(*b*) *Addition initiated by ultraviolet light.* A stirred solution of 1.00 g. (10.8 mmoles) of norbornadiene and 2.05 g. (10.8 mmoles) of *p*-toluenesulfonyl chloride in 50 ml. of cyclohexane was irradiated for 24 hr. in a Vycor flask, using the ultraviolet light from a Mazda AH-4 lamp. The cyclohexane was removed by evaporation and a pasty residue was obtained, which was chromatographed on 60 g. of activated alumina. Elution with 20% ethyl acetate in petroleum ether (b.p. 60–80°) gave a total of 1.62 g. (53.2%) of a white solid, m.p. 100–125°. Two recrystallizations from methanol gave X melting at 151.5–153.5°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Reactions of Free Radicals with Olefins. Reactions of *t*-Butoxy and *t*-Butyl Peroxy Radicals with 4-Vinylcyclohexene[1]

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Abstraction of hydrogen (rather than addition) is demonstrated as a preliminary step in the formation of *t*-butyl vinylcyclohexenyl peroxides from 4-vinylcyclohexene with *t*-butyl hydroperoxide in the presence of cobalt ions. The olefin is shown to be peroxidated mainly in the 6-position, with minor proportions peroxidated in the 3-position and 4-position. The ratio of isomers is taken as evidence also for a strong steric effect.

Slow photolysis of di-*t*-butyl peroxide in 4-vinylcyclohexene at 40° results in the formation of four times as much dehydrodimer as any other olefin-derived product, showing that the *t*-butoxy radical prefers abstraction under these conditions. In contrast, there is as much *t*-butoxylation as dehydrodimerization of the olefin when di-*t*-butyl peroxide is decomposed at 120° in 4-vinylcyclohexene in the presence of cupric ion. These variations may be explained by differences in the nature and relative concentrations of free radicals produced.

The work described in this paper is a part of a continuing study of the reactions of free radicals with olefins. The objective of the program is to provide additional information regarding the relative reactivity of different types of free radicals with a variety of unsaturated compounds, and to determine the point of attack and the nature of the products formed. The study is particularly aimed at providing information with model compounds which relates to free-radical processes involved in polymerization, in certain cross linking reactions, and in both thermal and oxidative degradation of polymers.

In hydroperoxide decompositions induced by cobalt ions or similar metal ions, the work of the late Professor M. S. Kharasch and his colleagues[3] suggested the presence of both peralkoxy and alkoxy radicals: for example, in butadiene, *t*-butyl hydroperoxide decomposed to give $t\text{-}C_4H_9OOCH_2\text{-}CH{=}CHCH_2OOt\text{-}C_4H_9$ and isomeric peroxide along with about one-half equivalent of *t*-butyl alcohol. The roles of these radical species were originally misunderstood. It was proposed that peroxidation of olefins with a hydroperoxide (Equation 1) proceeded by addition of the peroxy radical to the double bond, followed by loss of a hydrogen atom to give, for example, 1-peralkoxyoctene-2 from octene-1. However, the untenability of this mechanism has recently been acknowledged.[4] The peroxidation of such compounds as cumene and cyclohexanone[4,5] showed that hydrogen abstraction must occur in these cases because an initial addition of $RO_2\cdot$ was not a reasonable possibility. Reexamination of the octene-1 example disclosed the presence of 3-peralkoxyoctene-1, certainly a product of hydrogen abstraction rather than of peroxy radical addition.

$$2\,ROOH + R'H \longrightarrow ROOR' + ROH + H_2O \quad (1)$$

We had meanwhile applied the peroxidation technique to 4-vinylcyclohexene and independently concluded that the reaction must involve initial hydrogen abstraction in this case also.

The experimental work reported here involves the reaction of *t*-butoxy and *t*-butyl peroxy radicals with 4-vinylcyclohexene. This olefin provides both

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[1] Presented before the Division of Organic Chemistry, 137th Meeting, American Chemical Society, Cleveland, April 1960.

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[3] M. S. Kharasch, P. Pauson, and W. Nudenberg, *J. Org. Chem.*, 18, 322 (1953).

[4] M. S. Kharasch and A. Fono, *J. Org. Chem.*, 24, 72 (1959).

