

The ultraviolet spectrum of I is complex:  $\lambda_{\text{max}}^{\text{EtOH}}$  230 m $\mu$  (log  $\epsilon$  4.82), 273 (3.32), 304 (3.66), 314 (3.95), 319.5 (3.72), 329 (4.15). The infrared spectrum exhibits bands at 3.29(m); 3.36, 5.73(w); 5.92 and 5.95(doublet, s); 6.07; 6.86, 7.55, 8.66(s); 9.54(m); 10.08, 10.67, 11.42(s); 12.43(m); 13.10, and 14.38(s)  $\mu$ .

**Hydrogenation of 1,2-Dimethylenebenzocyclobutene.**—A sample of the diolefin I was prepared from 0.721 g. (2.87 mmoles) of diacetate XXII as described above, except that the purification by v.p.c. was omitted. Instead, the total material obtained in the distillation step was subjected directly to hydrogenation at atmospheric pressure in the presence of palladium-on-charcoal catalyst (0.05 g.) suspended in methanol (5 ml.). The hydrocarbon absorbed 40.0 ml. (S.T.P.) of hydrogen during 11 min. The reaction mixture was filtered through Celite to remove the catalyst and was poured into water (20 ml.). Extraction of the resulting suspension with 1 ml. of petroleum ether (b.p. 35–40°) followed by gas chromatography of the extract [15% Apiezon M on Sterchamol (0.2–0.4 mm. mesh), 0.25 inch  $\times$  6

ft., nitrogen at 160°] gave crude *cis*-1,2-dimethylbenzocyclobutene (XXVII, 0.060 g.). The analytical sample was obtained by a second pass of the crude material through the same gas chromatography column.

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>: C, 90.85; H, 9.15. Found: C, 90.86; H, 8.91.

**Conversion of 1,2-Dimethylenebenzocyclobutene (I) into Naphthalene.**—1,2-Dimethylenebenzocyclobutene (0.071 g., 0.55 mmole) was passed over a hot nichrome wire coil (ca. 700°) in a vacuum apparatus. The product (trapped on a cold-finger at –78°) was dissolved in 1 ml. of cyclohexane and the resulting solution was subjected to vapor phase chromatography (3 ft.  $\times$  0.25-inch column, 15% silicone grease on firebrick, nitrogen at 150°) to give naphthalene (0.013 g.), identical in melting point and infrared spectrum with authentic material.

**Acknowledgment.**—The authors gratefully acknowledge a grant by the National Science Foundation in support of this work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

## The Copper-Catalyzed Reaction of Peresters with Hydrocarbons<sup>1</sup>

By CHEVES WALLING AND ANDREAS A. ZAVITSAS

RECEIVED FEBRUARY 14, 1963

Experiments are described intended to test a mechanism for copper-catalyzed perester decompositions similar to that proposed by Kochi. Major steps are reduction of perester by Cu<sup>I</sup> to yield *t*-butoxy radicals, attack of *t*-butoxy radicals on hydrocarbon substrates, and oxidation of the resulting hydrocarbon radicals by Cu<sup>II</sup> to carbonium ions. Relative reactivities of seven hydrocarbons are shown to be the same in *t*-butyl peracetate and perbenzoate reactions as in *t*-butyl hypochlorite chlorination. The distributions of allylic acetates obtained from reaction of *t*-butyl peracetate and a number of alkenes are in good agreement with Kochi's findings, and it is suggested that the result is more consistent with an electron transfer process to give a relatively "free" carbonium ion than with ligand transfer. Products from perester reactions with allylbenzene and  $\beta$ -methylstyrene are shown to have undergone allylic rearrangements, although isomer distributions are different from the two alkenes. Examples of what appear to be carbonium ion rearrangements are found in the reaction of *t*-butyl peracetate with 6,6-dimethyl-1,3-cyclohexadiene to give *o*-xylene, and in the decomposition of 2,4,4-trimethyl-2-pentyl hydroperoxide to give isopentenes. The importance of side reactions in the perester decomposition which fail to regenerate Cu<sup>I</sup> is pointed out, and some limiting kinetic expressions are shown to be consistent with the kinetic data available.

The effect of traces of heavy metal ions on the decomposition of organic peroxides has long been recognized and finds important application in autoxidation processes and oxidation-reduction-initiated polymerization. Numerous synthetic applications have also appeared recently, and an understanding of the mechanisms of such reactions has obvious bearing on aerobic biochemical processes involving metal-containing enzymes.<sup>2</sup> A very interesting group of such metal-catalyzed reactions were described by Kharasch and his students in a series of papers beginning in 1958.<sup>3</sup> These investigators found that traces of copper (usually as cuprous chloride or bromide), and to some extent other transition metals, profoundly altered the course of reaction between organic peroxides and a variety of organic substrates, typical being the reaction of *t*-butyl perbenzoate with cyclohexene.<sup>3d</sup> In the presence of copper, high yields of 3-benzoyloxy cyclohexene and *t*-butyl alcohol are produced, while in its absence the reaction is slower and yields a rather indiscriminate mixture of products including bicyclohexenyl and benzoic acid. The reaction has had considerable synthetic elaboration.<sup>4–10</sup> Allylic substitution occurs with

a variety of olefins, although addition is observed with conjugated dienes and olefins lacking allylic hydrogen. Hydrogens  $\alpha$  to N (*t*-amines), O (alcohols, aldehydes and ethers) and S (thioethers) are attacked, and recently Story<sup>7</sup> has reported an interesting synthesis of 7-*t*-butoxynorbornadiene from norbornadiene and *t*-butyl perbenzoate. With *t*-hydroperoxides in place of peresters, labile hydrogens are said to be replaced by *t*-alkyl peroxy groups. Early reports also claimed that reaction of peresters with 1-olefins, allylbenzene and  $\beta$ -methylstyrene yielded allylic esters without shift of double bonds,<sup>3,11</sup> and Story<sup>7</sup> noted that the point of substitution in norbornadiene was not that anticipated in a normal radical process.

In part to account for this sort of specificity, Kharasch and Fono in 1959<sup>3b</sup> proposed a mechanism proceeding through a series of copper-stabilized radical-peroxide complexes, and similar "complex" mechanisms have been advanced by Denney,<sup>11</sup> and, in connection with a recent kinetic study, by Barnard and Yang.<sup>12</sup>

An alternative scheme not involving complexes and

(1) Taken from the Ph.D. Dissertation of Andreas A. Zavitsas, Columbia University, 1962. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) For a general discussion of earlier literature, cf. C. Walling, "Free Radicals in Solution" John Wiley and Sons, Inc., New York, N. Y., 1957, Ch. 9 and 11.

(3) (a) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **23**, 324 (1958); (b) **24**, 72 (1959); (c) M. S. Kharasch and G. Sosnovsky, *J. Am. Chem. Soc.*, **80**, 756 (1958); (d) M. S. Kharasch, G. Sosnovsky and N. C. Yang, *ibid.*, **81**, 5819 (1959); (e) G. Sosnovsky and N. C. Yang, *J. Org. Chem.*, **25**, 899 (1960).

(4) (a) G. Sosnovsky, *ibid.*, **25**, 874 (1960); (b) **26**, 281 (1961); (c) *Tetrahedron*, **13**, 241 (1961); (d) **18**, 15 (1962); (e) G. Sosnovsky and H. J. O'Neill, *Compt. rend.*, **254**, 704 (1962).

