

## 29. Radical Mechanisms in Saturated and Olefinic Systems. Part I. Liquid-phase Reaction of the *tert.*-Butoxy-radical with Olefins and with cycloHexane.

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The reactions occurring at 140° between the moderately energetic *tert.*-butoxy-radical and seven hydrocarbons have been studied with the object of determining the characteristic reactivities of the *tert.*-alkoxy-type of organic radical.

The *tert.*-butoxy-radicals, as derived by the thermal scission of di-*tert.*-butyl peroxide, display a reactive tendency towards the non-vinylc olefins and the alkylbenzenes which is practically confined to the dehydrogenation of  $\alpha$ -methylene groups, thereby producing olefin radicals which are capable of reacting in the appropriate (isomeric) resonance forms. These olefin radicals do not couple in any significant degree with *tert.*-butoxy-radicals, and hence achieve stabilisation by self-union, giving first dehydro-dimers, then (by the union of dimer radicals with monomer radicals) dehydro-trimers, and subsequently dehydro-tetramers, etc. The stoichiometrical relation between the peroxide and olefin consumed and the *tert.*-butanol and polymers produced strongly supports the mechanism advanced.

Vinylc ( $\Delta^1$ -)olefins, as represented by hept-1-ene, possess a dual reactive capacity, being capable of undergoing both ordinary additive polymerisation initiated by radicals and also dehydrogenation and subsequent dehydro-polymerisation like the non-vinylc forms. Hept-1-ene shows both reactivities with *tert.*-butoxy-radicals, the former (leading to essentially saturated polymers) in the higher degree.

Saturated hydrocarbons are attacked by *tert.*-butoxy-radicals at 140°, the secondary  $>\text{CH}_2$  groupings of cyclohexane being dehydrogenated to yield cyclohexyl radicals, which couple to give dicyclohexyl and thence by further dehydrogenation and coupling higher (mainly saturated) polymers.

The superior capacity for dehydrogenation of tertiary  $\alpha$ -methylidene groupings over secondary methylene, and secondary methylene over primary methyl appears to govern the path of reaction in the case of all unsaturated hydrocarbons, except where steric effects obtrude; and a similar reactivity sequence applies at a lower level to the groupings of saturated hydrocarbons.

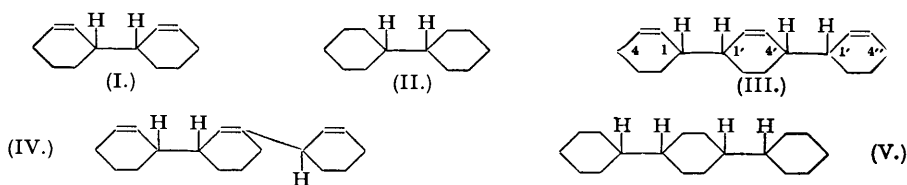
In the present series of papers it will be indicated that differently constituted free radicals show considerable differences in reaction capacity towards olefins in the exercise of the two main reactivities (substitution and addition) open to them. Most radicals seem to be capable of initiating olefinic substitution reactions by detaching  $\alpha$ -methylene hydrogen atoms, but relatively few—and these the more energetic ones—are able to add to the double bond of non-vinylc mono-olefins. Since in the thermal decomposition of hydroperoxides two kinds of radical are produced ( $\text{ROOH} \longrightarrow \text{RO}\cdot + \cdot\text{OH}$ ) whereas in that of *s*-dialkyl peroxides only one kind is produced ( $\text{ROOR} \longrightarrow 2\text{RO}\cdot$ ), there was good reason, when embarking on the investigation of radical reactivity, to choose first *s*-dialkyl peroxides as radical sources. Also there was good reason to select for the first studies the easily derived and manipulated *tert.*-butoxy-radical, although of course the experimentally convenient properties have as their counterpart a reactivity of only moderately energetic character. This moderately energetic reactivity has proved, however, to lead to very characteristic results and these will be contrasted in subsequent papers with the results accruing from the employment of more reactive radicals such as  $\cdot\text{OH}$ .

Di-*tert.*-butyl peroxide breaks down reasonably rapidly above 100°, and for present purposes the temperature of 140° has been selected as suitable both for the generation of radicals and for the attack of the radicals on the olefinic reagent. The peroxide and the various hydrocarbons in turn were heated together in the absence of oxygen in glass Carius tubes for periods varying from 12 to 48 hours. The relative proportions of peroxide to olefin, and the reaction time, were varied somewhat in different experiments, and the effect of the variations on the yield and nature of the reaction products determined.

*Reaction with cycloHexene.*—It was desirable for stoichiometrical reasons to make the quantity of peroxide employed the basis for all calculations of reaction yields. To ensure that all the radicals produced had an opportunity for reaction (with olefins), and correspondingly to minimise any tendency towards their explosive degradation, a large excess of the olefinic reactant was always used.

Reaction of di-*tert.*-butyl peroxide and *cyclohexene* in the molar ratio of 1 : 6 for 24 or 48 hours resulted in complete decomposition of the peroxide, which was converted mainly into *tert.*-butanol and to a minor extent into acetone. In addition to recovered *cyclohexene*, a mixture of *cyclohexene* "polymers" was obtained which contained no oxygenated constituents. By fractional distillation of the "polymer" mixture there were obtained three well-defined fractions, a "dimer"  $C_{12}H_{18}$ , a "trimer"  $C_{18}H_{26}$ , and a "tetramer"  $C_{24}H_{34}$ ; above this, a mixture of higher "polymers" remained which were capable of distillation only in high vacuum. These products were clearly dehydropolymers, and not true polymers  $(C_6H_{10})_n$ ; for convenience, however, in the following account the unqualified terms dimer, trimer, polymer, etc., are used to signify these dehydro-forms except where it is otherwise made clear.

*The dimer,  $C_{12}H_{18}$ .* This proved to consist entirely of the dicyclic diolefin, *dicyclohex-2-enyl* (I). The presence of two double bonds per  $C_{12}$  unit was confirmed both by iodine-value determinations and by catalytic hydrogenation. The tetrahydride derived by hydrogenation was pure *dicyclohexyl* (II); furthermore, the corresponding saturated bromine-adduct consisted wholly of the two known (doubtless stereoisomeric) tetrabromides,  $C_{12}H_{18}Br_4$ , of m. p.s 159—160° and 188—190° (cf. Berlande, *Compt. rend.*, 1941, 213, 484; Farmer and Michael, *J.* 1942, 513). The dimer itself agreed in its physical constants with synthetic *dicyclohex-2-enyl* derived by the action of magnesium on 3-bromocyclohexene.

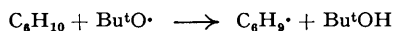


*The trimer,  $C_{18}H_{26}$ .* The trimeric fraction consisted of two isomeric *tercyclohexenyls*, (III) and (IV),\* and gave on hydrogenation a mixture of the corresponding hexahydrides,  $C_{18}H_{32}$ . One of these hexahydrides, the already known form of m. p. 162—163°, crystallised out, but about two-thirds of the mixture consisted of uncrystallised structural and stereo-isomers. On dehydrogenation with selenium the trimer gave a mixture of *p*- and *m*-terphenyl, and on treatment with bromine it gave a mixture of difficultly separable hexabromides, only three of which were isolated in substantially pure form. The apparently complete absence of *o*-terphenyl from the dehydrogenation product is significant in relation to the correctness of the mechanism advanced below.

*The tetramer,  $C_{24}H_{34}$ .* Many structural and stereo-forms were doubtless present in this polymer, and the only examination undertaken was that required to establish its tetraolefinic dehydro-constitution.

*Mechanism of Reaction.*—It is seen from the foregoing results that the di-*tert.*-butyl peroxide, when decomposed in *cyclohexene*, is transformed almost quantitatively into *tert.*-butanol and that those *cyclohexene* molecules which suffer attack become converted into a mixture of dehydropolymers *without loss of any of the original unsaturation*.

