molecule could have been formed. In the process, just over three-quarters of the digeranyl molecules had become converted into tetrameric aggregates by cross-linking, so that within these tetramer molecules most of the pairs of digeranyl chains were joined (on average) only by one cross-link, although occasional pairs (*ca.* 2 per 5 tetramers) were joined by two. Some reduction in the original degree of unsaturation occurred in these polymers also, and this again must be attributed to the occurrence of a minor degree of additive (radical to double bond) cyclisation.

The Cross-linking of Rubber.—In the case of rubber, with its average of *ca.* 5000 isoprene units per molecule, observations of cross-linking were made at 100° and at 140° with raw (" smooth smoked sheet ") and acetone-extracted samples, varying proportions of di-*tert.*-butyl peroxide being used as reagent. The specimens became progressively insoluble in benzene and other solvents and showed mechanical properties and swelling characteristics indicating the progressive occurrence of vulcanisation. Determination of the " equilibrium swelling constant " (Q_m) † of the vulcanised specimens, immediately after their preparation, permitted an estimate to be made of the average molecular weight between junction points (M_c) in the cross-linked chains, the latter value being inversely proportional to the number of new cross-links formed (Gee, *J. Polymer Sci.*, 1947, **2**, 451).

The numerical results obtained for the physical characteristics of the cross-linked samples are given in Tables I and II. These demonstrate very clearly that di-*tert.*-butyl peroxide is highly effective in producing good rubber vulcanisates, and the physical nature of the samples indicates that uniform vulcanisation has been effected. The values of Q_m and M_c steadily decrease with increasing peroxide concentration, thereby indicating a progressive increase in the degree of cross-linking.

The figure shows the effect of peroxide concentration on the tensile strengths of the samples The two curves show the characteristic features of well-defined maxima, the tensile strengths increasing with increasing amounts of peroxide up to a certain critical peroxide concentration, beyond which they fall very sharply.‡ The effect of the removal of non-rubber constituents (resin acids, antioxidants, *etc.*) from the rubber by acetone-extraction is to increase the maximum attainable tensile strength and also to reduce the peroxide concentration required to produce this maximum figure. For instance, raw " smoked sheet " requires *ca.* 2·9% of peroxide to give a maximum tensile strength of 178 kg. $cm.^{-2}$, whereas acetone-extracted " smoked sheet " gives a vulcanisate with a maximum tensile strength of 206 kg. $cm.^{-2}$ with only 1·45% of peroxide. The non-rubber constituents presumably compete with the polyisoprene chains for interaction with the peroxide, and so diminish the efficiency of the peroxide as a cross-linking agent.

As the peroxide concentration increases beyond a certain optimum value, the desirable properties of the vulcanisates (good tensile strength and elasticity) deteriorate; and with

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* The digeranyl employed contained a minor proportion of *iso*digeranyl in which one of the isoprenic units is modified (private communication).

† Q_m is defined as the volume of solvent (benzene) imbibed at equilibrium swelling by unit volume of rubber.

‡ The same phenomenon is observed with rubber-sulphur vulcanisates (Gee, *loc. cit.*).

TABLE I.

*Reaction of raw rubber with di-*tert.*-butyl peroxide* (6 *hours at* 140°).

Peroxide (g./100 g. of rubber).	Q_m.	10^3M_c.	T.s. (kg. cm.$^{-2}$).	E.b. (%).	Modulus (kg. cm.$^{-2}$). 100%.	300%.	500%.	700%.
0	—	—	54	925	3·1	3·6	4·9	18
1·45	4·4	7·5	141	645	5·4	13	29	—
2·1	3·9	6·1	145	580	7·4	18	60	—
2·5	3·7	5·7	162	570	6·2	20	82	—
2·9	3·4	4·7	178	555	11	22	93	—
3·4	2·6	3·1	123	470	8·2	25	—	—
5·4	2·2	2·3	29·5	250	13	—	—	—
7·65	2·1	2·2	16	85	—	—	—	—
10·1	1·3	1·0	12	40	—	—	—	—
15·7	1·0	0·85	12	20	—	—	—	—

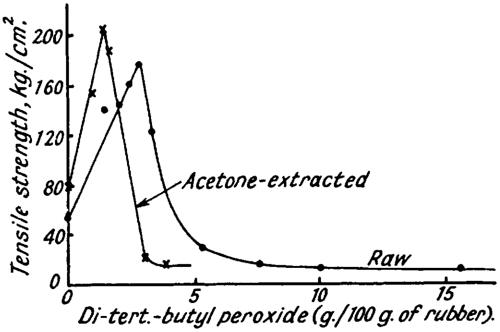
TABLE II.