(5) (a) S. O. Lawesson and C. Berglund, *Tetrahedron Letters*, **No. 2**, 4 (1960); (b) *Arkiv. Kemi*, **17**, 465, 475 (1961); (c) *Angew. Chem.*, **73**, 65 (1961); (d) *Acta Chem. Scand.*, **15**, 36 (1961); (e) S. O. Lawesson, C. Berglund and S. Grönwald, *ibid.*, **15**, 249 (1961); also subsequent papers.

(6) (a) J. K. Kochi, *J. Am. Chem. Soc.*, **83**, 3162 (1961); (b) **84**, 774 (1962); (c) **84**, 1572 (1962); (d) **84**, 3871 (1962); (e) *Tetrahedron*, **18**, 483 (1962). The last reference provides an excellent summary.

(7) P. R. Story, *J. Am. Chem. Soc.*, **82**, 2085 (1960); *J. Org. Chem.*, **26**, 287 (1961).

(8) J. R. Shelton and J. N. Henderson, *ibid.*, **26**, 2185 (1961).

(9) J. A. Bigot, *Rec. trav. chim.*, **80**, 825 (1961).

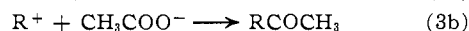
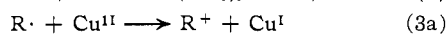
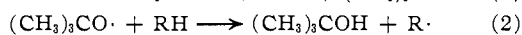
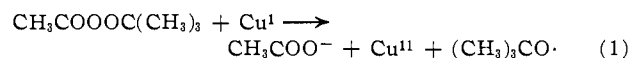
(10) B. Cross and G. H. Witham, *J. Chem. Soc.*, 1650 (1961).

(11) D. B. Denney, D. Z. Denney and G. Feig, *Tetrahedron Letters*, **No. 15**, 19 (1959).

(12) P. W. C. Barnard and N. C. Yang, *Chem. Ind. (London)*, 1573 (1961).

invoking only steps well established in other radical reactions can be written and apparently occurred quite independently to Kochi and his collaborators at the Shell Development Co. and to our group at Columbia shortly after the appearance of the preliminary communications. Impressive evidence for this scheme has recently been published by Kochi,<sup>6</sup> and this paper presents additional experimental data on the question.

Taking the reaction of *t*-butyl peracetate as an example, and RH as a compound with a reactive hydrogen, the principal reaction steps to be considered are

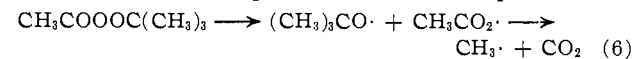


Considered in this manner, the reaction involves the formation of *t*-butoxy radicals by the oxidation-reduction reaction of the peroxide and cuprous ion (1), paralleling essentially the Haber-Weiss scheme for the reaction of ferrous ion with hydrogen peroxide,<sup>2</sup> the attack of free *t*-butoxy radicals on substrate (2), and the oxidation of the resulting radical R· either by electron transfer followed by neutralization of the carbonium ion by acetate (3) or by a one-step ligand transfer (4). In the equations the coordination state of the copper is not indicated (although it is obviously important, as discussed below). The over-all process is a chain reaction in copper which is recycled between the cuprous and cupric states.

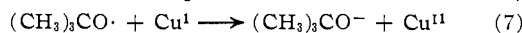
Obvious modifications of the scheme account for other products which may be observed. Hydroperoxides and diacyl peroxides can also give rise to alkoxy (or acyloxy) radicals by redox reactions.<sup>3,6</sup> With conjugated dienes or olefins without  $\alpha$ -hydrogens, double bond addition by alkoxy radicals may occur to produce alkoxy acetates.<sup>6</sup> Other nucleophiles may react with the carbonium ion produced in 3a or other ligands may undergo transfer.<sup>3,6,13,14</sup> Such competitions have been examined at some length by Kochi,<sup>6</sup> who has also shown that, with many saturated radicals R· possessing  $\beta$ -hydrogens, the chief consequence of reaction with copper is proton loss to give olefins, *i.e.*, the over-all equation



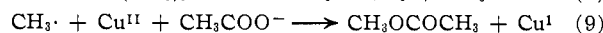
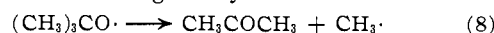
Finally, while reactions 1-5 would account for the major course of this class of reactions, a number of other known radical reactions would be expected to compete with the main sequence, influence its over-all rate, and account for various by-products observed. These include thermal decomposition of the initial peroxide



reduction of the intermediate alkoxy radical (a reaction analogous to another step in the Haber-Weiss scheme)



$\beta$ -scission of the alkoxy radical, probably followed by oxidation of the resulting methyl radical<sup>15</sup>



and coupling (or disproportionation) of alkyl radicals



(13) J. Kumamoto, H. E. De La Mare and F. F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960).

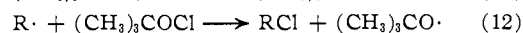
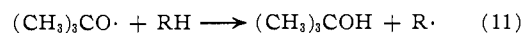
(14) F. Minisci and W. Pallini, *Gazz. chim. ital.*, **91**, 1030 (1961), and previous papers.

(15) Thus in an inert solvent (benzene) *t*-butyl perbenzoate is reported to give methyl benzoate in 34% yield.<sup>3d</sup>

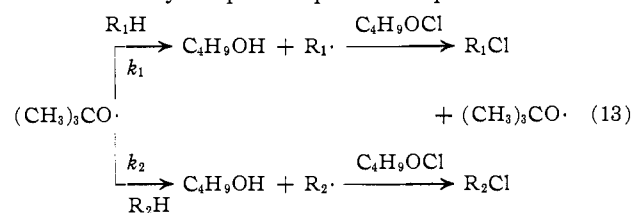
This reaction scheme as outlined permits a number of predictions which can be tested by experiment. These include: 1. If free *t*-butoxy radicals are involved in the reaction, relative reactivities of different substrates (or relative reactivities of different hydrogens in the same substrate) should be identical with those observed toward *t*-butoxy radicals produced in other reactions. 2. If an allylic radical is produced in 2, contrary to the early reports, it should normally give rise to isomeric products. Further, the same radical produced from allylic isomers should give the same mixture of products. 3. If a relatively "free" carbonium ion is produced in 3, typical carbonium ion rearrangements should be observed. 4. Over-all kinetics will depend not only on the rates of the main reaction (which in turn may vary with solvent and the state of coordination of copper), but also on the competition with side reactions 7-10. Peroxide disappearance should be faster than in the absence of copper, should be subject to oxygen inhibition and will probably increase with increasing reactivity of RH.

The work described in this paper has been directed toward testing each of these predictions.

**Competitive Experiments.**—Recent work in this Laboratory has shown that free-radical chlorinations employing *t*-butyl hypochlorite provide a very convenient technique for studying the properties of *t*-butoxy radicals.<sup>16,17</sup> The reaction proceeds very cleanly *via* the chain sequence



and relative reactivities of different substrates may be determined by simple competitive experiments



whence

$$k_1/k_2 = \log ([\text{R}_1\text{H}]_0/[\text{R}_1\text{H}]) / \log ([\text{R}_2\text{H}]_0/[\text{R}_2\text{H}]) \quad (14)$$

If in the copper-catalyzed peroxide reactions step 2 is correctly formulated, relative rates of disappearance of two hydrocarbons should be the same as in *t*-butyl hypochlorite chlorinations. Comparisons for two alkylbenzenes and four alkenes are shown in Table I. The alkenes all give excellent yields of allylic esters. Yields of benzylic esters were lower, and in agreement with Kharasch and Fono,<sup>3b</sup> we find that the copper-catalyzed peroxide reaction is unsuccessful with less reactive hydrocarbons, so that comparisons could not be extended to saturated alkanes. Possible reasons for this limitation and a more detailed discussion of products are given later in this paper.