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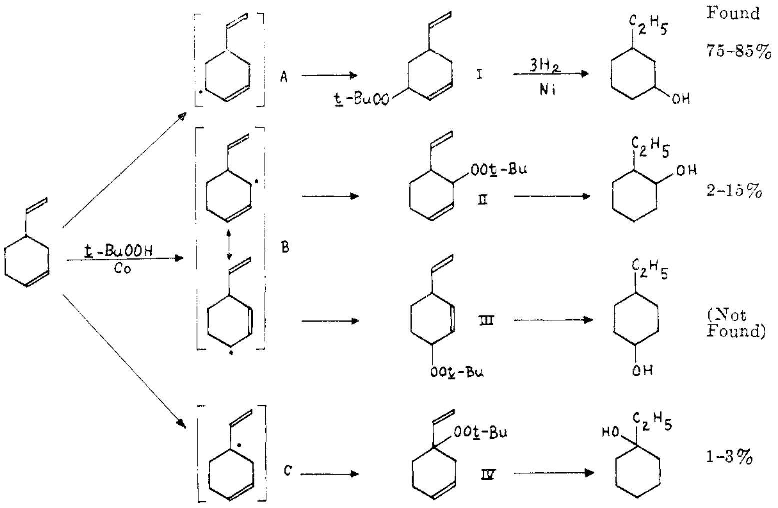

Fig. 1. Products by a hydrogen-abstraction mechanism in the *t*-butyl peroxidation of 4-vinylcyclohexene and subsequent hydrogenation

vinyl and internal unsaturation together with possible sites for hydrogen abstract from *alpha* methylene groups. The free radicals were generated by decomposition of *t*-butyl hydroperoxide and *t*-butyl peroxide as described later.

DISCUSSION

The *t*-butyl peroxidation was carried out in an excess of 4-vinylcyclohexene so as to favor monosubstitution. After the resulting peroxides were fully hydrogenated to the corresponding ethylcyclohexanols, infrared examination and preparation of derivatives showed that peroxidation had occurred predominantly in the 6-position of 4-vinylcyclohexene and that a minor proportion was per oxidated in the 3-position as illustrated in Fig. 1. These are the two positions *alpha* to the internal double bond. No 1-ethylcyclohexanol was isolated, but infrared spectra indicated that a trace quantity was present. Therefore, it may also be concluded that peroxidation occurred rarely in the 4-position of 4-vinylcyclohexene, although this is a tertiary carbon and alpha to the vinyl double bond. There was no evidence of peroxidation in the 1-position of 4-vinylcyclohexene, which might have been expected to occur *via* resonance stabilization of the radical, B, as shown in Fig. 1.

The occurrence of the peroxides I and II in the products shows that the first step of the peroxidation was hydrogen abstraction rather than addition to a double bond. The isomer ratios indicate considerable selectivity in the over-all substitution and probably in the hydrogen abstraction.

A likely agent for hydrogen abstraction in peroxidation is the alkoxy radical. Using *t*-butyl hydroperoxide with cyclohexene and octene-1, Kharasch and co-workers obtained at least as much *t*-butyl alcohol on a molar basis as peroxide,[3] and the same is true in *t*-butyl peroxidation of 4-vinylcyclohexene. While the formation of an equivalent amount of *t*-butyl alcohol does not prove that the abstraction was performed by *t*-butoxy radical, it certainly supports that interpretation.

Farmer and Moore[6] showed that cyclohexene yielded cyclohexene dehydrodimer when heated with di-*t*-butyl peroxide at 140°, showing that the *t*-butoxy radical does indeed abstract hydrogen from cyclohexene. We find that when a solution of di-*t*-butyl peroxide and 4-vinylcyclohexene at about 40° under nitrogen is irradiated, (2537 Å), at least 80% of the very small conversion of olefin results in the formation of vinylcyclohexene dehydrodimer, confirming the ability of *t*-butoxy to abstract hydrogen from this olefin, and demonstrating its reluctance to add to either of the double bonds under these conditions.

The *t*-butyl peroxidation of 4-vinylcyclohexene may be summarized as in Equation 2.

$$2\ t\text{-}C_4H_9OOH + C_8H_{12} \xrightarrow[\text{cobalt ions}]{45°-55°} t\text{-}C_4H_9OOC_8H_{11} + t\text{-}C_4H_9OH + H_2O \quad (2)$$

If this reaction were to have proceeded by the addition of *t*-butyl peroxy radical to 4-vinylcyclohexene, a major product would have been an unsaturated peroxide lacking a vinyl group, as the addition would have occurred preferentially at the vinyl double bond.[7] One evidence for hydrogen abstraction is therefore the fact that the product was mainly a mixture of doubly unsaturated peroxides which reduced to ethylcyclohexanols rather than to cyclohexylethanol. A second evidence is the presence of 2-ethylcyclohexanol among the reduction products (Fig. 1) which could not have arisen from an addition to 4-vinylcyclohexene. Finally, addition to the internal double bond followed by loss of hydrogen, should have afforded approxi-

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[6] E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1951).