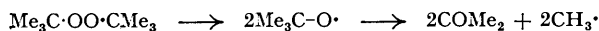
The mechanism advanced to explain these results involves initial homolytic scission of the O—O bond in the peroxide to give two *tert.*-butoxy-radicals. The latter stabilise themselves by abstracting hydrogen atoms from the  $\alpha$ -methylene groups of *cyclohexene* molecules with which they collide favourably, so yielding *tert.*-butanol and a *cyclohexenyl* radical (cf. Farmer and Michael, *loc. cit.*):



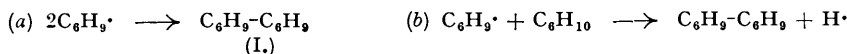
The existence of traces of acetone in these decompositions suggests that the peroxide undergoes, to a minor extent, unimolecular radical decomposition in a manner analogous to the vapour-phase pyrolysis of the peroxide in the absence of solvents as observed by Milas and Surgenor (*J. Amer.*

\* The position of the double bond assigned in the middle ring of (IV) is not easily demonstrable, but is that required for consistency with other observations.

*Chem. Soc.*, 1946, **68**, 205, 643; see also Milas and Perry, *ibid.*, p. 1938), and by Raley, Rust, and Vaughan (*ibid.*, 1948, **70**, 88):

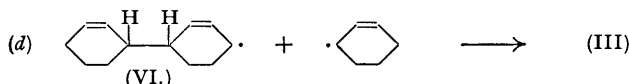


The cyclohexenyl radicals produced by the dehydrogenative action of *tert.*-butoxy-radicals may be expected to become stabilised by the radical-radical coupling reaction (a) to give the dimer (I). This process will undoubtedly have a low energy of activation, whereas (the alternative) radical stabilisation by the substitution reaction (b) seems from energy considerations to be unlikely to occur. It should be noted that the monomer radical may also participate to some extent in a hydrogen-transfer process (c), and in fact spectrographic evidence shows that this type of reaction definitely occurs when the *tert.*-peroxide is thermally decomposed in the presence of hept-1-ene (p. 135) or of 4-methylhept-3-ene (see Part II).

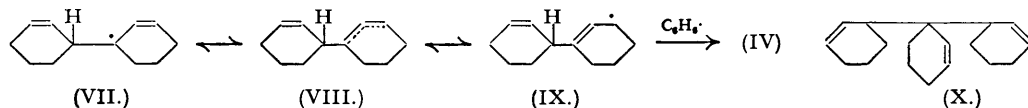


It is especially to be noted that the total absence of oxygenated components from the mixture of cyclohexene polymers demonstrates the highly specific reactivity of *tert.*-butoxy-radicals under the present reaction conditions. The latter radicals are obviously mainly limited in their reactivity to hydrogen abstraction from olefinic  $\alpha$ -methylene groups, so showing *negligible additive reactivity towards double bonds* ( $\text{RO}\cdot + \text{C}=\text{C} \longrightarrow \text{RO}-\text{C}-\text{C}\cdot$ ), and *negligible direct substitutive replacements at  $\alpha$ -methylene groups* ( $\text{RO}\cdot + \text{-CH}_2\text{-C}=\text{C-} \longrightarrow \text{RO}-\text{CH}-\text{C}=\text{C} + \text{H}\cdot$ ).

Turning now to the production of trimeric and higher products, the same basic concepts serve as a basis for formulating the further paths of reaction. The dimer molecules of dicyclohexenyl will, as they are formed in increasing numbers, inevitably compete with the monomer olefin molecules for reaction with *tert.*-butoxy-radicals, and thus they will give *tert.*-butanol and dicyclohexenyl radicals, the latter subsequently giving, by radical-radical unions comparable with (a), trimeric, and occasionally tetrameric products. Thus, for the production of (III), the radical coupling of the dimer radical (VI) with the monomer-radical as in (d) may be formulated.



Here, however, some consideration of possibilities is needed. Clearly, radical attack at one or other of the tertiary (inner)  $\alpha$ -methylidyne groups of the dimer (to give VII) is likely, in the absence of special circumstances, greatly to outweigh that at one or other of the two secondary (outer)  $\alpha$ -methylene groups (to give VI): it is likely, however, that special circumstances will be present, in that the approach of rather large *tert.*-butoxy- or olefin radicals to the inner  $\alpha$ -methylidyne carbon atoms may be to some extent sterically hindered, so causing enhancement



of the otherwise relatively unimportant degree of outer-carbon (secondary)  $\alpha$ -methylene attack. Since, in practice, the yield of stereoisomers of (III) amounts to as much as 33% (and possibly a little more) of the trimer fraction, the steric approach factor does, indeed, seem to have a material effect in enhancing substitution at the outer  $\alpha$ -methylene positions by hindering abstraction of hydrogen at the inner ones. But this is apparently not the only result of steric hindrance in affecting reaction of the inner positions, since the predominant substitution of the dimer molecule is found to occur, not just simply at either the inner or the outer positions, but at what appears at first sight to be one of the original (outer) ethylenic carbon atoms (to give IV). This substitutive effect may easily be interpreted as a direct consequence of resonance in the allylic system of the dehydro-dimer radical (VII), the mesomeric form (VIII) of which is impelled, largely by steric hindrance, to react predominantly *via* its radical form (IX). The relatively large-scale operations needed for the confirmation of the presence in very small proportions of the trimer isomer (X), derived from (VII) in the trimer fraction, could not be undertaken.

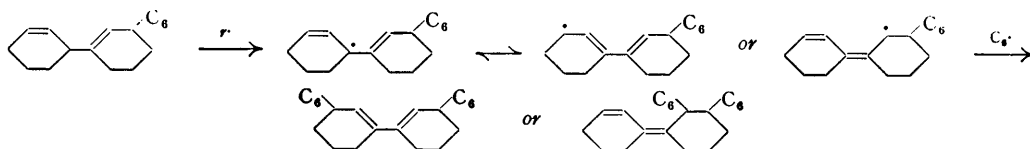
Below the trimeric stage of aggregation, branching in the polymer chain cannot occur; but

it is noteworthy that it appears as soon as circumstances permit. With the tetrameric and higher polymers the number of structurally-different branched forms may be expected to increase substantially owing to increase in the number of *tert.*- $\alpha$ -methylidyne groups, and simultaneously the number of stereoisomers of both branched and unbranched forms is likely to become rapidly larger.

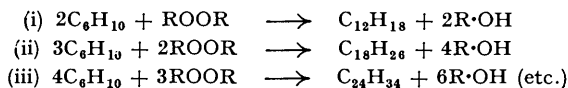
*Conjugation in High Polymers.*—A further interesting feature of the correspondence between allylic theory and experimental observation is the appearance of conjugation as soon as it become possible theoretically. For instance, whereas no conjugation is to be observed in the dimer and trimer fractions of radical-polymerised cyclohexene, yet it occurs, and its extent can be measured, in the tetramer, hexamer, etc., fractions. The measurements (see p. 139) permit the deductions that (1) the appearance of two double bonds in one ring is in practice precluded, and (2) the absorption which is to be observed at  $\lambda_{\text{max}}$ . 2430 Å. may be due to either (or both) of the two conjugated diene systems (XI) and (XII) (cf. Booker, Evans, and Gillam, *J.*, 1940, 1453;



Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72), the total occurrence of which is of the order of <5% in the tetramer and 10–20% in the hexamer and heptamer–octamer fractions. An unresolved band at  $\lambda_{\text{max}}$ . 2860 Å. may \* be due to relatively small amounts of conjugated trienes containing the systems (XIII) and (XIV), which give selective absorption at  $\lambda_{\text{max}}$ . ~2800 Å. (Koch, *Chem. and Ind.*, 1942, **61**, 273). Of course, such conjugation is to be expected theoretically as the outcome of allylic resonance during the conversion of a trimer into a tetramer. This is seen in the following scheme in which the branching cyclohexenyl groups are represented by  $C_6$ :



*Stoichiometrical Considerations.*—The yields of products may be represented as dependent on the basic equations:



By using these equations, the yields of *tert.*-butanol ( $R\cdot OH$ ) and cyclohexene polymers formed in the reaction have been correlated with the amount of peroxide decomposed. The correspondence between the observed peroxide expenditure and the total peroxide theoretically required for producing the various polymers is, as may be seen from Tables I and II, very good, and strongly supports the reaction mechanism advanced. It is to be noted that in the 1 : 6 molar run (Table I) all the peroxide has reacted after 24 or 48 hours' heating, but decomposition is incomplete after only 12 hours; also that the relative proportions of the polymer fractions have remained constant in experiments conducted with a constant peroxide/olefin ratio but different reaction times. Comparison of Tables I and II reveals that variation in the peroxide/olefin ratio causes a great difference in the relative yields of the individual polymers; *e.g.*, in the 1 : 6-molar run the polymer yields are of the order dimer 8, trimer 2.7, tetramer 1, whereas in the 1 : 2-molar run the order has changed to dimer 1.75, trimer 1.1, tetramer 1.0.