*Reaction of acetone-extracted rubber with di-*tert.*-butyl peroxide.*

Peroxide (g./100 g. of rubber).	Reaction conditions: hrs.	temp.	Q_m.	10^3M_c.	T.s. (kg. cm.$^{-2}$).	E.b. (%).	Modulus (kg. cm.$^{-2}$). 100%.	300%.	500%.	700%.
0	—	—	—	—	80	900	3·3	5·7	11	34
1·0	6	140°	4·3	7·4	155	705	7·3	14	32	154
1·45			4·1	6·8	206	660	6·5	16	56	—
1·7			4·1	6·8	190	625	6·6	17	64	—
3·1			2·6	3·0	22	210	12	—	—	—
3·95			2·1	2·2	16	100	16	—	—	—
51·5			0·74	0·44	—	—	—	—	—	—
2·4	24	99·5° ± 0·5°	8·7	—	109	905	—	6·7	14	43
3·0			8·0	—	>95	835	—	6·9	14	46
3·5			7·2	—	>116	875	—	6·6	15	49
4·5			6·6	—	148	890	—	6·7	16	55
5·0			6·2	—	>137	865	—	6·9	16	55
3·0	72	99·5° ± 0·5°	5·5	—	184	815	—	11	30	104
3·55			6·0	—	172	820	—	9·4	26	90

peroxide concentrations of *ca.* 5—16% the samples show a substantial loss of rubber-like properties, displaying brittleness, low tensile strength, and negligible elasticity. The results thus demonstrate that cross-linking of rubber chains must be restricted within very narrow limits to give useful products.

Cross-linking of rubber at 140° (6 *hours*).



The increase in oxygen content of the peroxide-vulcanised samples was only very small (0·34—0·355%), as based on direct oxygen determination (Chambers, Rubber Technology Conf., London, 1948, Preprint No. 16), for much of the peroxide was converted into a mixture of *tert.*-butanol and acetone: in one rather extreme case investigated [peroxide equal to 48·2% (w/w) of the rubber; 6 hours' heating], these represented (respectively) 41·1% and 36·6% of the peroxide taken. Thus the major, and probably the sole olefinic reaction in the peroxide-vulcanisation of rubber is still dehydro-cross-linking, producing ultimately a three-dimensional net-structure in which all the cross-links are C–C bonds. Decomposition of some of the *tert.*-butoxy-radicals to yield acetone will simultaneously give methyl radicals ($Me_3C–O\cdot \longrightarrow Me_2CO + Me\cdot$), a part of which may dimerise without any cross-linking effect, and the remainder participate in the dehydrogenation which precedes cross-linking ($RH + Me\cdot \longrightarrow MeH + R\cdot$; $R\cdot + R\cdot \longrightarrow$ R–R, where R is an isoprene unit of a rubber chain). The likelihood, however, of a portion of the dehydrogenating capacity being lost through acetone-formation will become less as the peroxide concentration decreases, and is probably insignificant up to the optimum concentration value of the rubber. The scanty incorporation of *tert.*-butoxy-radicals in the rubber, as indicated by the low oxygen content, is in sharp contrast to the heavy incorporation of (the more electrophilic) benzoyloxy-radicals in the corresponding treatment of rubber with dibenzoyl peroxide (van Rossem *et al.*, *Kautschuk*, 1931, **7**, 202, 220; Farmer and Michael, *J.*, 1942, 513); moreover, the contrast corresponds to a notable difference between the two peroxidic reagents, since the extensive and wasteful formation of ester characterising the benzoyl compound has no counterpart (ether formation) in the case of the alkyl compound.

TABLE III.

Reaction of acetone-extracted rubber with diethyl peroxide.