[7] M. S. Kharasch and M. Sage, *J. Org. Chem.*, 14, 537 (1949).

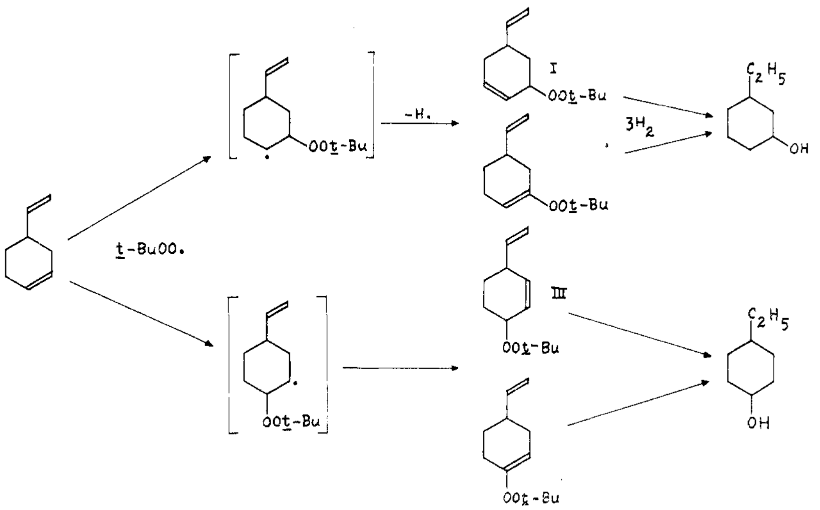

Fig. 2. Supposed products of *t*-butyl peroxy radical added to the internal double bond of 4-vinylcyclohexene

mately equal amounts (after hydrogenation) of 3-ethylcyclohexanol and 4-ethylcyclohexanol, as shown in Fig. 2. Actually, the amounts of these alcohols were not equal. The 3-ethylcyclohexanols accounted for most of the product and no infrared peaks characteristic of 4-ethylcyclohexanol were observed. By the abstraction route also (Fig. 1) both alcohols could be formed but they would not be expected to be in equal amount. For these reasons, the peroxidation of 4-vinylcyclohexene is concluded to proceed *via* abstraction of hydrogen to produce vinylcyclohexenyl radicals. Induced decomposition of the hydroperoxide by reaction with free radicals would merely produce more $RO_2\cdot$ which could in turn abstract hydrogen to reform the hydroperoxide and a free radical. Consequently, the observed vinylcyclohexenyl peroxide may be considered to result from a coupling of the appropriate free radicals:

$$2\,ROOH \xrightarrow[\text{cobalt ions}]{} RO\cdot + RO_2\cdot + H_2O \qquad (3)$$

$$RO\cdot + R'H \longrightarrow ROH + R'\cdot \qquad (4)$$

$$RO_2\cdot + R'\cdot \longrightarrow RO_2R' \qquad (5)$$

Kharasch and Fono[4,5] have recently postulated in detail further reaction steps to account for substitutive peroxidations by the action of alkoxy and peralkoxy radicals produced by hydroperoxide decomposition induced by ions of metals such as cobalt. The substituted product R′OOR is attributed in the later papers to reaction of the metallic ion with a hydrogen-bonded complex:

$$R'\cdot + ROOH \longrightarrow R'\cdot H{:}OOR \qquad (6)$$

$$Me^{++} + R'\cdot H{:}OOR \longrightarrow R'OOR + Me^{+} + H^{+} \qquad (7)$$

An alternative interpretation is available which accounts for the formation of peroxides, ethers, and dehydrodimers under varying conditions. In substitutive peroxidations (where both RO· and $RO_2\cdot$ are present) the peroxide R′OOR could be formed by initial abstraction of hydrogen by RO· and coupling of ROO· with R′· as in reactions 4 and 5. In alkoxylations with ROOR, (where $RO_2\cdot$ is absent) ROR′ could be formed similarly by coupling of RO· with R′· to produce ROR′, when the concentration of RO· is sufficiently large. Where RO· is in very small concentration, as in the slow photolysis of di-*t*-butyl peroxide in 4-vinylcyclohexene, the coupling of R′· is favored, to give R'_2, in this case the dehydrodimer of vinylcyclohexene. The much more rapid, copper-induced decomposition of the same mixture at 120° gave a mixture of ROR′, R'_2, and tars:

$$ROOR + R'H \xrightarrow[\text{CuCl}_2]{} R'_2 + ROR' + ROH, \text{ etc.} \qquad (8)$$