From Table I it is evident that selectivities observed in the copper-catalyzed reactions of *t*-butyl peracetate and perbenzoate are identical within experimental error with those obtained in the *t*-butyl hypochlorite chlorination. The hypochlorite results also agree reasonably with those obtained previously at 40°, considering the expected drop in selectivity with increased temperature. Thus relative reactivities of ethylbenzene:cumene:*trans*-2-hexene are 1:1.02:1.43 compared with 1:1.44:2.84.<sup>18</sup> The low reactivity of *cis*-4-methyl-2-pentene observed in all cases is interesting, and we attribute it

(16) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

(17) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

(18) Calculated from Table VII of ref. 17.

TABLE I  
 COMPARISON OF HYDROCARBON REACTIVITIES AT 70°

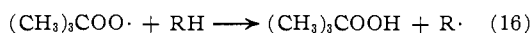
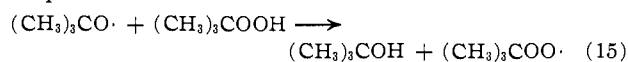
R <sub>1</sub> H	R <sub>2</sub> H	$k_1/k_2^a$			
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OCl	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OOAc	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OOBz	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OOH
Ethylbenzene	Cumene	0.98 ± 0.03	1.03 ± 0.03	1.03 ± 0.03	0.96 ± 0.03
Cumene	1-Octene	0.43 ± .03	0.42 ± .02	0.44 ± 0.03	0.61 ± .05
<i>trans</i> -2-Hexene	1-Octene	1.40 ± .02	1.36 ± .03	...	1.75 ± .05
<i>trans</i> -2-Heptene	1-Octene	1.42 ± .03	1.34 ± .03	1.38 ± 0.05	1.77 ± .04
<i>trans</i> -4-Methyl-2-pentene	1-Octene	1.76 ± .05	1.65 ± .05	1.74 ± .06	2.90 ± .20
<i>cis</i> -4-Methyl-2-pentene	1-Octene	0.79 ± .05	0.67 ± .04	0.69 ± .04	0.85 ± .05

<sup>a</sup> In the presence of Cu salts for peroxides. Uncertainties indicated are the spread of duplicate experiments analyzed in triplicate.

to the fact that for the transition state to assume a conformation favorable for overlap with the  $\pi$ -electron system requires extensive interference between methyl groups. Direct steric hindrance to attack on the tertiary allylic hydrogen seems unimportant, since models indicate little difference in hindrance in the *cis* and *trans* isomers.

Further evidence for the participation of the *t*-butoxy radical in the perester reactions comes from an examination of the products from 2-pentene. Here attack may occur on either primary or secondary allylic hydrogens. With *t*-butyl hypochlorite allylic chloride distribution is 67% 4-chloro-2-pentene, 22% 1-chloro-2-pentene and 11% 3-chloro-1-pentene, whence attack at carbons 1 and 3 is 33:67. In the *t*-butyl peracetate reaction we obtain a mixture of allylic acetates containing 68% 4-acetoxy-2-pentene, 29% 3-acetoxy-1-pentene and 3% 1-acetoxy-2-pentene corresponding to a ratio of 32:68.

Selectivities found with *t*-butyl hydroperoxide differ significantly from those observed in other cases, indicating that the over-all sequence of reactions is more complicated than reactions 1-4 and that a somewhat more selective species is involved. Although we have not investigated the matter in detail, except to note that the products in acetic acid are still predominantly acetates, a possible explanation is some incursion of the steps



The *t*-butyl peroxy radical should be a more selective species,<sup>19</sup> and Thomas<sup>20</sup> has recently reported that the exchange



occurs rapidly with a rate constant similar to that for 16 where RH = cumene. Since 17 is thermoneutral while 15 should be exothermic, the latter would be expected to be even more rapid. Alternatively, *t*-butyl peroxy radicals could also be produced by Cu<sup>II</sup> oxidation of hydroperoxides, a reaction having precedent in other oxidation-reduction systems.<sup>2</sup>

**Products of Peroxide Reactions.**—As noted in our preliminary discussion, oxidation of allylic radicals by Cu<sup>II</sup> should lead to mixtures of allylic isomers. While such a result is contrary to early reports,<sup>3,11</sup> Kochi finds that 1-butene and 1-pentene yield mixtures of 1-acyloxy-2-alkenes and 3-acyloxy-1-alkenes. Further, as sequence 1-4 predicts, 1-butene and *cis*- and *trans*-2-butene give the same mixture of products,<sup>6a,b,c</sup> and reaction of 1,3-butadiene leads to both 1,2- and 1,4-addition<sup>6c</sup> (the question of *cis-trans* isomer distribution has not been studied in these systems).

Our own results are summarized in Table II.

In agreement with Kochi's findings, a series of 1-olefins including 1-octene and 1-hexene give mixtures of allylic acetates containing approximately 85% 3-

(19) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

(20) J. R. Thomas and C. A. Tolman, *ibid.*, **84**, 2079 (1962).

TABLE II

PRODUCT DISTRIBUTIONS IN COPPER-CATALYZED REACTIONS OF *t*-BUTYL PERACETATE AT 70°

Substrate	Catalyst	Ester products <sup>a</sup>	
1-Pentene	CuCl	3-Acetoxy-1-pentene	89 ± 3
		1-Acetoxy-2-pentene	11 ± 3
1-Hexene	CuCl	3-Acetoxy-1-hexene	86 ± 3
		1-Acetoxy-2-hexene	14 ± 3
1-Octene	CuCl	3-Acetoxy-1-octene	86 ± 5
		1-Acetoxy-2-octene	14 ± 5
	Cu(OAc) <sub>2</sub>	3-Acetoxy-1-octene	89 ± 3
		1-Acetoxy-2-octene	11 ± 3
	Cu(OAc) <sub>2</sub> -pyridine	3-Acetoxy-1-octene	70
		1-Acetoxy-2-octene	30
2-Pentene	CuCl	4-Acetoxy-2-pentene	68 ± 3
		3-Acetoxy-1-pentene	29 ± 2
	CuCN-dipyridyl	1-Acetoxy-2-pentene	3 ± 1
		4-Acetoxy-2-pentene	67
		3-Acetoxy-1-pentene	27
		1-Acetoxy-2-pentene	6
Cyclohexene	Various	3-Acetoxy-cyclohexene	100
		4-Acetoxy-1,5-cyclooctadiene	71 ± 3
1,5-Cyclooctadiene	Cu 2-ethylhexoate	6-Acetoxy-1,4-cyclooctadiene	29 ± 3
Cumene	CuCl	$\alpha$ -Acetoxycumene	100 <sup>c</sup>
Allylbenzene	CuCl	3-Acetoxy-3-phenylpropene	71 ± 4 <sup>d</sup>
		3-Acetoxy-1-phenylpropene	29 ± 4
	Cu(OAc) <sub>2</sub>	3-Acetoxy-3-phenylpropene	67 ± 4 <sup>e</sup>
		3-Acetoxy-1-phenylpropene	33 ± 4
	CuCl <sup>b</sup>	3-Acetoxy-3-phenylpropene	53
		3-Acetoxy-1-phenylpropene	47
$\beta$ -Methylstyrene	CuCl or Cu(OAc) <sub>2</sub>	3-Acetoxy-3-phenylpropene	100 <sup>f</sup>
		3-Acetoxy-3-phenylpropene	52
	CuCl <sup>b</sup>	3-Acetoxy-1-phenylpropene	48