The relative yields of the different polymeric grades provide further illustration of the different susceptibility to radical attack of primary, secondary, and tertiary C–H bonds. On a statistical basis high yields of trimer and the higher polymers would not be expected, since the peroxide undergoes decomposition in a large excess of olefin, so that the monomeric olefin molecules will always be more abundant than the dimer molecules, and might therefore be expected to react preferentially with the peroxide. The relative susceptibility to attack, however, declines so considerably in the direction  $C^t-H > C^s-H > C^p-H$ , that this factor

\* Conjugated dienones also absorb at  $\lambda_{\text{max}}$ . 2690–3170 Å., the precise value being dependent on the character of the alkyl substituents, so the observed spectrographic value is not completely conclusive of triene conjugation.

counterbalances the collision-frequency factor sufficiently to have a very pronounced effect on the higher-polymer yields.

TABLE I.

Reaction of di-*tert.*-butyl peroxide \* with cyclohexene.† (Temp. 140°; molar ratio 1 : 6.)

| Heating period :      | 12 Hours.  |                         |                                | 24 Hours.  |                         |                                | 48 Hours.  |                         |                                |
|-----------------------|------------|-------------------------|--------------------------------|------------|-------------------------|--------------------------------|------------|-------------------------|--------------------------------|
|                       | Wt.,<br>g. | Total<br>polymer,<br>%. | Peroxide<br>acctd.<br>for, %.§ | Wt.,<br>g. | Total<br>polymer,<br>%. | Peroxide<br>acctd.<br>for, %.§ | Wt.,<br>g. | Total<br>polymer,<br>%. | Peroxide<br>acctd.<br>for, %.§ |
| Products.             |            |                         |                                |            |                         |                                |            |                         |                                |
| <i>tert.</i> -Butanol | 43.0       | —                       | 87.25                          | 47.4       | —                       | 96.2                           | 46.0       | —                       | 93.3                           |
| Total polymer mixture | 42.0       | (25.6%<br>cyclohexene)  |                                | 45.5       | (27.75%<br>cyclohexene) |                                | 45.0       | (27.45%<br>cyclohexene) |                                |
| Dimer                 | 25.8       | 61.45                   | 47.75                          | 28.15      | 61.85                   | 52.1                           | 27.2       | 60.45                   | 50.35                          |
| Trimer                | 8.8        | 20.95                   | 21.8                           | 9.5        | 20.9                    | 23.55                          | 9.75       | 21.75                   | 24.2                           |
| Tetramer              | 3.3        | 7.85                    | 9.2                            | 3.55       | 7.8                     | 9.9                            | 3.5        | 7.8                     | 9.8                            |
| Higher polymers ‡     | 3.8        | 9.05                    | 11.8                           | 3.85       | 8.45                    | 11.95                          | 4.2        | 9.3                     | 13.05                          |
| Total                 | —          | 99.3                    | 90.55                          | —          | 99.0                    | 97.5                           | —          | 99.3                    | 97.4                           |

\* Weight taken, 48.7 g. † Weight taken, 164.0 g. ‡ Assumed to be (on average) hexamer.

§ Owing to the distillation technique used, the various polymer fractions isolated could not be quite pure molecular-weight species but would contain small amounts of the next higher—and lower—polymers. This, of course, introduces slight inaccuracies into the peroxide-equivalence values as given.

TABLE II.

Reaction of di-*tert.*-butyl peroxide with cyclohexene. (Temp. 140°; heating period 24 hours.)

| Products.             | Molar ratio 1 : 4.* |                        |                            | Molar ratio 1 : 2.† |                        |                            |
|-----------------------|---------------------|------------------------|----------------------------|---------------------|------------------------|----------------------------|
|                       | Wt., g.             | Total<br>polymer, %.   | Peroxide<br>acctd. for, %. | Wt., g.             | Total<br>polymer, %.   | Peroxide<br>acctd. for, %. |
| <i>tert.</i> -Butanol | 46.3                | —                      | 93.9                       | 46.0                | —                      | 93.3                       |
| Total polymer mixture | 44.4                | (40.6%<br>cyclohexene) |                            | 35.8                | (65.5%<br>cyclohexene) |                            |
| Dimer                 | 20.4                | 45.95                  | 37.75                      | 7.14                | 19.95                  | 13.2                       |
| Trimer                | 9.5                 | 21.4                   | 23.55                      | 4.56                | 12.75                  | 11.3                       |
| Tetramer              | 4.6 (a)             | 10.35                  | 12.85                      | 4.1                 | 11.45                  | 11.45                      |
| Higher polymers       | 8.0 (b)             | 18.0                   | 24.9                       | 18.7 (c)            | 52.25                  | 59.85-61.1                 |
| Total                 | —                   | 95.7                   | 99.05                      | —                   | 96.4                   | 95.8-97.05                 |

\* Weights taken : peroxide 48.7 g., cyclohexene 109.3 g.

† Weights taken : peroxide 48.7 g., cyclohexene 54.65 g.

(a) Tetramer sample (A) (p. 140). (b) Polymer sample (B), average composition hexameric [Found :  $M$  (in benzene), 470. Calc. for  $C_{36}H_{50}$  :  $M$ , 482] (p. 140)]. (c) Polymer sample (C), average composition between heptamer and octamer [Found : C, 89.55; H, 10.25%;  $M$  (in benzene), 605, 615.  $C_{42}H_{58}$  requires C, 89.6; H, 10.4%;  $M$ , 562.  $C_{48}H_{66}$  requires C, 89.65; H, 10.35%;  $M$ , 642] (p. 140)].

*Reaction with Dicyclohexenyl.*—When the peroxide and olefin reacted together in the molar ratio of 1 : 2 for 48 hours at 140°, all the peroxide decomposed, yielding *tert.*-butanol (92% of theoretical yield isolated). Of particular significance were the facts : (1) that 35.8% of the olefin was recovered unchanged, (2) that 18.5% of the olefin was converted into quatercyclohexenyl,  $C_{24}H_{34}$   $\bar{4}$ , and (3) that 40.75% of the olefin was converted into a mixture of undistillable polymers having an average composition corresponding to the octamer  $C_{48}H_{66}$   $\bar{8}$ . These results confirm earlier findings that the radical-coupling procedure is not confined to the first or dimerisation stage of polymerisation engendered by radical-olefin interaction ( $2RH \xrightarrow{-2H} 2R \cdot \rightarrow R-R$ ). Here sufficient *tert.*-butoxy-radicals were available to convert all the  $C_{12}$  olefin molecules taken into the  $C_{24}$  dimer; but, in practice, a third of the monomer molecules escaped attack, and a corresponding proportion of *tert.*-butoxy-radicals became available for hydrogen-abstraction, leading to higher polymer formation.

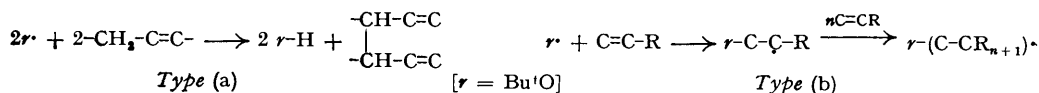
*Reaction with Hept-1-ene.*—Considerable interest attached to the behaviour of the *tert.*-butoxy-radical towards a typical  $\Delta^1$ - or vinylic mono-olefin since olefins of this groups possess in common a strong tendency towards additive polymerisation, the initial step consisting in the addition of a radical (and a wide range of radicals appear to be effective) to one end of the double bond of a monomer molecule—a tendency, which, as seen above, appears to be wholly replaced by a hydrogen-abstraction tendency in the case of non-vinylic mono-olefins.

When the di-*tert.*-butyl peroxide was heated at 140° with hept-1-ene in the molar ratio of

1 : 4, 85.5% of the peroxide passed into *tert.*-butanol and only a small proportion (6.35%) of the heptene was recovered. The bulk of the olefin had been converted into polymeric materials, the fractionation of which gave three heptene dehydro-dimers A, B, and C, containing traces of oxygenated constituents, together with a large proportion (equivalent to *ca.* 76% of olefin taken) of an undistillable polymer having on average a hexameric composition. The three dimer fractions and the polymer residue all showed a considerably lower degree of unsaturation (as revealed by quantitative catalytic hydrogenation, C/H ratios, and infra-red spectrography) than that appropriate to the original hept-1-ene.