Peroxide (g./100 g. of rubber).	Reaction conditions: hrs.	Reaction conditions: temp.	Q_m.	T.s. (kg. cm.$^{-2}$).	E.b. (%).	Modulus (kg. cm.$^{-2}$). 300%.	Modulus (kg. cm.$^{-2}$). 500%.	Modulus (kg. cm.$^{-2}$). 700%.
1·2	6	140° ± 0·5°	7·0	> 90	830	6·6	13	43
1·5			6·7	>102	830	7·6	14	53
2·8			5·4	>116	790	8·9	20	69
3·7			5·1	161	825	9·8	19	82
0·94	6	99·5° ± 0·5°	*	36	835	5·7	7·6	21
1·9			*	34	825	5·0	7·0	18
2·7			*	33	780	4·9	7·8	23
3·6			*	41	825	4·0	8·0	23

* Q_m values too high to be obtained accurately.

It was attractive to investigate whether by use of a rather more energetic alkoxy-radical than the *tert.*-butyl compound superior peroxide-vulcanisates could be obtained from natural rubber by operating at temperatures well below the usual reaction temperature of 140°. To this end the ethoxy-radical, derived by thermal decomposition of diethyl peroxide, was employed. The relevant physical properties of the cross-linked rubbers obtained at 140° and at *ca.* 100° are given in Table III. These, however, reveal that no advantage accrues by using the more reactive but less easily manipulated peroxide. Whether or not the cross-linked products obtained by use of the ethoxy-radical resemble those obtained by use of the *tert.*-butoxy-radical in being almost entirely free from combined ethoxy-groups remains to be investigated. It is possible that ethoxy-radicals are sufficiently energetic (unstabilised) to unite reasonably rapidly with olefinic radicals and/or with olefinic double bonds to ensure that a substantial degree of wasteful and deleterious ethoxylation of the vulcanisate occurs: $RH \xrightarrow{-H\cdot} R\cdot \xrightarrow{\cdot OEt} R–OEt$; $–C{=}C– + \cdot OEt \longrightarrow –\overset{\bullet}{C}–\overset{|}{C}–OEt$. Also it seems probable that a greater degree of thermal decomposition of the ethoxy-radical will occur ($CH_3–CH_2–O\cdot \longrightarrow CH_3\cdot + H–CHO$) than is the case with the *tert.*-butoxy-radical.

EXPERIMENTAL.

(Microanalyses by Dr. W. T. Chambers, Miss E. Farquhar, and Mrs. H. Hughes. Spectrographic observations by Dr. H. P. Koch.)

Cross-linking of 1-*Methyl*cyclo*hexene.*—The methyl*cyclo*hexene (50 g., 0·5 mol.; b. p. 109—110°/760 mm., $n_D^{19\cdot5}$ 1·4503) and di-*tert.*-butyl peroxide (18·25 g., 0·125 mol.) were heated in a Carius tube sealed under nitrogen, at 140° for 24 hours. The product (66·0 g.), a colourless mobile liquid, gave on distillation the fractions: (i) b. p. 82—110° (44·2 g.); (ii) b. p. <86°/1 mm. (0·35 g.); (iii) b. p. 86—94°/1 mm. (10·15 g.); (iv) b. p. 94—146°/1 mm. (0·45 g.); (v) b. p. 146—149°/1 mm. (3·85 g.); (vi) b. p. 203—204·5°/1 mm. (2·4 g.); (vii) a colourless, glass-like residue in the still (*ca.* 4·0 g.) which was not further investigated. Fraction (i) gave on aqueous extraction, 18·0 g. of water-soluble compounds, which consisted mainly of *tert.*-butanol (isolated as described in Part I), b. p. 82—82·5°/760 mm.; only traces of acetone were present, these being identified and determined as the 2 : 4-dinitrophenylhydrazone, m. p. 124—125° (yield 0·11 g., equiv. to 0·027 g. of acetone). The non-aqueous layer was unchanged methyl-

*cyclo*hexene (25·0 g.) which, after being dried ($CaCl_2$) and distilled over sodium, had b. p. 109—110°/760 mm., $n_D^{17\cdot5}$ 1·4510.