<sup>a</sup> Total ester yields 85% or greater unless indicated; numbers after individual products are per cent of total ester. <sup>b</sup> Reaction of *t*-butyl hydroperoxide in acetic acid. <sup>c</sup> Total ester 30%. <sup>d</sup> Total ester 45-50%. <sup>e</sup> Total ester 35-40%. <sup>f</sup> Total ester 40-45%.

acetoxy-1-alkene and 15% 1-acetoxy-2-alkene, rather than a single isomer, the 3-substituted 1-alkene.<sup>21</sup> Similarly, 2-pentene and 1-pentene give the same ratio of 3-acetoxy-1-pentene and 1-acetoxy-2-pentene within the precision of our measurements, and 1,5-cyclooctadiene yields two products, in one of which allylic shift of a double bond has occurred. Our results with allylbenzene and  $\beta$ -methylstyrene are less clear-cut. Allylbenzene gives approximately a 2:1 mixture of 3-acetoxy-3-phenylpropene and 3-acetoxy-1-phenylpropene, while  $\beta$ -methylstyrene gives consistently pure 3-acetoxy-3-phenylpropene, the less stable allylic isomer. On the other hand, reaction with *t*-butyl hydroperoxide in acetic acid yielded the same product mixture from both allylic isomers. Yields were low (<50%) in all cases and a number of other unidentified products were also produced including what appear to be dimeric or polymeric materials. Considerable attention was devoted to these systems which proved difficult to analyze reliably since some isomerization occurred during G.L.C. analysis.<sup>22</sup> Reproducible results were finally

(21) Presumably early reports,<sup>3d</sup> based upon physical constants and infrared spectra, failed to detect the small amount of non-terminal alkene, now easily separated by G.L.C. techniques.

(22) Similar difficulties have been encountered by D. B. Denney, who reports inability to confirm his early result<sup>11</sup> on the stereospecificity of these reactions (private communication). See also D. Z. Denney, A. Applebaum and D. B. Denney, *J. Am. Chem. Soc.*, **84**, 4969 (1962).

obtained by hydrogenating reaction mixtures, and then analyzing the resulting mixtures of saturated esters, but we have no good explanation to offer for the variations observed.

A large number of reactions with cyclohexene were carried out and this system was found to give high yields of 3-acetoxycyclohexene under a variety of conditions, including reaction with *t*-butyl or cumene hydroperoxide in acetic acid. Since these hydroperoxides are inexpensive and readily available, this probably constitutes the simplest synthesis of 3-acetoxycyclohexene available. Our result here and with allylbenzene and  $\beta$ -methylstyrene contrasts with the report by Kharasch and Fono<sup>8b</sup> that *t*-butyl hydroperoxide and cumene in acetic acid gives no acetate, but *t*-butyl cumyl peroxide. Whether this difference is the consequence of the change in substrate has not been investigated,<sup>23</sup> but we find that, in our hands, cumene reacts with *t*-butyl peracetate to give only a 30% yield of ester (2-phenyl-2-propyl acetate), plus  $\alpha$ -methylstyrene and dicumene.

A notable feature of all the 1-alkene reactions is that the mixture of allylic products formed consists chiefly of the 3-acetoxy-1-alkene. This result, which differs markedly from the isomer distribution observed in radical reactions,<sup>24</sup> points strongly to a product-determining step which is non-radical in nature as demanded by the Kochi reaction sequence. The situation has been discussed in some detail by Kochi, who concludes that the high yield of 3-acetoxy-1-alkene is evidence for a largely ligand transfer sequence (4) rather than purely electron transfer (3) to give an essentially "free" carbonium ion. Although he presents an ingenious rationalization for a high yield of 3-acyloxy-1-alkene in a ligand transfer reaction, and notes that significant changes in allylic isomer ratios occur in the presence of Cu<sup>II</sup> complexes with  $\alpha,\alpha$ -dipyridyl or 1,10-phenanthroline,<sup>6e,25</sup> we do not believe that available data adequately support his conclusion. The question of what isomer distribution is to be expected from reaction of an essentially free carbonium ion should be answered by results of experiments in which such species are produced in solvolyses, but here the problem may be complicated by competing SN2 and SN2' processes, the participation of a multiplicity of types of ion pairs, and the possibility of product equilibration.

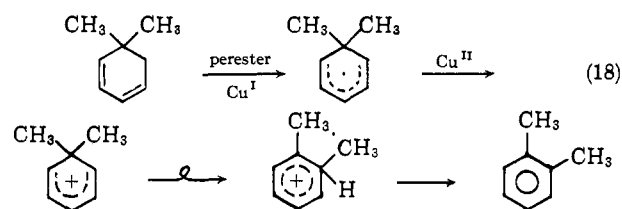
The situation has been reviewed by De Wolfe and Young<sup>26</sup> who have pointed out that a minimum criterion for a "free carbonium ion" process is "zero spread" (no difference) between product compositions obtained from allylic isomers. Such zero spread has been observed with a few primary-tertiary allylic systems in water where they give approximately 85:15 1:2 alkene products. In less polar solvents, and in all cases with primary-secondary allylic systems, the 1:2 alkene ratio in the products decreases, but the "spread" becomes appreciable. Thus Kochi finds that when the allylic chlorobutenes are treated with silver acetate in acetic acid, the 1:2 alkene ratios are 0.93 and 0.84. If one accepts the idea that such systems showing relatively small "spreads" are approaching free carbonium ion reactions, one concludes that the isomer distribution obtained from a really "free" carbonium ion must be quite solvent dependent, the amount of 3-substituted-1-alkene decreasing in less polar solvents. On the other

hand, electrophilic addition of halogen acids and halogens to butadiene might also serve as a model for processes involving intermediate allylic carbonium ions. Here the ratio of 1,2- to 1,4-addition is reported to be about 4:1, even in highly non-polar solvents.<sup>27</sup>

Kochi and we have both shown that allylic products from copper-catalyzed peroxide reactions show isomer distributions which seem to be almost solvent independent in media ranging from benzene to aqueous *t*-butyl alcohol, a result which he uses as an argument for a ligand transfer process. However, Kochi has also shown<sup>6d</sup> that in reaction of allylic radicals (from radical addition to butadiene) with cupric chloride (which he considers a pure ligand transfer) the major product is a 1,4-disubstituted-2-butene. Such results can be rationalized by assuming very different allylic isomer distributions from transfers of different ligands. Although the subject certainly needs further study, at present it seems rather simpler to us to assume that solvolyses in acetic acid are not good models of "free" carbonium ion reactions, and that cupric ion oxidations of allylic radicals giving predominantly 3-substituted-1-alkenes are primarily electron transfer reactions giving products approaching "free carbonium ions." As ligand transfer increases, products shift to those expected from radical displacements since a pure ligand transfer reaction is essentially a simple radical displacement analogous to radical displacement on carbon tetrachloride.