Infra-red spectrographic analysis showed that the recovered portion of the heptene employed now contained distinct traces of unsaturation of type R—CH=CH—R; also the three dimer and the higher-polymer fractions all showed a considerable proportion of the latter type of unsaturation in addition to the original vinylic unsaturation. Absorption bands consistent with the presence of small amounts of ether groups and possibly traces of carbonyl groups also characterised the dimer fractions.

The main conclusions to be drawn from these results are: (1) Much of the peroxide decomposes to give *tert.*-butanol. (2) Extensive polymerisation of the olefin is promoted, but there is a complete lack of correspondence between the relative proportions of recovered heptene, dimer fractions, and higher polymer obtained in this case compared with those obtained in all other cases of non-vinylic mono-olefins examined. (3) The polymers show a significant decrease in unsaturation and an extensive rearrangement of the original vinylic unsaturation. (4) It is to be inferred that two different types of polymerisation are being effected side by side by the action of the *tert.*-butoxy-radicals, *viz.*, (a) radical-linking at  $\alpha$ -methylene carbon atoms to give dehydro-polymers of the type described above,\* and (b) true additive polymerisation of the type well known in the peroxide-catalysed production of high polymeric materials from innumerable vinylic olefins, and terminated by one or other of the usual methods involving disproportionation, radical coupling, or hydrogen abstraction from external molecules.



The true additive polymerisation reactions of type (b), of course, entail substantial loss of original olefinic unsaturation, and the fact that the major product is a nearly saturated polymer of fairly high molecular weight indicates that these reactions compete very favourably with those of type (a). The appearance of non-vinylic unsaturation in the monomeric and polymeric reaction products is doubtless due in the main † to resonance in the allylic radical systems produced by hydrogen abstraction, whereby radicals R— $\dot{\text{C}}\text{H-CH=CH}_2$  pass extensively into their counterparts, R—CH=CH— $\dot{\text{C}}\text{H}_2$ , before undergoing mutual coupling or each regaining a hydrogen atom. It is of especial interest that some hept-1-ene molecules change their unsaturation in this way, so illustrating the occurrence of exchange reactions between heptene radicals and heptene molecules (R— $\dot{\text{C}}\text{H-CH=CH}_2 \longleftrightarrow \text{R-CH=CH-}\dot{\text{C}}\text{H}_2 \xrightarrow{\text{R-CH}_2\text{-CH=CH}_2} \text{R-CH=CH-CH}_2 + \text{R-}\dot{\text{C}}\text{H-CH=CH}_2$ ). Also, it is to be noted that, although all the non-vinylic olefins examined (including those discussed later) tend fairly completely to give the dehydro-type of polymer with *tert.*-butoxy-radicals, yet this representative example of the vinylic type of olefin is able to give, under conditions of reaction which provide an abundance of *tert.*-butoxy-radicals, an appreciable proportion of dehydropolymerisation alongside the predominant additive polymerisation.

*Reaction with Alkylbenzenes.*—As might be expected, *tert.*-butoxy-radicals attack alkylbenzenes with moderate facility, the aryl nucleus acting as olefinic activating group to the  $\alpha$ -methylene carbon atom in the side chain, and the alkyl group(s) attached to the latter (if any) as subsidiary activating groups (Ar  $\curvearrowright$  CH<sub>2</sub>  $\longleftarrow$  R). Thus when di-*tert.*-butyl peroxide is decomposed at 140° in presence of toluene, there are formed dibenzyl and substituted dibenzyls, the latter representing dehydro-trimers, -tetramers, etc., of toluene. Likewise, at the same temperature, the peroxide gives with ethylbenzene a mixture of *meso*- and racemic 2 : 3-diphenylbutanes, CHMePh·CHMePh, together with dehydro-trimers, etc., but with

\* To a very minor extent coupling of olefin and butoxy-radicals occurs to give ethers, as revealed by infra-red spectrography.

† Possibly chain-stopping hydrogen-rejections are to some extent responsible ( $r\text{-[CH}_2\text{-CH-R]}\cdot \longrightarrow r\text{-[CH}_2\text{-CH-R]}_{n-1}\text{-CH=CHR}$ ).

*isopropylbenzene* it yields only the homogeneous dimer, 2 : 3-dimethyl-2 : 3-diphenylbutane,  $\text{CMe}_2\text{Ph}\cdot\text{CMe}_2\text{Ph}$ ,\* and no higher polymers.

The approximate yields of polymeric products obtained at  $140^\circ$  from the three alkylbenzenes are given in Table III. The production of a single product from *isopropylbenzene* is to be expected, since only one  $\alpha$ -methylene C-H bond (but that a tertiary one) is present in the monomer, and none at all in the dimer; in contrast, the considerable proportion of trimer and tetramer formed from toluene is doubtless to be attributed to the reactivity of the secondary, and secondary and tertiary  $\alpha$ -methylene C-H bonds present respectively in the dimeric and trimeric products. As regards comparison of the influence of the primary, secondary, and tertiary  $\alpha$ -methylene C-H bonds characterising the three alkylbenzenes (respectively) in promoting reaction with the peroxidic reagent, no valid deduction is to be drawn from the values in Table III; and, indeed, in respect of such relative reactivity it should be mentioned that contemporaneous kinetic studies by Raley *et al.* (*loc. cit.*) on the liquid-phase decomposition of di-*tert.*-butyl peroxide in solvents of widely varying chemical character demonstrate that the rate-determining step in all cases is the unimolecular scission of the peroxidic O-O bond, since the variation in the first-order rates of decomposition is but small.

TABLE III.

Yield (%) of products at  $140^\circ$ .\*

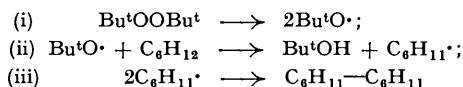
|                           | Toluene                     | Ethylbenzene                 | <i>iso</i> Propylbenzene     |                              |
|---------------------------|-----------------------------|------------------------------|------------------------------|------------------------------|
|                           | (sealed tube<br>(24 hours). | (atm. press.)<br>(24 hours). | (atm. press.)<br>(46 hours). | (sealed tube)<br>(24 hours). |
| Monomer (recovered) ..... | 39                          | 69                           | 57                           | 14.5                         |
| Dimer .....               | 20                          | 26                           | 43                           | 85.5                         |
| Trimer .....              | 10                          | } 5                          | —                            | —                            |
| Higher polymer .....      | 31                          |                              | —                            | —                            |

\* In all these examples, except that of *isopropylbenzene* in the experiment at atmospheric pressure, a 100% excess of hydrocarbon (not taken into account in calculating yields) was employed above that required for a 2 : 1 molar hydrocarbon/peroxide ratio.

It is very noticeable in these experiments with alkylbenzenes that the thermal decomposition of the *tert.*-butoxy-radical (to give acetone) which in the case of simple olefinic hydrocarbons competes very unfavourably with the hydrogen-abstraction function, is considerably enhanced, accounting, for example, in the case of toluene for the very significant proportion of *ca.* 8% of the peroxide consumed.

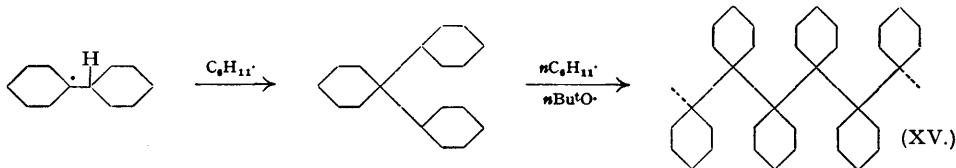
*Reaction with cycloHexane.*—Qualitative tests with saturated hydrocarbons showed that decomposing di-*tert.*-butyl peroxide exercised a similar "polymerising" action to that observed with non-vinylic olefins. As an example of such reaction within the group of saturated hydrocarbons, that with *cyclohexane* was selected since at the monomeric stage all the methylene groups are secondary and equivalent. This hydrocarbon, taken in large excess, was heated for 24 hours at  $140^\circ$  with the peroxide, the products comprising much *tert.*-butanol (92.5% yield), traces of acetone, and a mixture of hydrocarbon polymers with unchanged *cyclohexane*. Dicyclohexyl formed 22.6% of the polymer mixture, and *tercyclohexyl*,  $\text{C}_{18}\text{H}_{32}$  (probably a mixture of isomers), a very much smaller fraction. The major portion of the product (*ca.* 52%) was an orange polymeric residue, essentially of hydrocarbon character, containing apparently an average of 7—8 *cyclohexane* units per molecule (*M*, 630). This polymer, on spectrographic analysis, showed some unsaturation, including, apparently, *cyclohexadiene* groupings; but quantitative determination of the unsaturation, or the gaining of evidence as to the extent of its appearance in conjugated diene groups, was frustrated by the insolubility of the polymer.