The method used to accomplish the alkoxylation of 4-vinylcyclohexene was adapted from a preliminary communication of Kharasch and Fono[5] on radical reactions modified by the presence of copper salts. In a more complete recent report,[8] these authors suggest that unstable copper organic complexes are intermediates. However, they stress that decompositions of peroxides and related compounds are appreciably faster when copper induced, a circumstance which leads us to suppose that concentration effects resulting from different rates of radical generation may also play a part in the modifications which are observed.

In view of the recent report of Brill[9] that 4-vinylcyclohexene is oxidized primarily (though probably not exclusively) to 4-hydroperoxy-4-vinylcyclohexene, the selective avoidance of this position in peroxidation, and the preferred orientation toward the 6-position, is particularly striking. It suggests the operation of a strong steric factor. The availability of only one tertiary hydrogen at the 4-position as compared to two abstractable hydrogens at each of the methylenes in the 3- and

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[8] M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 606 (1959).

[9] W. F. Brill, *J. Org. Chem.*, **24**, 257 (1959).

6-positions would favor reaction at these positions as observed in our work.

The effect of polar factors should also be considered as alkoxy radicals and peralkoxy radicals should be strongly electron-seeking, and this characteristic could affect their selectivity.[10] The greater electronegativity of $RO_2\cdot$ would tend to make it less selective than $RO\cdot$. The variations in electron density at the carbon-hydrogen bonds of 4-vinylcyclohexene is probably small, however, and the fact that initiation by molecular oxygen and propagation by $RO_2\cdot$ gives a different selectivity from that of $RO\cdot$ again lends more weight to a steric argument.

It nevertheless seems to us that in understanding reactions of alkoxy and peralkoxy radicals, their electrophilic nature should be considered. The observations of McBay and colleagues[11] regarding the competitive coupling of radicals are pertinent: whether it be because of field repulsion of like substituents or the electron availability at radical sites (or both), coupling will tend to occur between the unlike radicals. If we may assume that with respect to electrophilic character, $RO_2{}^{2}\cdot > RO\cdot >> R'\cdot$, then it is to be expected that in the presence of comparable concentrations of all three radicals, in systems where other reactions are minimized, the major product will be RO_2R' and not ROR' or $R'R'$. Similarly, ROR' will form when $RO_2\cdot$ is absent, and $R'R'$ when both $RO_2\cdot$ and $RO\cdot$ are in short supply.

SUMMARY

Hydrogen abstraction (rather then radical addition) appears to be the initial step leading to the formation of peroxides and other substitution products in the reactions reported here. The marked selectivity in 4-vinylcyclohexene peroxidation may be attributed to steric effects. 4-Vinylcyclohexene was alkoxylated with di-*t*-butyl peroxide in the presence of a cupric salt, but slow photolysis (in the absence of cupric ion) produced only the dehydrodimer. The difference may be attributed to the more rapid generation of radicals occurring in the metal-catalyzed decomposition of the peroxide. In both alkoxylations and peroxidations it is proposed that variations in the relative concentrations of the free radicals, together with some contribution from polar and steric factors, provide an adequate explanation of the observed behavior.

EXPERIMENTAL

Reagents. The 4-vinylcyclohexene was supplied by Phillips Petroleum Company, pure grade, 99 mole percent minimum purity. It was distilled at reduced pressure in a 20-plate Oldershaw column under nitrogen, within 48 hr. of use: n_D^{20}, 1.4635. The *t*-butyl hydroperoxide was of 99% purity,[12] obtained from Lucidol reagent by fractionation at reduced pressure in the Oldershaw column. The di-*t*-butyl peroxide was Lucidol reagent, redistilled, n_D^{20}, 1.3877. Cobalt naphthenate was used in the form of Nuodex cobalt catalyst 6% cobalt.