**Rearrangements in Copper-Catalyzed Reactions.**— Since preponderant evidence now indicates that radical rearrangements occurring *via* 1,2-shifts of hydrogen or alkyl groups do not compete successfully with other radical processes at ordinary temperatures, the occurrence of such rearrangements would provide excellent evidence for carbonium ion intermediates in radical oxidations.<sup>28</sup> Kochi has made a preliminary report of such a rearrangement of a neopentyl radical,<sup>6b</sup> and Story, by a deuterium-labeling experiment,<sup>29</sup> has demonstrated that his synthesis of 7-*t*-butoxynorbornadiene is also a rearrangement process.

We also find examples of such 1,2-shifts of alkyl groups. When *t*-butyl peracetate is treated with 6,6-dimethyl-1,3-cyclohexadiene (containing some of its unconjugated isomer, 3,3-dimethyl-1,4-cyclohexadiene) we obtain a 6% yield of *o*-xylene, although none is formed in the absence of copper or of perester.



Apparently *o*-xylene is the sole product of substitution on the diene and its formation strongly indicates a carbonium ion intermediate. The major products are 3-acetoxy-4-*t*-butoxy-6,6-dimethylcyclohexene (80%) and 3-acetoxy-4,4-dimethyl-6-*t*-butoxycyclohexene (8%), the consequences of *t*-butoxy radical addition. Here no rearrangement occurs, perhaps because it would involve loss of the resonance energy of the allylic carbonium ion, and, as in the case of butadiene, 1,2-addition is preferred. Rearrangement was also observed in the copper-catalyzed decomposition of 2,4,4-

(23) Kochi<sup>6d</sup> also reports that acetates rather than peroxides are obtained from the reaction of *t*-butyl hydroperoxide and butadiene in the presence of acetic acid.

(24) Thus, in allylic chlorination of 1-alkenes with *t*-butyl hypochlorite, products are chiefly (80-90%) 1-chloro-3-alkenes.<sup>11</sup> Similarly, radical additions to butadiene give chiefly 1,4-products.

(25) We also confirm this result with Cu dipyridyl complex and also with Cu(OAc)<sub>2</sub> in pyridine; cf. Table II.

(26) R. H. De Wolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

(27) C. J. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Ch. 12.

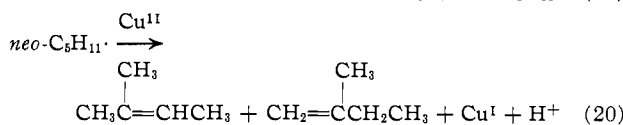
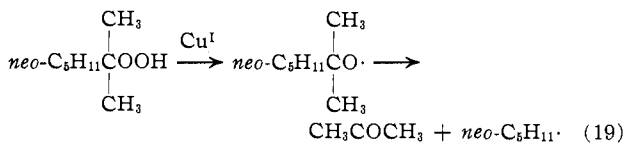
(28) C. Walling, "Free Radical Rearrangements" in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

(29) P. R. Story, *Tetrahedron Letters*, 414 (1962).

trimethyl-2-pentyl hydroperoxide. Thermal decomposition of this peroxide is reported to give a mixture of products including approximately 50% neopentyl alcohol, but no *t*-pentyl alcohol.<sup>30</sup>

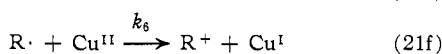
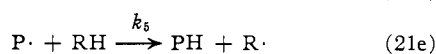
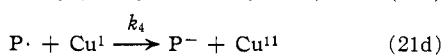
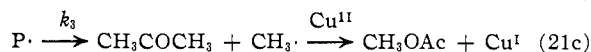
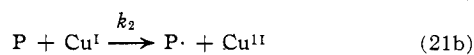
When the pure hydroperoxide was decomposed at 70° in the presence of Cu 2-ethylhexoate, a quantitative yield of acetone resulted, together with neopentane (30%), neopentyl alcohol (55%), 2-methyl-2-butene (10%) and 2-methyl-1-butene (1.8%). Copper-catalyzed decomposition in *o*-dichlorobenzene plus acetic acid also gave acetone, neopentyl acetate, and small amounts (3–8%) of neopentane, neopentyl alcohol and the same methylbutenes.

Although some of the products may arise from the thermal decomposition, the methylbutenes seem best accounted for by the sequence



The facile cleavage of the 2,4,4-trimethyl-2-pentoxy radical is consistent with other observations on alkoxy radical cleavage which increases in rate with increasing resonance stabilization of the radical produced,<sup>31</sup> and the neopentane may arise from competing hydrogen abstraction by neopentyl radicals.

**Rate Phenomena in Copper-Catalyzed Reactions.**—If reactions 1–10 represent the significant steps in copper-catalyzed peroxide reactions, they also define the reaction kinetics. Repeating them here for convenience, in a more abbreviated notation



where P = *t*-butyl peracetate and P· = *t*-C<sub>4</sub>H<sub>9</sub>O·.<sup>32</sup> We see that, while the main sequences 21b,e,f oxidize and reduce copper at equal rates, side reactions 21d and g consume or fail to regenerate cuprous ion which must be regenerated by oxidation of additional radicals, produced *via* the thermal decomposition 21a. Although the entire system of reactions yields too complicated a rate expression to be illuminating, two limiting cases illustrate the consequences of this oxidation reduction balance.<sup>33</sup>

(30) J. Hoffman and C. E. Boord, *J. Am. Chem. Soc.*, **77**, 3139 (1955). Presumably the neopentyl alcohol arises from a heterolytic rearrangement rather than a radical decomposition.

(31) For recent quantitative results and summary of older data, cf. C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963).

(32) For simplicity the CH<sub>3</sub>COO· radical produced in 21a is assumed to have the same reactive properties as P·. If it behaves differently, some expressions would be changed by, at most, a factor of 2. Also, although electron transfer is indicated in 21f, ligand transfer is kinetically equivalent.

(33) In both we neglect 21c since it is essentially equivalent to 21e–f but leads to a much more complex expression.

**Case I:** steps 21a,b,d,e,f important, all R· radicals oxidized by Cu<sup>II</sup>, but Cu<sup>I</sup> wasted *via* 21d. Here we may write three steady-state expressions, for copper

$$k_2[\text{P}][\text{Cu}^{\text{I}}] + k_4[\text{P}\cdot][\text{Cu}^{\text{I}}] = k_6[\text{R}\cdot][\text{Cu}^{\text{II}}] \quad (22)$$

and for P· and R·

$$2k_1[\text{P}] + k_2[\text{P}][\text{Cu}^{\text{I}}] = k_4[\text{P}\cdot][\text{Cu}^{\text{I}}] + k_5[\text{P}\cdot][\text{RH}] \quad (23)$$

$$k_5[\text{P}\cdot][\text{RH}] = k_6[\text{R}\cdot][\text{Cu}^{\text{II}}] \quad (24)$$

These suffice to eliminate radical concentrations, and, by reasonably straightforward algebra

$$-d[\text{P}]/dt = k_1[\text{P}] + k_2[\text{P}][\text{Cu}^{\text{I}}] = k_1[\text{P}](k_5[\text{RH}]/k_4[\text{Cu}^{\text{II}}]) \quad (25)$$