The large yield of *tert.*-butanol and the substantial amount of dicyclohexyl suggest that reaction followed a similar course to that discussed above for olefins :

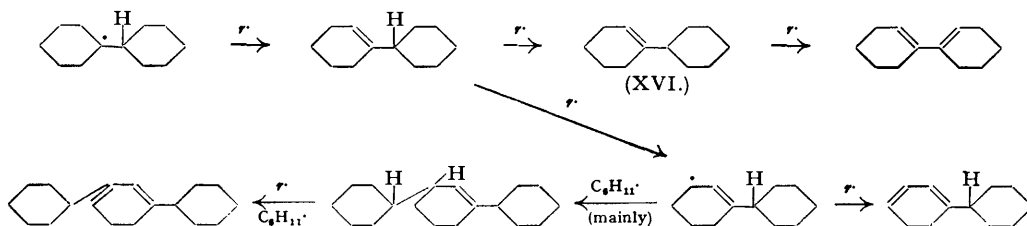


\* Kharasch *et al.* (*J. Org. Chem.*, 1945, **10**, 401) have demonstrated the formation of the two 2 : 3-diphenylbutanes from ethylbenzene and dimethyldiphenylbutane from *isopropylbenzene* by the action of radicals from decomposing diacetyl peroxide. Since our experiments were completed, Raley, Rust, Seubold, and Vaughan (*J. Amer. Chem. Soc.*, 1948, **70**, 88, 95, 1336) have reported observations concerning di-*tert.*-butyl peroxide and toluene and *isopropylbenzene* similar to those described here.

The main point of interest in this case is that dehydro-polymerisation beyond the dimeric stage involves selection of the point of dehydrogenative attack between tertiary  $\text{>CH}$  and (numerous) secondary  $\text{>CH}_2$  groupings; and if such selection meticulously favours attack at the former (which probably is not quite the case) then reaction must pass through the stages:



except to the extent that a subsidiary procedure for the stabilisation of cyclic hydrocarbon radicals occurs, involving a second dehydrogenation step (immediately following the first \*) in the place of coupling:



In view of the yield and average (*ca.* octameric) complexity of the polymer it seems likely that dehydrogenation and coupling at the tertiary carbon atoms proceed with only occasional variations caused by two-stage dehydrogenations, which latter must lead, where they occur, to departure from the regular double-row-parallel-plane arrangement formulated in (XV). The coupling, however, seems to be occasionally varied by the inclusion of a *tert.*-butoxy-group in place of *cyclohexyl*.

#### EXPERIMENTAL.

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

*Di-tert.-butyl Peroxide.*—The peroxide was prepared by both methods given by Milas and Surgenor (*J. Amer. Chem. Soc.*, 1946, **68**, 205). That prepared from *tert.*-butyl hydroperoxide and *tert.*-butyl hydrogen sulphate had b. p. 109.0—110.0°/761.5 mm.,  $n_D^{20}$  1.3905 (Found: C, 65.45; H, 12.65. Calc. for  $\text{C}_8\text{H}_{18}\text{O}_2$ : C, 65.7; H, 12.4%). Prepared from *tert.*-butanol and hydrogen peroxide, the pure peroxide had b. p. 109.0—110.0°/760 mm.,  $n_D^{20}$  1.3882 (Found: C, 65.7; H, 12.3%). Milas and Surgenor (*loc. cit.*) give b. p. 109.0—109.2°/760 mm.,  $n_D^{20}$  1.3872; Vaughan and Rust (U.S.P. 2,395,523, Feb. 26th, 1946) give b. p. 108—110°,  $n_D^{20}$  1.3893.

*Reaction of Di-tert.-butyl Peroxide with cycloHexene.*—The reaction was conducted under various conditions of molar ratio and reaction time, the following being a representative example. The olefin (164 g., 2.0 mols., b. p. 82.50°/744.5 mm.,  $n_D^{20}$  1.4463) with di-*tert.*-butyl peroxide (48.7 g., 0.33 mol.) was heated for 48 hours at 140° in Carius tubes sealed in an atmosphere of pure nitrogen. The product (212.0 g.) was a colourless mobile liquid which on fractionation through a 10-in. Vigreux column under nitrogen gave a forerun of b. p. 74—83°/764 mm. (160.6 g.). After removal of the last traces of volatile material by warming the residue at 50° for a short time at the water-pump, there remained a colourless oily product (45.0 g.); this was distilled at oil-pump pressure, giving the fractions: (i) b. p. 68—71°/1 mm. (27.2 g.),  $n_D^{20}$  1.5095, (ii) b. p. 130—140°/1 mm. (9.75 g.), (iii) b. p. 180—192°/1 mm. (3.5 g.), and an undistillable residue (*ca.* 4.2 g.), which set to a glass on cooling.

*Reaction products.* The forerun, consisting of a mixture of *tert.*-butanol, unchanged *cyclohexene*, and a trace of acetone, was extracted 6 times with water (6 × 50 g.) whereby 46.0 g. of water-soluble material were obtained. This extract was found to be almost entirely *tert.*-butanol. In one experiment the aqueous extract was distilled, giving an azeotrope of *tert.*-butanol and water, b. p. 80°/763 mm., the butanol component of which (separated and dried by potassium hydroxide, and subsequently distilled over sodium) boiled at 80—82°/765 mm., and was identified by formation of its phenylurethane (m. p. and mixed m. p. with an authentic specimen 135—136°) (Found: C, 68.5; H, 8.3; N, 7.0. Calc. for  $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}$ : C, 68.4; H, 7.83; N, 7.25%). In a similar experiment the aqueous extract was treated with an excess of saturated 2:4-dinitrophenylhydrazine solution (in 2*N*-hydrochloric acid). Acetone

\* The tendency for this two-stage dehydrogenation to occur in hydroaromatic rings is understandably much greater than is the case for open-chain olefins (*cf.* Part V). The susceptibility of *tert.*-*cyclohexyl* groups, such as occur in (XVI), to similar attack, is, doubtless, of a much lower order.



2 : 4-dinitrophenylhydrazone separated (0.24 g.  $\equiv$  0.05 g. of acetone), which on crystallisation from light petroleum (b. p. 100—120°) had m. p. 122—123°, and mixed m. p. with an authentic sample 123—124° (Found : C, 45.7; H, 4.55. Calc. for  $C_8H_{10}O_4N_4$  : C, 45.4; H, 4.2%). The yield of *tert*-butanol represented 93.3% of the peroxide taken, the yield of acetone being insignificant (equivalent to <0.1% of peroxide). The recovered *cyclohexene* (114.5 g.) was dried ( $CaCl_2$ ) and when distilled over sodium (in nitrogen) had b. p. 83.0°/763 mm. Ultra-violet spectrographic analysis of a sample of this olefin showed the almost complete absence of conjugated diene (Found : 0.05—0.1% of *cyclohexa-1 : 3*-diene), and the complete absence of benzene.