Reaction of t-butyl hydroperoxide with 4-vinylcyclohexene. The reaction was carried out according to the method of Kharasch and co-workers[3,4] in either of two ways:

A. The cobalt catalyst was added at intervals to the magnetically stirred mixture, for example, 0.8 mole of *t*-butyl hydroperoxide in 2.9 moles 4-vinylcyclohexene under nitrogen. Total catalyst concentration was varied from 0.2 mole percent based on initial hydroperoxide, to 2 mole percent. The larger amount of catalyst led to a higher proportion of tarry material, accounting at the maximum for as much olefin as was monoperoxidated. With 0.2 mole percent of catalyst, the amount of higher-boiling materials accounted for less than 60% as much olefin as was monoperoxidated. The yield of *t*-butyl vinylcyclohexenyl peroxides was 51–52% in either case, based on initial *t*-butyl hydroperoxide.

B. The cobalt catalyst (0.1 mole percent) was added all at once, by capsizing through magnetic stirring a floating glass boat containing the catalyst, under a nitrogen atmosphere. The continuously stirred reaction mixture, for example, 0.59 mole of *t*-butyl hydroperoxide in 3.8 moles 4-vinylcyclohexene was then allowed to warm and was maintained at 50–55° for 3 hr. by external heating. In this case the yield of *t*-butyl vinylcyclohexenyl peroxides was 0.164 mole, 56% of the theoretical yield based on the initial *t*-butyl hydroperoxide. Higher-boiling and tarry material amounted to 7.9 g., accounting for less than 40% as much olefin as was peroxidated.

In either method, low-boiling materials were removed by distillation at reduced pressure. The *t*-butyl vinylcyclohexenyl peroxide mixture was separated and purified by vacuum distillation; or alternatively, the entire peroxide mixture after removal of low-boiling materials was hydrogenated over Raney nickel.

Identification of t-butyl vinylcyclohexenyl peroxides. Infrared spectra showed absorption indicating the retention of vinylcyclohexenyl unsaturation—*i.e.*, vinyl and *cis*-internal double bonds respectively: 3.25, 3.30, 5.5, 6.08, 10.06, 11.0, 15.2; 3.30, 6.1, 13.6 μ. The presence of the *t*-butyl group was indicated primarily by the absorptions at 7.21, 7.33 μ; carbon-oxygen bond by strong absorption at 8.36 μ. A band at 11.4 μ was attributed to O—O stretching. Physical properties were consistent with a mixture of monovinylcyclohexenyl compounds: b.p. 26–33° at 0.02 mm; n_D^{20}, 1.461–1.463; pungent odor.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27; mol. wt., 196. Found[13]; C, 73.4; H, 10.2; mol. wt., 152 (Rast).

Decomposition is presumed to have lowered the molecular weight. Peroxide fractions became contaminated, on standing, with conjugated ketone (5.93 μ) and hydroxyl (2.9 μ) presumed to be *t*-butyl alcohol.

Over reduced platinum oxide (Adam's catalyst) in ethanol[14] at room temperature and atmospheric pressure of hydrogen, 3.62 g. of *t*-butyl vinylcyclohexenyl peroxides absorbed 959 ml. of hydrogen (S.T.P.) or 2.3 moles per mole of peroxide. From the reaction mixture both *t*-butyl ethylcyclohexyl peroxide (2 g.) and a mixture of ethylcyclohexanols (0.6 g.) were isolated, confirming partial hydrogenation of the peroxide bond. The *t*-butyl ethylcyclohexyl peroxide (boiling 49–50° at 0.7 mm; n_D^{20}, 1.4405) was identified by its infrared spectrum, analysis, and further reduction.

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(10) E. C. Kooyman, R. Van Helden, and A. F. Bickel, *Kon. Ned. Akad, Weten*, **46**, 75 (1959).

(11) H. C. McBay, O. Tucker, and P. T. Groves, *J. Org. Chem.*, **24**, 536 (1959).

(12) Iodometric analysis: V. R. Kokatnur and M. Jelling, *J. Am. Chem. Soc.*, **63**, 1432 (1941).

(13) Elemental analyses and molecular weight determinations by Drs. Weiler and Strauss, Oxford, England.

(14) R. P. Linstead, J. A. Elvidge, and M. Whalley, *A Course in Modern Techniques of Organic Chemistry*, Butterworth's, London, 1955, p. 84.

Absorptions due to unsaturation are absent in its spectrum; the *t*-butyl, C—O and O—O bonds remain.

Anal. Calcd. for $C_{12}H_{24}O$: C, 71.95; H, 12.08; mol. wt. 200. Found[14]: C, 72.12; H, 12.09; mol. wt., 236.