If  $k_2[\text{P}][\text{Cu}^{\text{I}}] \gg k_1[\text{P}]$

$$[\text{Cu}^{\text{I}}]^2 = k_1k_5[\text{RH}]/k_2k_4 \quad (26)$$

and

$$-d[\text{P}]/dt = [\text{P}](k_1k_2k_5[\text{RH}]/k_4)^{1/2} \quad (27)$$

**Case II:** steps 21a,b,e,f,g important, radical oxidation is incomplete and competes with bimolecular coupling of radicals. Here the steady-state expressions become

$$k_2[\text{P}][\text{Cu}^{\text{I}}] = k_6[\text{R}\cdot][\text{Cu}^{\text{II}}] \quad (28)$$

$$2k_1[\text{P}] + k_2[\text{P}][\text{Cu}^{\text{I}}] = k_5[\text{P}\cdot][\text{RH}] \quad (29)$$

$$k_5[\text{P}\cdot][\text{RH}] = k_6[\text{R}\cdot][\text{Cu}^{\text{II}}] + 2k_7[\text{R}\cdot]^2 \quad (30)$$

from which, assuming  $k_2[\text{P}][\text{Cu}^{\text{I}}] \gg k_1[\text{P}]$

$$-d[\text{P}]/dt = k_2[\text{P}][\text{Cu}^{\text{I}}] = k_6[\text{Cu}^{\text{II}}](k_1[\text{P}]/k_7)^{1/2} \quad (31)$$

Cases I and II and the resulting kinetic expressions 27 and 31 represent the reaction under somewhat simplified limiting conditions. At very low copper concentrations, where radical oxidation is incomplete, case II kinetics should be approximated, rates will be proportional to total copper present (assuming  $[\text{Cu}^{\text{II}}] \gg [\text{Cu}^{\text{I}}]$ ) and to  $[\text{P}]^{1/2}$ . At higher copper concentrations, as reactions 4 and 6 account for consumption of essentially all radicals, kinetics should approach case I, the reaction becoming first order in peroxide, half order in substrate [RH], and independent of copper. The point of transition will depend upon the ease of radical oxidation of a particular radical R· *via* 21f, and in the case I region, relative rates of peroxide decomposition in the presence of different substrates will be proportional to the square root of their reactivities toward *t*-butoxy radicals in step 21e. In the absence of a reactive substrate, the only reaction available for cuprous ion regeneration is 21c and little copper catalysis is to be expected.<sup>34</sup>

An interesting feature of the kinetic equations 27 and 31 is that, although peroxide decomposition occurs almost entirely by the oxidation-reduction reaction 21b, the rate constant for the thermal decomposition 21a occurs in the over-all rate expressions to the half power, since the thermal reaction is required to regenerate "wasted" cuprous ion. In the case II region, the over-all activation energy  $E_a = 1/2(E_1 + E_2 + E_3 - E_4)$ , or since  $E_4$  and  $E_5$  are probably very small,  $E_a \cong 1/2(E_1 + E_2)$ . No account is taken in the development of the coordination state of copper, it simply being assumed that some steady-state distribution of coordinated species exists in any given experiment. Obviously, however, rate constants for steps involving copper will vary with its state of coordination.

Although no detailed study of the kinetics of these copper-catalyzed reactions has appeared, a number of more or less qualitative observations are consistent with the kinetic scheme outlined. In agreement with

(34) Rapid decomposition should, however, be anticipated with peroxides yielding alkoxy radicals undergoing more rapid  $\beta$ -scission, and has been observed by Kochi. Expressions equivalent to 27 and 31 may be easily derived for such cases.

other reports, we find that copper, peroxide and a reactive substrate are all required for rapid reaction. The reactions are also significantly retarded by air as would be anticipated since oxygen not only removes R· radicals without reducing copper, but may also oxidize Cu<sup>I</sup> directly. Qualitatively, rates appear to increase with substrate reactivity, and the reaction with cumene, which is relatively slow, produces considerable dicumene, indicating that reaction 21g is important. Evidently the cumyl radical is oxidized with greater difficulty than are allylic radicals.

Barnard and Yang<sup>12</sup> in a preliminary report on the kinetics of the *t*-butyl perbenzoate-cyclohexene reaction have noted that the reaction is first order in peroxide and that the rate rises rapidly with copper concentrations at low levels of copper, and more slowly at higher concentrations, indicating transition from case II to case I. Preliminary kinetic measurements in this Laboratory<sup>35</sup> on *t*-butyl peracetate in acetic acid and acetonitrile have given pseudo-first-order plots between about 10–70% reaction and demonstrated the retarding effect of oxygen. Pseudo-first-order rates show little dependence on copper concentration above 10<sup>-3</sup> M and roughly square root dependence on the excess cyclohexene present. In short, the limited data available seem in accord with our proposed kinetic scheme.

### Experimental

**Materials.**—Except as described further below, all reagents, solvents, etc., were commercial materials, purified by distillation if necessary and purity checked by physical constants and G.L.C. (gas-liquid chromatography).

***t*-Butyl peracetate and hydroperoxide** were samples supplied by the Lucidol Division of Wallace and Tiernan Corp., Buffalo, N. Y. The peracetate was obtained as a 75% solution in benzene which infrared and n.m.r. analysis indicated to contain no significant impurities. It was used as such, the benzene providing a convenient internal standard for some G.L.C. analyses. The hydroperoxide contained about 10% impurities, chiefly water and *t*-butyl alcohol. It was purified by subjecting 50-ml. samples to water aspirator vacuum for 12 hr. at room temperature. Losses by this simple technique were about 20% and the product titrated as over 98% pure. Cumyl hydroperoxide (89%) was used without purification.

**2,4,4-Trimethyl-2-pentyl hydroperoxide** was prepared by modification of Hoffman's method.<sup>36</sup> Several attempts using 90% H<sub>2</sub>O<sub>2</sub> either gave low yields or led to vigorous decomposition. To a 2-liter round-bottom flask equipped with stirrer, dropping funnel and thermometer was added 674 g. (5.9 moles) of 30% H<sub>2</sub>O<sub>2</sub> and the whole cooled to 4° in an ice-bath. A mixture of 366 ml. of 96% H<sub>2</sub>SO<sub>4</sub> and 261 ml. of water precooled to 10° was added over 30 min., maintaining the flask temperature below 15°. 2,4,4-Trimethyl-1-pentene (189 g., 1.68 moles) was next added over 10 min. with vigorous stirring. No temperature rise was noted at this point, but the characteristic odor of the hydroperoxide was immediately present. The ice-bath was replaced with a large water-bath and the reaction mixture stirred at room temperature. The organic layer was removed, washed thrice with sodium bicarbonate solution, dried over sodium carbonate and exposed to water aspirator vacuum for 2 hr. Titration of the residue showed a 78% hydroperoxide content. Purification of a portion *via* the sodium salt proved unsuccessful, so the remainder was distilled to give 98% peroxide, b.p. 44–45° (0.9 mm.).

*Anal.* Calcd. for C<sub>8</sub>H<sub>18</sub>O<sub>2</sub>: C, 65.67; H, 12.45. Found: C, 65.11; H, 11.96.