*The dimer.* Fraction (i), a colourless oily liquid, consisted mainly of the dimeric olefin *dicyclohex-2-enyl* (Found : C, 88.0; H, 11.2%). On careful fractionation over sodium (in nitrogen) it gave the pure hydrocarbon, b. p. 62—63°/0.5 mm. (68—69°/1.0 mm.),  $n_D^{20}$  1.5092 (Found : C, 88.65; H, 11.23%; I.V., 302.5, 302.2; *M* (micro-Rast), 167.5. Calc. for  $C_{12}H_{18}$  : C, 88.8, H, 11.2%; I.V. 313.6; *M*, 162). Quantitative catalytic hydrogenation of the olefin in pure ethanol (Adams's catalyst) gave a value of 1.97 double bonds per molecule (Calc. for  $C_{12}H_{18}$  :  $\frac{1}{2}$ ). A larger portion (1.5 g.) of the olefin, similarly hydrogenated in ethanol (20 c.c.), absorbed in *ca.* 6 hours 398 c.c. of hydrogen at N.T.P. (Calc. : 415 c.c.), so giving *dicyclohexyl*, which on distillation over sodium had b. p. 72—73°/*ca.* 1 mm.,  $n_D^{20}$  1.4803; the yield was 1.3 g. (86.5%) (Found : C, 86.65; H, 13.4. Calc. for  $C_{12}H_{22}$  : C, 86.65; H, 13.35%). The olefin (2.0 g.) in chloroform (20.0 c.c.), cooled to  $-10^\circ$ , absorbed during 1 hour (with stirring) 3.75 g. of bromine (in 20 c.c. of chloroform). The colourless crystalline product (5.75 g., 96.6%) consisted of a mixture of two, presumably stereoisomeric, *dicyclohexenyl* tetrabromides, which were separated by repeated fractional crystallisation from chloroform. The more soluble isomer, prismatic plates, m. p. 159—162°, predominated (Found : C, 29.9; H, 3.8; Br, 66.65. Calc. for  $C_{12}H_{18}Br_4$  : C, 29.9; H, 3.76; Br, 66.75%); the less soluble isomer, large rectangular prisms, was present in only small yields, m. p. 188—190° (Found : C, 29.85; H, 3.75; Br, 66.75%). Both tetrabromides have been reported in the literature, the former as having m. p. 159° (Farmer and Michael, *J.*, 1942, 513), and the latter m. p. 189—190° (Berlande, *Compt. rend.*, 1941, **213**, 484).

For comparison with the dimer, *dicyclohex-2-enyl* was obtained from 3-bromocyclohexene and magnesium. The bromide was prepared by the method of Ziegler *et al.* (*Annalen*, 1942, **551**, 80); the *N*-bromosuccinimide (36.6 g.) and *cyclohexene* (103 c.c.) were refluxed in carbon tetrachloride (150 c.c.) for 30 minutes in the presence of a little benzoyl peroxide as catalyst. The succinimide (20.2 g. Calc. : 20.35 g.) which separated from the cold reaction mixture was filtered off. Removal of the solvent through a column, and distillation of the residue, gave 3-bromocyclohexene (25.0 g., 75%), b. p. 58—60°/12 mm.,  $n_D^{20}$  1.5309 (Found : C, 44.75; H, 5.6. Calc. for  $C_6H_9Br$  : C, 44.75; H, 5.65%). When this bromide (20.0 g.), dissolved in ether (75 c.c.), was added during 40 minutes to magnesium (2.0 g.), just covered with ether, and the mixture warmed, reaction soon began. When it had subsided, the product was stirred for an hour, then decomposed with ice-cold ammonium chloride solution, and the ethereal layer separated and dried ( $CaCl_2$ ). The extracted *dicyclohexenyl* when distilled over sodium (in nitrogen) had b. p. 62—63°/0.5 mm.,  $n_D^{20}$  1.5093 (yield 9.4 g., 94%) (Found : C, 88.5; H, 11.35. Calc. for  $C_{12}H_{18}$  : C, 88.8; H, 11.2%). Addition of bromine to this product (2.0 g.), as described above, gave a mixture of tetrabromides (5.95 g., 100%), resolvable into a major isomer of m. p. 160° (Found : C, 29.85; H, 3.85; Br, 66.3%), and a minor one of m. p. 189—190° (Found : C, 29.9; H, 3.8; Br, 66.4%), identical with those previously obtained.

*The trimer.* Fraction (iii) was a colourless, viscous liquid which on refractionation over sodium (in nitrogen) distilled mainly at 133—134°/1 mm., and had  $n_D^{20}$  1.5330. It represented the "trimeric" olefin *tercyclohexenyl*,  $C_{18}H_{28}$   $\frac{1}{3}$  [Found : C, 88.9; H, 10.85%; I.V., 282, 284, 287; *M* (micro-Rast), 239.  $C_{18}H_{28}$  requires C, 89.2; H, 10.8%; I.V., 315; *M*, 242].

Quantitative catalytic hydrogenation of the olefin in glacial acetic acid (Adams's catalyst) showed 2.94 double bonds per molecule. A larger portion (5.0 g.), hydrogenated in a mixture of glacial acetic acid (25 c.c.) and ethyl acetate (15 c.c.) at room temperature and pressure, took up 1435 c.c. of hydrogen at N.T.P. (Calc. : 1390 c.c.). The reaction mixture, from which crystals had already separated, gave, when worked up, a crude saturated hydrocarbon (4.95 g.), from which by distillation (i) a partly crystallising oil, b. p. 147—150°/2 mm. (3.5 g.), and (ii) a colourless crystalline residue (1.45 g.) were obtained. The latter, together with the solid from fraction (i) (0.2 g.), represented the high-melting form of 1 : 4'-*tercyclohexyl*, forming colourless, feathery plates, m. p. 162—163° (Found : C, 86.9; H, 13.0. Calc. for  $C_{18}H_{32}$  : C, 87.0; H, 13.0%), from ethyl acetate (von Braun, Irmisch, and Nelles, *Ber.*, 1933, **66**, 1471, give m. p. 162°; Corson and Ipatieff, *J. Amer. Chem. Soc.*, 1937, **59**, 646, give m. p. 159.5—161°). On redistillation, the colourless liquid from fraction (i) had b. p. 122—128°/1 mm.,  $n_D^{20}$  1.5072. It could not be crystallised and consisted, presumably, of a mixture of stereoisomers of 1 : 4'- and 1 : 3'-*tercyclohexyl* (Found : C, 87.05; H, 12.6%). For the low-melting form of the 1 : 4'-isomer, Corson and Ipatieff (*loc. cit.*) reported m. p. 54—56°, and later (*ibid.*, 1938, **60**, 747) for the two forms of the 1 : 3'-isomer the m. p.s. 62.5—63.5° and 57—59°.

Dehydrogenation of the trimeric olefin (2.0 g.) was effected by heating it with powdered selenium (6.0 g.), in nitrogen, for 40 hours at 320° (metal-bath). Evolution of hydrogen selenide began almost immediately. The product, which solidified on cooling, was extracted with boiling benzene. The extract gave a solid (1.8 g.), which by sublimation over molten sodium at 0.05 mm. (bath-temp. 200—250°) gave a colourless crystalline mass (1.53 g.) melting over the range *ca.* 50° to *ca.* 175°. Crystallisation of this product from benzene gave *p*-terphenyl (0.4 g.) as lustrous plates, m. p. 211—212° (lit. 213°) (Found : C, 93.35; H, 6.15. Calc. for  $C_{18}H_{14}$  : C, 93.9; H, 6.1%). The benzene mother-liquor was evaporated to dryness, and the resulting solid (0.99 g.) repeatedly crystallised, whereby the following fractions were obtained : (i) a mixture of *p*- and *m*-terphenyl (0.6 g.); (ii) *m*-terphenyl as colourless needles, m. p. 82° (softening)—84° (0.15 g.) (Found : C, 94.0; H, 6.1%), and (iii) a less pure *m*-terphenyl, m. p. 82—83° (0.13 g.). (The highest recorded m. p. for this substance is 87°.)

Addition of bromine (1.5 c.c. in 20 c.c. of chloroform) to the olefin (2.0 g.) in chloroform (20 c.c.) at 0° yielded a difficultly separable mixture of isomeric *tercyclohexenyl hexabromides* (5.4 g.). Fractional crystallisation of this mixture from chloroform gave the following fractions: (a) a very insoluble, colourless, crystalline powder (0.1 g.), m. p. 285—287° (sublimation) (Found: C, 29.95; H, 3.7; Br, 66.55.  $C_{18}H_{26}Br_6$  requires C, 29.95; H, 3.62; Br, 66.4%); (b) a colourless microcrystalline powder, m. p. 249—250° (ca. 50 mg.); (c) the major product, colourless micro-crystals, m. p. 217—219° (Found: C, 29.95; H, 3.7; Br, 67.0%).