Reduced by a sodium dispersion in xylene,[15] 1.25 g. of *t*-butyl ethylcyclohexyl peroxide yielded 0.25 g. of *t*-butyl alcohol and 0.6 g. of mixed ethylcyclohexanols.

Over Raney nickel[16] in ethanol at room temperature and 4 atm. of hydrogen in the Parr hydrogenation apparatus, 22.7 g. of *t*-butyl vinylcyclohexenyl peroxide produced a pressure drop of 28 p.s.i. Under these conditions the theoretical pressure drop was 27 p.s.i. for 3 moles of hydrogen per mole peroxide.

Identification of ethylcyclohexanols. The individual ethylcyclohexanols in fractionally distilled hydrogenation mixtures were identified through preparation of alcohol derivatives by standard procedures, and by infrared analysis. A similar infrared analysis of a mixture of ethylcyclohexanols has been reported.[17] Authentic 1-ethylcyclohexanol in crystalline form was supplied by Dr. K. W. Scott of Goodyear Tire and Rubber Co.; authentic 2-ethylcyclohexanols and 3-ethylcyclohexanols, respectively, were prepared by hydrogenation of 2-ethylphenol and 3-ethylphenol in ethanol over Raney nickel[16] at 150° in hydrogen at 1400 p.s.i., under the direction of Dr. A. P. Arnold at Cleveland Industrial Research, Inc. 4-Ethylcyclohexanols were prepared similarly from 4-ethylphenol by Dr. T. P. Yen and S. T. Quigley at Goodyear Tire and Rubber Company. The hydrogenation mixtures were fractionated by distillation at reduced pressures but the pure isomers were not generally separable in this manner. All seven of the isomeric ethylcyclohexanols were thus available pure or in *cis-trans* mixtures to enable comparisons with authentic derivatives and spectra. The purity of each ethylphenol isomer, redistilled Eastman Organic Chemicals 4514, P4520, and P4503, was assured by infrared examination.

Ethylcyclohexanol mixtures from hydrogenation of the peroxides were also oxidized to the corresponding ketones, using chromic acid.[18] Derivatives were prepared and isolated: *cis*-3-ethylcyclohexyl phenylurethan, m.p., 100°.

Anal. Calcd. for $C_{15}H_{21}NO$: C, 72.8; H, 8.56; N, 5.67; Found[13]: C, 73.3; H, 8.45; N, 5.80;

cis, or *trans-2*-Ethylcyclohexyl naphthylurethan, m.p., 153.5° (range, two degrees).

Anal. Calcd. for $C_{19}H_{23}NO$: C, 76.7; H, 7.80; N, 4.71. Found: C, 77.2; H, 8.04; N, 4.62.

2,4-Dinitrophenylhydrazone, m.p., 126° .

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: C, 54.9; H, 5.92; N, 18.29. Found: C, 55.0; H, 6.05; N, 18.15.

3-Ethylcyclohexanone semicarbazone, m.p., 161.5°.

Anal. Calcd. for $C_9H_{17}ON_3$: C, 58.9; H, 9.35. Found: C, 58.5; H, 9.28.

In each case the derivative when mixed with the corresponding authentic derivative failed to depress the melting point. (Melting points are not corrected.)

Using Perkin-Elmer spectrophotometers, Model 21 and/or Model 137, infrared spectra were made of all peroxide hydrogenation products, which were in all cases mixtures of ethyl cyclohexanols imperfectly separated by distillation and occassionally contaminated with ethylcyclohexanones and *t*-butyl ethylcyclohexyl peroxides. Semiquantitative estimates were made of the proportions of each isomer in each fraction by selecting the peaks having a minimum of interference from other isomers and assuming Beer's law to hold. As indicated in Fig. 1, considerable latitude is allowed for the error in this procedure. In the case of 2-ethylcyclohexanol *cis-trans* mixtures,[19] absorption at 11.37, 11.82, and 12.2 μ served to indicate the presence of 2-isomers, but each of these peaks occurs close to absorptions for 3-isomers, which are the major components in these solutions, so that our accuracy is probably poorest for 2-ethylcyclohexanols. Based on the 11.82 band, the proportion was estimated to be 5%. 1-Ethylcyclohexanol may be recognized by absorptions at 8.57, 8.90, 10.56, and 11.09 μ; based on the absorption at 8.57 μ, the concentration was calculated to be 2%. *trans*-3-Ethylcyclohexanol, the low-boiling isomer,[18,20] has characteristic absorptions, e.g., at 9.65, 9.86, 10.33, 11.66, 12.27 μ; *cis*-3-ethylcyclohexanol: 9.00, 9.53, 10.45, 11.92 μ. In *cis-trans* 3-ethylcyclohexanol mixtures the absorbance-concentration plots were linear at 11.92, 12.27 μ. using these, the proportion of *cis*-3-ethylcyclohexanol in all fractions of one peroxidation run was estimated to be 31%; *trans*-3-ethylcyclohexanol, 46%.