***t*-Butyl hypochlorite** was supplied by Dr. A. Padwa.<sup>31</sup>

**5,5-Dimethyl-1,3-cyclohexadiene** was prepared by reduction of 5,5-dimethyl-1,3-cyclohexadione (Dimedon) and dehydration of the resulting alcohol. Conventional reduction of 66.4 g. (0.47 mole) of the dione with LiAlH<sub>4</sub> in ether gave 45 g. of crude diol, b.p. 85–90° (15 mm.). A center cut had *n*<sub>D</sub><sup>20</sup> 1.4653 and infrared spectrum with strong -OH absorption and bands at 1143, 1180 and 1365 cm.<sup>-1</sup> (-C(CH<sub>3</sub>)<sub>2</sub>). It also showed weak absorption in the carbonyl region, but since unreduced material would not interfere with the dehydration the crude product was used without further purification.

The diol (20 g.) was dehydrated by dropwise addition to KHSO<sub>4</sub>, 3 drops of H<sub>2</sub>SO<sub>4</sub> and 150 ml. of boiling decahydronaphthalene in a 500-ml. flask with reflux condenser and distilling

head. The product was distilled and collected as formed. Redistillation gave 8 g. (57%) of colorless diene, b.p. 133°. The infrared spectrum showed characteristic -C(CH<sub>3</sub>)<sub>2</sub> bands and the ultraviolet a  $\lambda_{\max}$  at 256 m $\mu$  in cyclohexane with no shoulders at higher wave length. Since  $\lambda_{\max}$  for 1,3-cyclohexadiene is 256 m $\mu$ , and cyclohexadienes with alkyl groups at the double bonds show  $\lambda_{\max}$  260–267 m $\mu$ , no alkyl group migration occurred during the dehydration. Analysis by G.L.C. peak collection and ultraviolet spectra of each showed that the product, however, contained about 20% of the unconjugated isomer, 3,3-dimethyl-1,4-cyclohexadiene. Dehydration without H<sub>2</sub>SO<sub>4</sub> gave a product containing 50% unconjugated isomer.

**Competitive experiments** were carried out in sealed degassed tubes and analyzed for hydrocarbon consumption by G.L.C. (silicone column) essentially as in our previous work with *t*-butyl hypochlorite.<sup>16,17</sup> A small amount of CuCl was used as catalyst in the peroxide experiments, and samples were heated in a 70° thermostat until reaction was complete (1–7 days). The hypochlorite experiments were initiated photochemically (incandescent lamp). Each hydrocarbon pair was run at least in duplicate and analyzed in triplicate. Experimental errors in Table I are average deviations of individual experiments from the mean.

**Product Identification and Isomer Distribution.**—Products and distribution of allylic isomers listed in Table II were determined as described below for typical experiments.

**Cyclohexene Reactions.**—Cyclohexene (5 ml.), *t*-butyl peracetate (2 ml.), chlorobenzene (1 ml. as internal standard) and a trace of CuCl (<1 mole % based on peroxide) were heated for 20 hr. in a sealed tube at 70°. At the end of this time no peroxide remained. Gas-liquid chromatographic analysis indicated the following yields of products: acetone, 2%; *t*-butyl alcohol, 96%; and 3-acetoxycyclohexene, 95%. A trace of gas (<5%) was also evolved. This was collected and identified as CO<sub>2</sub>. The 3-acetoxy cyclohexene was isolated by G.L.C. and identified by physical constants, infrared and n.m.r. spectra. In preparative scale experiment 35 ml. (0.35 mole) of cyclohexene, 15 ml. (0.2 M) of acetic acid, 7.0 ml. of 95.4% *t*-butyl hydroperoxide (0.067 M), 2 ml. of chlorobenzene and 0.07 g. (1 mole %) of CuCl were refluxed gently for 22 hr. Gas-liquid chromatographic analysis showed *t*-butyl alcohol, a small amount of water, and an 88% yield of 3-acetoxycyclohexene. In a similar experiment with cumene hydroperoxide the yield was 92%.

**1-Octene Reactions.**—Heating 3 ml. of 1-octene, 1 ml. of *t*-butyl peracetate, 1 ml. of chlorobenzene and a trace of CuCl for 20 hr. at 70° in a sealed tube led to complete reaction of peroxide and formation of a precipitate with the appearance of cupric acetate. Gas-liquid chromatographic analysis showed acetone (4%), *t*-butyl alcohol (95%) and octenyl acetates (89%). The acetates appeared as two peaks, 87 and 13%, respectively. The major peak was collected and identified as 3-acetoxy-1-octene on the basis of its infrared spectrum, ester bands at 1740 and 1245 cm.<sup>-1</sup> and bands indicating a terminal double bond at 990 and 928 cm.<sup>-1</sup>. The minor peak was collected and showed acetate bands and absorption at 961 cm.<sup>-1</sup> (*trans*-non-terminal double bond) in the infrared. Hydrogenation in cyclohexane with 10% Pd-on-charcoal at 3 atm. H<sub>2</sub> gave a saturated ester, infrared spectrum identical with *n*-octyl acetate. The relative quantities of the two acetates did not change on standing with acetic acid and cupric acetate, and the individual esters showed no isomerization on repeated G.L.C. analysis. The mixed esters were also added to a cyclohexene-peracetate-CuCl mixture, heated to complete reaction and reanalyzed. No isomerization was detected.

Essentially the same isomer distribution (82–90% 3-acetoxy-1-octene) was obtained in similar experiments using CuCl-Cu(OAc)<sub>2</sub>, CuCl<sub>2</sub> or CuBr. Cupric acetate in the presence of pyridine (3 ml. of 1-octene, 1.5 ml. of *t*-butyl peracetate and 1.5 ml. of pyridine) gave a black solution, 5% acetone, 94% *t*-butyl alcohol, 10% acetic acid and 10% esters (68% 3-acetoxy-1-octene, 32% 1-acetoxy-2-octene). The major product apparently involved attack on pyridine, but was not investigated further. No significant reaction between 1-octene and *t*-butyl peracetate occurred in 16–22 hr. at 70° in the presence of Co(OAc)<sub>2</sub>, CoCl<sub>2</sub> or MnCl<sub>2</sub>.

**1-Pentene and 1-hexene reactions** were carried out and products identified in the same manner. From 1-pentene, G.L.C. analysis showed 1% methyl acetate, 4% acetone, 95% *t*-butyl alcohol and 88% pentenyl esters. The esters were separated and identified as 88% 3-acetoxy-1-pentene and 12% 1-acetoxy-2-pentene.

Similarly, a 1-hexene reaction gave 89% esters, 84% 3-acetoxy-1-hexene and 16% 1-acetoxy-2-hexene. A 1-hexene experiment in the presence of pyridine gave 5% acetone, 90% *t*-butyl alcohol and only 11% esters, containing 71% 3-acetoxy-1-hexene, 29% 1-acetoxy-2-pentene.

**2-Pentene Reactions.**—Reaction of 5 ml. of 2-pentene (an approximately equal mixture of *cis* and *trans* isomers), 1.5 ml. of *t*-butyl peracetate and 1 mole % cupric acetate at 70° gave an 89% yield of three pentenyl acetates. Two had identical retention times with those of the products from 1-pentene and were identified as 3-acetoxy-1-pentene (29%) and 1-acetoxy-2-pentene

(35) Unpublished experiments by Dr. T. Tanaka.

(36) J. Hoffman, *Org. Syntheses*, **40**, 76 (1960).