Fraction (iii), a colourless oily liquid, was identified as *dimethyl*dicyclo*hexenyl*. Though molecularly homogeneous, it doubtless consisted of a mixture of structural isomers. Redistillation over sodium, in nitrogen, gave a main fraction, b. p. 74—78°/0·5 mm., n_D^{20} 1·5116 [Found, for two different samples: C, 88·35, 88·55; H, 11·80, 11·65%; *M* (micro-Rast), 214, *M* (benzene), 233. $C_{14}H_{22}$ requires C, 88·35; H, 11·65%; *M*, 190]. This olefinic dimer absorbed hydrogen (Adams's catalyst) equivalent to 2·0 double bonds per mol. A larger portion (1·37 g.) in absolute ethanol (150 c.c.), when hydrogenated over palladium–charcoal (200 mg.), absorbed 305·0 c.c. of gas at N.T.P. (Calc.: 322·9 c.c.) to give the tetrahydride, dimethyldi*cyclo*hexyl. This, when distilled over sodium, gave two fractions: (i) b. p. 64—68·0°/0·5 mm., n_D^{20} 1·4827 (0·56 g.) (Found: C, 86·7; H, 13·45%); and (ii) b. p. 68·0°/0·5 mm., n_D^{20} 1·4831 (0·47 g.) (Found: C, 86·6; H, 13·5. Calc. for $C_{14}H_{26}$: C, 86·5; H, 13·5%). Both fractions were colourless mobile liquids, stable towards potassium permanganate solution and towards bromine.

Treatment of the dimeric olefin (in chloroform) at 0° with bromine led to the absorption of 2·0 mols. of halogen. The product, however, on removal of the solvent rapidly evolved hydrogen bromide and darkened; no solid tetrabromides could be isolated.

The colourless, viscous liquid forming fraction (v) was redistilled over sodium in nitrogen. It had b. p. 144—148°/1 mm., n_D^{20} 1·5339, and gave analytical values corresponding to *trimethylter*cyclo*hexenyl* [Found: C, 88·75, 88·8; H, 11·25, 11·35%; *M* (in benzene), 268, 280, 300; unsaturation value (catalytic hydrogenation), $\overline{\overline{|}}_{2\cdot87}$. $C_{21}H_{32}$ requires C, 88·65; H, 11·35%; *M*, 284, $\overline{\overline{|}}_{3}$]. This triolefinic trimer fraction probably contained a number of structural isomers.

Fraction (vi) was an extremely viscous, colourless semi-glass, which on distillation over sodium gave a small fraction, b. p. <186°/0·1 mm., and a main fraction, b. p. 186—192°/0·1 mm., the latter doubtless consisting of the *tetramer* (Found: C, 89·0; H, 11·35. $C_{28}H_{42}$ requires C, 88·8; H, 11·2%).

Cross-linking of 4-*Methylhept*-3-*ene*.—The olefin, prepared by dehydration of 4-methylheptan-4-ol (b. p. 70—78°/20—23 mm., n_D^{20} 1·4258) with *ca.* 0·5% of iodine, had b. p. 116—117·0°/738 mm., n_D^{20} 1·4175; infra-red spectrographic analysis indicated its main type of unsaturation to be of trialkylethylene type, R·CH:CR′R″, but there was also a small amount of the *as*-dialkylethylene type RR′C:CH$_2$ present, indicative of the 4-methyleneheptane isomer. Other types of unsaturation were definitely absent.

A mixture of the olefin (112 g.; 4 mols.) and the peroxide (36·5 g.; 1 mol.) was heated at 140° for 24 hours in nitrogen-filled Carius tubes. The colourless liquid product (148·0 g.) gave on distillation the fractions: (i) b. p. 80—120°/742 mm. (89·3 g.), (ii) b. p. <28°/21 mm., n_D^{20} 1·4187 (8·9 g.), and (iii) a liquid residue, n_D^{20} 1·4641 (47·9 g., equiv. to 42·7% of the original olefin), consisting entirely of olefinic hydrocarbon constituents (Found: C, 86·35, 86·1; H, 13·65, 13·65%). A portion (46·8 g.) of fraction (iii) gave on redistillation in nitrogen the following fractions: (iv) b. p. <71°/0·05 mm., n_D^{20} 1·4510 (2·0 g.); (v) b. p. 67°/0·01 mm.—72°/0·05 mm., n_D^{20} 1·4586 (25·3 g.), and a residue (vi), n_D^{20} 1·4775 (19·0 g.) (Found: C, 86·15; H, 13·4%), which was not further investigated.

The fraction (i) gave on extraction with water (300 g. + 200 g.) a mixture of water-soluble constituents (36·0 g.). Treatment of the extract with 2 : 4-dinitrophenylhydrazine solution (in 2N-hydrochloric acid) gave acetone 2 : 4-dinitrophenylhydrazone (0·32 g., equiv. to 0·08 g. of acetone). The only other water-soluble material was *tert.*-butanol (*ca.* 36·0 g., equiv. to 97·3% of the peroxide employed).