4-Ethylcyclohexanols have strong or moderate absorptions at 8.74, 10.10, 10.50, 11.15 μ, probably *cis;* and 9.17, 9.50, 10.36, 11.15 μ, probably *trans.* The peaks least likely to show interference from other components of these mixtures are those at 10.10, 10.50, 11,15 μ. In undiluted, hydrogenated product mixtures in 0.02 to 0.045-mm. infrared cells, none of these absorptions was detected unequivocally in any fraction. Carbonyl absorption at 5.84 μ persisted in the spectra of the hydrogenated products, lower-boiling fractions. Very small absorptions in these fractions near 7.45, 7.62, 10.35, and 11.55 μ were attributed to 3-ethylcyclohexanone.

Ethylcyclohexyl peroxides contribute few distinctive absorptions but the presence of peroxides is indicated in some runs by a broad band at 11.4 μ.

Mixtures of ethylcyclohexanols were not found to be separable on the gas chromatograph, using a two-foot column, silicone grease on celite, F and M Scientific Corp., Model 124. The carrier was helium gas at 50 ml. per minute. Column temperatures 115° and 140° were used.

Photolysis of di-t-butyl peroxide in 4-vinylcyclohexene. A magnetically stirred mixture of 300 g. of di-*t*-butyl peroxide and 180 g. of 4-vinylcyclohexene was irradiated 24 hr. with a quartz-jacketed 8 watt germicidal lamp (General Electric G8T5, 2537 Å) partially immersed in the solution, the entire system under a nitrogen atmosphere. Under these conditions the temperature of the mixture was maintained by the lamp at 39–40° without external heating or cooling. By distillation of the reaction mixture, under reduced pressure, *t*-butyl alcohol (about 3 g.), and unchanged di-*t*-butyl peroxide and 4-vinylcyclohexene were removed. The residue, 3.8 g., representing 2.1% conversion of the 4-vinylcyclohexene, was a slightly tarry liquid. Of this vinylcyclohexene-derived material, 3.0 g. (80%)[21] was separated by distillation (on redistillation, boiling at 59° at 0.12 mm.; n^{20}_{D}, 1.5190) and identified as vinylcyclohexene dehydrodimer. The infrared spectrum showed the presence of practically all of the absorptions characteristic of 4-vinylcyclohexene, the only marked exception being the moderately strong 4-vinylcyclohexene peak at 8.77 μ, (unassigned), absent in the dehydrodimer. A sample, 0.4695 g., absorbed 191 ml. hydrogen (S.T.P.; 4.0 moles hydrogen per mole) over Adam's catalyst at one atmosphere.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found[13]: C, 89.72; H, 10.38.

t-Butoxylation of 4-vinylcyclohexene with di-t-butyl peroxide.

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(18) J. J. Lamneck and P. H. Wise, *J. Am. Chem. Soc.*, **76**, 5108 (1954).

(19) J. Entel, C. H. Rouf, and H. C. Howard, *J. Am. Chem. Soc.*, **73**, 4152 (1951).

(20) Assignment based on work with analogous compounds: E. L. Eliel, R. G. Haber, *J. Org. Chem.*, **23**, 2041 (1958). W. Huckel, M. Meier, E. Jordan, and W. Seeger, *Ann.*, **616**, 46 (1958).

(21) The remaining 20% was a higher-boiling tarry mixture.