*The tetramer.* Redistillation of fraction (iii) over sodium (in nitrogen) gave a colourless, extremely viscous liquid, b. p. 180—193°/1 mm.,  $n_D^{20}$  1.5478, having the composition of *quatercyclohexenyl* [Found: C, 89.05; H, 10.7%; I.V. 282, 284; *M* (micro-Rast), 313.  $C_{24}H_{34}$  requires C, 89.35; H, 10.65%; I.V., 313.5; *M*, 322]. Although molecularly homogeneous, it doubtless contained many structural isomers. This tetrameric mixture (29.62 mg.), dissolved in glacial acetic acid (5.0 c.c.), absorbed 8.65 c.c. of hydrogen at 13° and 753 mm. (*i.e.*, 3.98 mols. per molecule) in presence of Adams's catalyst (10 mg.).

*Ultra-violet spectrographic analysis of the polymeric products.* The di- and *tercyclohexenyls* isolated showed no selective absorption consistent with the presence of conjugated dienes. *Quatercyclohexenyl* from the 1:6 run (Table I), in *cyclohexane-ethanol* (9:1) as solvent, showed selective absorption near  $\lambda_{max}$  2450 Å.,  $E_{1cm}^{1\%}$  ~45, and also at  $\sim\lambda_{max}$  2830 Å.,  $E_{1cm}^{1\%}$  ~50. The same olefin from the 1:4 run (Product A, Table II), in *cyclohexane-ethanol* (1:1) as solvent, showed selective absorption at  $\lambda_{max}$  2430 Å.,  $E_{1cm}^{1\%}$  50, and at  $\lambda_{max}$  2860 Å.,  $E_{1cm}^{1\%}$  65. The polymeric mixture obtained as the undistillable residue from the 1:4 run (Product B, Table II), in *cyclohexane-ethanol* (1:1) showed selective absorption at  $\lambda_{max}$  2430 Å.,  $E_{1cm}^{1\%}$  140, and at  $\lambda_{max}$  2860 Å.,  $E_{1cm}^{1\%}$  45. The polymeric mixture in the 1:2 run (Product C, Table II) gave similar bands at  $\lambda_{max}$  2430 Å.,  $E_{1cm}^{1\%}$  180, and at  $\lambda_{max}$  2860 Å.,  $E_{1cm}^{1\%}$  90.

*Reaction of Di-tert.-Butyl Peroxide with Dicyclohex-2-enyl.*—The olefin (16.2 g.; b. p. 68—70°/1 mm.) and di-*tert.*-butyl peroxide (7.3 g.) were heated at 140° for 48 hours in an evacuated sealed tube. The product (23.0 g.) gave on distillation the following fractions: (i) *tert.*-butanol, b. p. 80—82.5°/751 mm. (6.8 g., equivalent to 92% of the peroxide taken); (ii) unchanged olefin, b. p. 64—67°/ca. 1 mm.,  $n_D^{20}$  1.5090 (5.8 g. or 35.8% of the olefin taken) (Found: C, 88.45; H, 11.4%); (iii) an oil of b. p. 180—190°/1 mm.,  $n_D^{20}$  1.5468 (3.0 g.); and (iv) the residue in the still (6.6 g.), which set on cooling to a bright orange resin.

Fraction (iii) resembled in all respects the *quatercyclohexenyl* previously obtained from *cyclohexene* [Found: C, 89.35; H, 10.8%; I.V., 289, 292; unsaturation value (catalytic hydrogenation),  $\frac{58.84}{100}$ . Calc. for  $C_{24}H_{34}$ : C, 89.36; H, 10.64%; I.V., 315.5;  $\bar{M}$ , 314].

Fraction (iv) consisted mainly of a *cyclohexene polymer* mixture having, on average, "octameric" complexity [Found: I.V., 307.3, 307.5; *M* (micro-Rast), 666.  $C_{48}H_{68}$  requires I.V., 316; *M*, 643].

*Reaction of Di-tert.-butyl Peroxide with Hept-1-ene.*—The olefin was prepared by the reaction of allyl bromide with *n*-butylmagnesium bromide (cf. Wilkinson, *J.*, 1931, 3057) and fractionated (in nitrogen) over sodium through a 3-ft. Widmer column. It had b. p. 92.0—93.2°/746 mm.,  $n_D^{20}$  1.3999 (Found: C, 85.6; H, 14.8. Calc. for  $C_7H_{14}$ : C, 85.6; H, 14.4%).

A mixture of the olefin (85.0 g.) and di-*tert.*-butyl peroxide (31.7 g.) was heated at 140° for 24 hours in nitrogen-filled Carius tubes. The product (116.0 g.), a light yellow oil, gave on fractionation the fractions: (i) b. p. 75—86° (32.5 g.), (ii) b. p. 84—100°/1 mm.,  $n_D^{20}$  1.4410 (9.1 g.) (Found: C, 84.6; H, 14.35%), and (iii) a residue (64.5 g.).

*Examination of the fractions.* Aqueous extraction of the forerun (i) gave *tert.*-butanol (27.1 g., *i.e.*, 85.5% of the peroxide taken) and recovered olefin (5.4 g.), the latter of which, after being dried (CaCl<sub>2</sub>) and distilled over sodium, had b. p. 94.0—96.5°/766 mm.,  $n_D^{20}$  1.4000.

A portion (5.0 g.) of fraction (ii), on refractionation over sodium through a 6-in. column, gave the three sub-fractions: (iiA), b. p. 58—70°/0.1 mm.,  $n_D^{24}$  1.4420 (1.1 g.) [Found: C, 85.2; H, 14.35%; *M* (in benzene), 196. Calc. for  $C_{14}H_{28}$ : C, 85.6; H, 14.35%; *M*, 196. Calc. for  $C_{14}H_{26}$ : C, 86.5; H, 13.5%; *M*, 194]; (iiB), b. p. 70—76°/0.1 mm.,  $n_D^{24}$  1.4440 (1.85 g.) [Found: C, 85.8; H, 14.45; *M* (in benzene), 207, 208, 209]; (iiC), b. p. 76—78°/0.1 mm.,  $n_D^{24}$  1.4430 (1.65 g.) [Found: C, 85.1; H, 14.6%; *M* (in benzene), 211]. Quantitative catalytic hydrogenations of these sub-fractions in glacial acetic acid, over Adams's catalyst, gave the following hydrogen uptake values: (iiA), 98.6 c.c. (N.T.P.)/g., 97.85 c.c./g.; (iiB), 83.8 c.c./g.; (iiC), 93.7 c.c./g. (Calc. for  $C_{14}H_{28}$ : 114.3 c.c./g. Calc. for  $C_{14}H_{26}$ : 231.0 c.c./g.).

The original residue, fraction (iii), was a mixture of polymeric hydrocarbons of unsaturation value considerably lower than that of the parent olefin [Found: C, 85.7; H, 14.0%; *M* (in benzene), 590];  $n_D^{20}$  1.4737. It absorbed 34.7 c.c./g. (N.T.P.) (Adams's catalyst) (Calc. for  $C_{42}H_{84}$ : C, 85.6; H, 14.4%; *M*, 588; Hydrogen uptake, 38.1 c.c./g.).

*Infra-red spectrographic analysis of hept-1-ene and the derived olefins.* The various samples of the heptene products were examined as the pure liquids in rock-salt absorption cells of path length 0.1 mm. on a Hilger double-beam research instrument run on a single-beam photographic recording. The synthetic hept-1-ene employed had very strong bands at 909 and 990 cm<sup>-1</sup>. Selective absorption of other characteristic frequencies was absent. The recovered hept-1-ene contained, in addition to the 909 and 990 cm<sup>-1</sup> bands, an extremely weak band at 965 cm<sup>-1</sup>. The dimer sub-fractions (iiA), (iiB), and (iiC) had spectra very similar to one another. In addition to strong absorption at 910 and 990 cm<sup>-1</sup>, they displayed a strong band at 965 cm<sup>-1</sup> and other bands at 1082 and 1198 cm<sup>-1</sup> and a weak band at 887 cm<sup>-1</sup>. In the (residual) polymer mixture (iii), by far the strongest absorption occurred at 965 cm<sup>-1</sup>.