The olefin present in fractions (i) and (ii) was combined, and redistilled (in nitrogen) over sodium. It gave a monomeric fraction, b. p. 117·0—120·0°/755 mm., n_D^{20} 1·4184.

Fraction (v), a colourless oily liquid, was obviously the dimer, *hexadecadiene* [Found: C, 86·1; H, 13·6%; *M* (in benzene), 246. $C_{16}H_{30}$ requires C, 86·4; H, 13·6%; *M*, 222]. A portion of the redistilled dimer (3·1 g.), dissolved in absolute ethanol (50 c.c.), absorbed over palladium–charcoal (1·0 g.) at room temperature and pressure 535 c.c. (N.T.P.) of hydrogen, *i.e.*, 85·6% of the theoretical amount. The hexadecane so obtained was a colourless liquid, b. p. 64—67°/0·1 mm., n_D^{20} 1·4439 (2·3 g.) (Found: C, 84·9; H, 14·95. Calc. for $C_{16}H_{34}$: C, 84·85; H, 15·15%). The product was stable towards aqueous potassium permanganate for a long time.

Infra-red spectrographic examination of the recovered methylheptene revealed a higher ratio of CH$_2$:CRR′ to R·CH:CR′R″ than existed in the original olefin, and also showed a band at 963 cm.$^{-1}$ consistent with the presence of a trace of R·CH:CHR′, which was absent from the original olefin. In the methylheptene dimer the ratio of CH$_2$:CRR′ to R·CH:CR′R″ was about the same as in the original olefin. The appearance of a strong new band at 975 cm.$^{-1}$ and the broadening at the olefinic absorption band at 1640 cm.$^{-1}$ are attributed to a new form of unsaturation, RR′R″C·CH:CHR‴, not present in the original olefin. In the fully-hydrogenated methylheptene dimer the olefinic absorption in the 1650 cm.$^{-1}$ region and the strong bands at 847 cm.$^{-1}$ and 975 cm.$^{-1}$, assigned to R·CH:CR′R″ and R·CH:CHR′, respectively, were all absent.

Cross-linking of 2 : 6-*Dimethylocta*-2 : 6-*diene*.—The olefin, b. p. 56°/14 mm., n_D^{20} 1·4490 (13·8 g.; 3 mols.), was heated with the peroxide (4·9 g., 1 mol.) in a nitrogen-filled Carius tube at 140° for 24 hours. Distillation of the product (18·5 g.) gave *tert.*-butanol, together with unchanged olefin, leaving an olefinic polymer residue (6·9 g., equiv. to 50% of olefin taken), having n_D^{24} 1·4945 [Found: C, 87·3; H, 12·45%; *M* (in benzene), 362, 372]. Micro-hydrogenation of the polymer indicated a considerable reduction in unsaturation (Found: $\overline{\overline{|}}_{1\cdot63}$ to $\overline{\overline{|}}_{1\cdot65}$ per C_{10} unit). Infra-red spectrographic examination of the polymer indicated, in addition to the original type of unsaturation, appreciable amounts of RR′C:CH$_2$ and R·CH:CHR′ double-bond structures.

Cross-linking of Digeranyl.—The olefin (kindly supplied by Dr. D. Barnard) had b. p. 181·0—181·3°/13·5 mm., n_D^{20} 1·4831 (Found : C, 87·7; H, 12·65%; $\overline{\vert=}_{4\cdot05}$. Calc. for $C_{20}H_{34}$: C, 87·5; H, 12·5%; $\overline{\vert=}_{4}$). A mixture of the olefin (8·22 g.; 1·5 mol.) and the peroxide (2·92 g., 1 mol.) was sealed in a Carius tube under 0·01 mm. of nitrogen, and heated at 140° for 24 hours. The product was transferred to a horizontal pot-still with a water-cooled condensing finger. Evaporative distillation at <0·01 mm. gave, first, volatile products, and then the following fractions : (i) at 50—53°, consisting mainly of digeranyl, n_D^{20} 1·4850 (1·61 g.; equiv. to 19·6% of olefin taken) [Found : C, 87·4; H, 12·6%; *M* (in benzene), 279, 295]; (ii) at 53°, a liquid, $n_D^{20\cdot2}$ 1·4859 (0·115 g.; equiv. to 1·4% of olefin taken); (iii) a colourless very viscous residue, n_D^{20} 1·5168 (6·40 g.; equiv. to 77·85% of olefin taken) [Found : C, 87·75; H, 12·1%; M (in benzene), 985, 990]. Microhydrogenation of fraction (iii) showed that it contained *ca.* 72% (Found : 71·6, 72·1%) of the unsaturation of the original digeranyl. The results of infra-red analysis of fraction (iii) were similar to those for the dimethyloctadiene residue given above.