A magnetically stirred mixture of 165 g. of 4-vinylcyclohexene, 36 g. of di-*t*-butyl peroxide and 0.3 g. of cupric chloride hydrate was gently refluxed 5 hr. under nitrogen, the pot temperature varying from 115–125°. The reaction vessel was fitted with a six-inch glass-helix-packed column and distilling head with controlled take-off. Effluent vapors were trapped and oxygen excluded by a liquid-nitrogen cooled trap and a mercury check-valve which also served to maintain the system pressure slightly above atmospheric pressure. During the course of the reaction, 27 g. of *t*-butyl alcohol and 7 g. of di-*t*-butyl peroxide were collected as distillate. After filtration of the mixture and fractionation of the filtrate, a further 0.5 g. of *t*-butyl alcohol was recovered and 2 g. of di-*t*-butyl peroxide; 110 g. of 4-vinylcyclohexene was recovered. Identification of products was not complete but 4 g. of *t*-butyl vinylcyclohexenyl ether (boiling 30° at 0.2 mm.; n_D^{20}, 1.462) and 4 g. of vinylcyclohexene dehydrodimer were isolated. The infrared spectrum of the *t*-butyl vinylcyclohexenyl ether contains the major olefinic absorptions of 4-vinylcyclohexene; the absorptions at 7.21 and 7.34 μ, assigned to *t*-butyl; a strong band at 8.40 μ, C—O stretching; and a very strong, broad band at 9.4 μ, typical of ethers. A 0.36-g. sample absorbed 85 ml. hydrogen (S.T.P.; 2.0 moles hydrogen per mole) over Adam's catalyst in ethanol at one atmosphere at room temperature.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.9; H, 11.2; mol. wt., 180. Found[13]: C, 78.4; H, 11.2; mol. wt., 192. Subsequent gas chromatographic analysis showed the presence of two as yet unrecognized impurities, totalling possibly 7% of the sample.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Structure of 2,6-Dibenzalcyclohexanone Dimer

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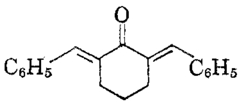
A solution of 2,6-dibenzalcyclohexanone in boiling toluene is converted to an equilibrium mixture of the starting ketone and its dimer. Subsequent transformations have established the structure 9 for this dimer.

Solutions of 2,6-dibenzalcyclohexanone (1) in boiling acetic anhydride, acetic acid, benzene and ethanol have been reported[1] to yield a colorless dimer, m.p. 187–188°. The dimer was reported[1] to exhibit an ultraviolet maximum at 292 mμ (ϵ 42,500) with infrared bands at 1695, 1608, 754, and 697 cm.$^{-1}$ and to form a dioxime, m.p. 197–198°, and a tetrahydro derivative, m.p. 217–218°. From these observations, as well as the failure to isolate benzoic acid from a permanganate oxidation, the structure II was tentatively suggested for this dimer.

As it was not apparent why the reaction conditions described should convert the unsaturated ketone 1 to structure 2 or to any other dimer containing two carbonyl groups,[2] the formation and constitution of the dimer have been reinvestigated. Our attempts to prepare the dimer by refluxing an ethanol solution of 1 for 120 hours, a process reported to form the dimer in 90% yield, were uniformly unrewarding. In one instance in which an ethanol solution of 17.7 g. of the dimer had been refluxed for 121 hours, chromatography of the mother liquors remaining after separation of the starting material afforded 10 mg. of the crude dimer, m.p. 184–187°. However, the use of the higher-boiling solvents acetic anhydride, bromobenzene and toluene permitted formation of the dimer in reasonable yield. Use of boiling toluene with a reaction period of two days was found most convenient and permitted the isolation of the dimer, m.p. 192–193° dec., in 21% yield. The dimerization proceeded equally well when the reaction mixture was protected from light indicating that the dimerization was not a photochemical transformation. After a solution of the dimer in bromobenzene had been refluxed for twenty hours, the pure, monomeric unsaturated ketone 1 was isolated in 60% yield. Solutions of the ketone 1 and the dimer in boiling toluene were heated until equilibrium was established. In these toluene solutions, containing the equivalent of 0.30*M* 2,6-dibenzalcyclohexanone (1), equilibrium was established when 50–55% of the dimer was present.



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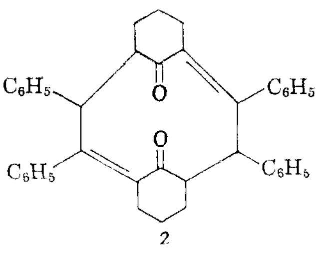

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(1) (a) P. Y. Yeh, *J. Taiwan Pharm. Assoc.*, 5, 2 (1953); (b) P. Y. Yeh, C. T. Chen, S. Y. Ro, and C. H. Wang, *J. Am. Chem. Soc.*, 77, 3415 (1955).

(2) Although the formation of photodimers containing cyclobutane rings is well known [A. Mustafa, *Chem. Revs.*, 51, 1 (1952)], there was no indication (ref. 1) that light was required to transform the ketone 1 to its dimer.