*Reaction of Di-tert.-butyl Peroxide with Alkylbenzenes.—Products from toluene.* A mixture of the peroxide (18.25 g., 1 mol.) and toluene (46.0 g., 4 mols.; b. p. 100.0—100.2°/761 mm.,  $n_D^{20}$  1.4974) was heated at 140° for 24 hours in a Carius tube sealed under nitrogen. When the tube was opened a considerable amount of gas was evolved. The liquid product (ca. 64 g.) gave on distillation the following three fractions: (i) b. p. 79—110° (31.5 g.), containing (a) unchanged toluene, (b) peroxide, (c) *tert.*-butanol (12.3 g.) (phenylurethane, m. p. 135.5—136°. Found: C, 68.3; H, 7.65; N, 7.4. Calc. for  $C_{11}H_{15}O_2N$ : C, 68.4; H, 7.8; N, 7.25%), and (d) acetone (1.1 g.) (2 : 4-dinitrophenylhydrazone, m. p. 124—125°. Found: C, 45.45; H, 4.35. Calc. for  $C_9H_{10}O_4N_2$ : C, 45.4; H, 4.25%); (ii) b. p. 110° (15.15 g.),  $n_D^{20}$  1.4927, consisting mainly of unchanged toluene; (iii) b. p. 84—85°/0.1 mm. (0.4 g.); (iv) dibenzyl, b. p. 85—86°/0.1 mm., m. p. 51.0—51.5° (4.2 g.) (Found: C, 92.25; H, 7.75. Calc. for  $C_{14}H_{14}$ : C, 92.25; H, 7.75%); (v) b. p. 86—138°/0.1 mm. (0.4 g.); (vi) a saturated oil, b. p. 138—144°/0.1 mm.,  $n_D^{20}$  1.5872 (2.3 g.), consisting mainly of but slightly impure 1 : 2 : 3-*triphenylpropene* (Found: C, 92.05; H, 7.6.  $C_{21}H_{20}$  requires C, 92.6; H, 7.4%); and (vii) a slightly oxygenated undistillable residue (7.15 g.), which set to a clear light yellow glass (Found: C, 90.75; H, 7.65%).

*Products from Ethylbenzene.*—The peroxide (36.5 g., 1 mol.) and ethylbenzene (106 g., 4 mols.; b. p. 135°/755 mm.,  $n_D^{20}$  1.4959) were heated on an oil-bath under an efficient reflux at 140° for 24 hours, a slow stream of purified nitrogen being passed through the apparatus. The product (142.0 g.) gave on distillation a liquid, b. p. 83—136°/760 mm. (125.0 g.), shown by aqueous extraction to contain *tert.*-butanol (ca. 12.7 g.) and a residue. Removal of the last traces of ethylbenzene from the latter by heating it on a water-bath under slightly diminished pressure gave a partly crystallising product (16.3 g.), from which crystals of *meso*-2 : 3-diphenylbutane (7.5 g.), m. p. 125—126° were isolated (Found: C, 91.5; H, 8.75. Calc. for  $C_{16}H_{18}$ : C, 91.35; H, 8.65%); Conant and Blatt (*J. Amer. Chem. Soc.*, 1928, **50**, 551) record m. p. 124—125°, and Ott (*Ber.*, 1928, **61**, 2139) records m. p. 126—127°. The oily liquid (8.8 g.) accompanying the crystals gave on distillation a fraction, b. p. 85—86°/1 mm. (6.3 g.), from which more solid of m. p. 126° (0.9 g.) was separable, leaving a colourless oily liquid (5.4 g.) consisting mainly of racemic 2 : 3-diphenylbutane. On redistillation of this liquid over sodium it had b. p. 136°/9 mm.,  $n_D^{20}$  1.5537 (Found: C, 91.25; H, 8.8%). Kharasch, McBay, and Urry (*J. Org. Chem.*, 1945, **10**, 401) give b. p. 106°/2 mm.,  $n_D^{20}$  1.5517. Isomerisation of the racemic to the *meso*-form of diphenylbutane (m. p. 126°) was effected by heating the former in an evacuated sealed tube at 250° for 17 hours in the presence of a small quantity of iodine (<1 mg. per g. of hydrocarbon); the yield was 42%. The residue (2.5 g.) in the still was a colourless viscous liquid, consisting of higher polymeric hydrocarbons.

*Products from isoPropylbenzene.*—A mixture of the peroxide (12.2 g.; 1 mol.) and *isopropylbenzene* (20.0 g., 2 mols.; b. p. 148.0—148.5°/725 mm.,  $n_D^{20}$  1.4910) was heated under an efficient reflux condenser on an oil-bath at 140° for 46 hours, purified nitrogen being passed through the apparatus. The product, on fractionation, gave: (i) mainly *tert.*-butanol (5.1 g.), b. p. 82—83° (phenylurethane, m. p. 136°); (ii) unchanged peroxide, b. p. 110—114° (6.2 g.); (iii) unchanged hydrocarbon, b. p. 150—152° (11.25 g.), and (iv) still residue, solid 2 : 3-dimethyl-2 : 3-diphenylbutane (8.45 g.), which crystallised from absolute ethanol in long colourless needles, m. p. 118—119° (Found: C, 90.6; H, 9.4. Calc. for  $C_{18}H_{22}$ : C, 90.7; H, 9.3%). Klages (*Ber.*, 1902, **35**, 2638) gives m. p. 119—120°, and Kharasch *et al.* (*loc. cit.*) m. p. 115°.

In a second experiment the peroxide (12.2 g.; 1 mol.) and *isopropylbenzene* (40.0 g., 4 mols.), after being heated in nitrogen-filled Carius tubes at 140° for 24 hours, gave: (i) *tert.*-butanol (9.8 g., equiv. to 79.5% of the peroxide taken), (ii) acetone (0.5 g.) estimated and identified as its 2 : 4-dinitrophenylhydrazone (2.15 g.), (iii) a mixture of unchanged peroxide and hydrocarbon (23.3 g.), and (iv) dimethyldiphenylbutane, m. p. 118—119.5° (17.1 g.; 85.5%, based on the peroxide consumed).

*Reaction of Di-tert.-butyl Peroxide with cycloHexane.*—The peroxide (24.3 g., 1 mol.) and spectroscopically pure *cyclohexane* (84.0 g., 6 mols.;  $n_D^{20}$  1.4262) were heated together in Carius tubes at 140° for 24 hours. The product (107.9 g.), a light yellow liquid, gave on distillation a forerun, b. p. 70—91°/766 mm. (92.5 g.), shown by aqueous extraction and treatment of the aqueous extract with 2 : 4-dinitrophenylhydrazine solution (2*N*-hydrochloric acid) to contain *tert.*-butanol (22.8 g., equiv. to 92.45% of peroxide taken), acetone (0.085 g.), and unchanged *cyclohexane* (ca. 69 g.,  $n_D^{20}$  1.4261).

The polymeric product (13.6 g., equiv. to 16.2% of the hydrocarbon taken) was a viscous yellow liquid which on fractionation gave: (i) b. p. <100°/11 mm.,  $n_D^{20}$  1.4711 (0.34 g.); (ii) b. p. 100.0—102.3°/11 mm.,  $n_D^{20}$  1.4784 (3.08 g.); (iii) b. p. <124°/0.1 mm.,  $n_D^{20}$  1.4825 (0.57 g.); (iv) b. p. 124—134°/0.1 mm.,  $n_D^{20}$  1.5035 (0.57 g.); and (v) an orange polymeric residue (7.1 g.) which on cooling set to a brittle solid glass. Fraction (ii), consisting mainly of *dicyclohexyl*, gave on refractionation over sodium a small forerun, b. p. <99.5°/10 mm.,  $n_D^{20}$  1.4792, together with a main fraction, b. p. 99.5—100.0°/10 mm.,  $n_D^{20}$  1.4801 (Found: C, 86.8; H, 13.4. Calc. for  $C_{12}H_{22}$ : C, 86.65; H, 13.35%). Fraction (iv) was mainly *tercyclohexyl*, but contained a small amount of oxygenated material [Found: C, 86.3; H, 12.6%; *M* (in benzene), 242. Calc. for  $C_{18}H_{32}$ : C, 87.0; H, 13.0%; *M*, 248]. Fraction (v) was mainly a mixture of polymeric hydrocarbons but also contained a small amount of oxygen [Found: C, 87.0; H, 11.5%; *M* (in benzene), 630]. An ultra-violet spectrographic examination of this polymer indicated the presence of unsaturation and, in particular, showed selective absorption near  $\lambda_{max}$  2550 Å., which is attributed to the presence of not more than 5% of conjugated *cyclohexadiene* groupings.