*Cross-linking of Natural Rubber with Di-*tert.*-butyl and Diethyl Peroxide.*—The former peroxide, prepared according to Milas and Surgenor (*J. Amer. Chem. Soc.*, 1946, **68**, 205), had b. p. 109·0—110·0°/760 mm., n_D^{20} 1·3882 (Found : C, 65·7; H, 12·3. Calc. for $C_8H_{18}O_2$: C, 65·7; H, 12·4%). The diethyl peroxide, prepared by Wiley's method (U.S.P. 2,357,298/1944), had b. p. 62·5—63·5°/759·5 mm., $n_D^{16\cdot1}$ 1·3711, $n_D^{20\cdot5}$ 1·3690 (Found : C, 53·15; H, 11·25. Calc. for $C_4H_{10}O_2$: C, 53·3; H, 11·2%). Harris and Egerton (*Proc. Roy. Soc.*, 1938, *A*, **168**, 1) give b. p. 58—59°/625 mm., $n_D^{16\cdot5}$ 1·3715, and Wiley (*loc. cit.*) gives b. p. 61—65°, n_D^{23} 1·3700.

The rubber hydrocarbon used was a sample of smooth " smoked sheet " rubber. The acetone-extracted sample was prepared by extracting strips of the rubber in a nitrogen atmosphere for 24 hours, followed by drying of the swollen strip *in vacuo* for 3—5 days at 10^{-5} mm.

The experimental technique generally used was as follows : Strips of the rubber (*ca.* 4 × 0·5 × 0·1 in.) of known weight were left in contact with the calculated amounts of the appropriate peroxide in tubes sealed in an atmosphere of purified nitrogen. After 24—48 hours' contact it was assumed that even distribution of the peroxide in the rubber had been attained. The samples were quickly weighed and, while cooled in liquid air to prevent loss of peroxide, were sealed in Carius tubes in a nitrogen atmosphere of *ca.* 0·05 mm. pressure and then heated for the appropriate time (6—72 hours) and at the appropriate temperature (99·5° ± 0·5°, or 140° ± 0·5°).

The mechanical properties and equilibrium swelling constants (Q_m) in benzene (Gee, *loc. cit.*) of all the samples were measured immediately after reaction. These data are given in Tables I—III.

The volatile by-products obtained in the reaction between di-*tert.*-butyl peroxide and rubber were examined as follows :

Method 1. A sample of acetone-extracted rubber was dried for 4 days at 10^{-5} mm. and then immediately analysed (Found : C, 86·3; H, 11·45; O,* 0·98, 0·965; ash, 0·25%). This sample was heated with di-*tert.*-butyl peroxide (51·5 g./100 g. of rubber) for 6 hours at 140°. The liquid which separated from the product was shown to be mainly *tert.*-butanol, together with some acetone, but no peroxide. The rubber derivative (a hard brittle solid having no rubber-like properties) was acetone-extracted and dried for 7—9 days at 10^{-5} mm. (Found : C, 87·3, 86·6; H, 11·3, 11·55; O,* 1·32, 1·32; ash, 0·95%).

Method 2. A sample of rubber (17·0 g.), as in (1), was allowed to imbibe the peroxide (8·2 g.) in an atmosphere of nitrogen during 2 weeks, the resulting mixture then being heated under nitrogen for 6 hours at 140°. The liquid product (5·8 g.), which separated out after the reaction, was pumped off at 1 mm. pressure and condensed in a liquid-air trap. It was a colourless liquid boiling entirely over the range 56—80° and was shown to consist of a mixture of acetone (36·6% of peroxide taken), determined and identified as its 2 : 4-dinitrophenylhydrazone, m. p. 124—125° (mixed m. p. 125°), and *tert.*-butanol (equiv. to 41·1% of peroxide taken), identified as its phenylurethane, m. p. and mixed m. p. 136°. No unchanged peroxide was found.

THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
48, TEWIN ROAD, WELWYN GARDEN CITY, HERTS.

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* Direct determination.