(3%), so the third was evidently 4-acetoxy-2-pentene (68%). Chlorination of the same 2-pentene with *t*-butyl hypochlorite gave (two experiments) 3-chloro-1-pentene (12.9 and 11.9%), 1-chloro-2-pentene (22.6 and 21.5%), 4-chloro-2-pentene (64.0 and 66.7%).

**1,5-Cyclooctadiene Reactions.**—Reaction between 3.5 ml. of 1,5-cyclooctadiene and 1.5 ml. of *t*-butyl peracetate in the presence of 1 ml. of chlorobenzene and a trace of cupric 2-ethylhexanoate was complete in 16 hr. at 70°. Analysis showed a trace of acetone, 98% *t*-butyl alcohol and 96% of a mixture of two esters in ratio of 71:29. The major peak was collected and identified as 4-acetoxy-1,5-cyclooctadiene on the basis of its n.m.r. spectrum (5 peaks).

$\tau$	Identification	Relative area
4.68	Vinyl	5
4.79	Allylic H-C-O	
7.59	Allylic $\alpha$ to acetoxy	6
7.74	Allylic	
8.10	CH <sub>3</sub> COO-	3

The other product was accordingly considered to be 6-acetoxy-1,4-cyclooctadiene, and the two peaks, collected together, were analyzed.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>: C, 72.25; H, 8.49. Found: C, 72.53; H, 8.35.

**Cumene Reactions.**—A mixture of 75 ml. (0.53 mole) of cumene, 45 ml. (0.22 mole) of 75% *t*-butyl peracetate, 150 ml. of benzene, 10 ml. of acetic acid and 0.15 g. (0.7 mole %) of cupric acetate were refluxed together for a week. Volatile materials including cumene and acetic acid were removed under reduced pressure at 40° and examined by G.L.C. A 10% yield of  $\alpha$ -methylstyrene was detected and identified by collection and infrared spectrum. The residue (18 g.) was distilled and a fraction (11 g.) collected up to 110° (2 mm.). It was identified as  $\alpha$ -acetoxy-cumene (28% yield) on the basis of infrared and n.m.r. spectra and analysis.

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 74.13; H, 7.92. Found: C, 74.56; H, 8.03.

On cooling, a portion of the remaining 7 g. crystallized. The crystals were separated and recrystallized from ether; m.p. 114.5°. They were identified as 2,3-diphenyl-2,3-dimethylbutane (dicumene) by infrared and n.m.r. spectra and m.m.p. with authentic material.

**Allylbenzene Reactions.**—Heating a mixture of 15.5 g. (0.13 mole) of allylbenzene, 6.5 ml. (0.034 mole) of 75% *t*-butyl peracetate and 1 mole % CuCl at 70° for 35 hr. led to complete reaction. Gas-liquid chromatographic analysis indicated two high boiling products, A and B, B having the same retention time as authentic cinnamyl acetate. However, relative peak areas were found to depend upon G.L.C. column temperature, the ratio A:B decreasing from 71:29 at 160° to 14:86 at 210° on a DEGS (diethylene glycol polysuccinate) column. On the assumption that isomerization was taking place, the reaction mixture was hydrogenated at 40 p.s.i. pressure using 10% Pd-on-charcoal in cyclohexane. Gas-liquid chromatographic analysis now showed two high-boiling components, areas 72:28, retention times identical with authentic 1-phenyl- and 3-phenylpropyl acetates. The relative peak areas were now independent of column temperature. The hydrogenated reaction mixture was distilled and two fractions collected. The first, b.p. 111–112° (21 mm.), was identified as 96% 1-phenylpropyl acetate by G.L.C. analysis and infrared spectrum. The second, b.p. 113–135° (21 mm.), was shown by G.L.C. analysis and comparison of infrared spectra with known mixtures to be a 2:1 mixture of 3-phenyl- and 1-phenylpropyl acetates. Considerable residue remained from the distillation. The reaction was repeated and the products distilled without

hydrogenation. The esters were collected together at 80–118° (9 mm.) (46% yield). Infrared spectra showed bands at 993(s), 964(s), 913(s) and 889(w) cm.<sup>-1</sup> indicating both terminal and *cis* and *trans* double bonds. Quantitative ultraviolet analysis showed 28% cinnamyl acetate ( $\lambda_{\max}$  250 m $\mu$ ,  $\epsilon$  16,100 in cyclohexane). Hydrogenation and G.L.C. analysis of the ester fraction indicated 71% 1-phenyl- and 29% 3-phenylpropyl acetates and no other peaks. On the basis of these results it was concluded that G.L.C. analysis after hydrogenation provided the most reliable method of ester analysis, and a number of similar experiments were carried out on small samples at 70° as shown below.

Conditions	Yield of esters, %	Cinnamyl acetate, %
Cu(OAc) <sub>2</sub>	45	35
CoCl <sub>2</sub>	42	58
Co(Ac) <sub>2</sub>	35	69
<i>t</i> -Butyl hydroperoxide		
HOAc, CuCl		48

**$\beta$ -Methylstyrene reactions** were carried out and analyzed after hydrogenation as above. With either CuCl or Cu(OAc)<sub>2</sub> the only hydrogenated ester detected was 3-phenylpropyl acetate (yield 40–45%) identified by retention time and infrared spectrum. With *t*-butyl hydroperoxide in the presence of acetic acid the product contained 47% 3-phenyl- and 53% 1-phenylpropyl acetate.

**Reactions of 5,5-Dimethyl-1,3-cyclohexadiene.**—The 80:20 mixture of 5,5-dimethyl-1,3-hexadiene and 3,3-dimethyl-1,4-hexadiene (2.0 ml.), 1.5 ml. of *t*-butyl peracetate, 3 ml. of chlorobenzene and 7 ml. of acetic acid plus 1 mole % Cu(OAc)<sub>2</sub> were heated for 24 hr. at 70°. Gas-liquid chromatographic analysis showed 6% *o*-xylene, identified by retention time, infrared and ultraviolet spectra, and two peaks of longer retention time 8 and 80%. Collected together they analyzed for the addition product of the perester to the diene and each had infrared spectra consistent with such a structure.

*Anal.* Calcd. for C<sub>14</sub>H<sub>24</sub>O<sub>3</sub>: C, 69.96; H, 10.06. Found: C, 69.30; H, 9.35.

The major peak was identified as 3-acetoxy-4-*t*-butoxy-6,6-dimethylcyclohexene on the basis of its n.m.r. spectrum, peaks at 4.62 (vinyl), 5.03 (allylic H-C-O), 7.86 (*sec*-H-C-O), 8.12 (acetoxy), 8.45 (*sec*-cyclohexane), 9.02, 9.05 and 9.11 (-C(CH<sub>3</sub>)<sub>3</sub>)  $\tau$ , areas of 4.62, 5.03 and 8.45  $\tau$  peaks 2:1:2.

The minor peak was tentatively identified as the corresponding 1,4-addition product, 3-acetoxy-4,4-dimethyl-6-*t*-butoxycyclohexene. The reaction was repeated with cupric 2-ethylhexoate with identical results, based on G.L.C. analysis. Heating the reaction products for an additional 48 hr. at 70° produced no change in the *o*-xylene yield. Blanks without copper salt and without perester gave no *o*-xylene.

**Decomposition of 2,4,4-Trimethyl-2-pentyl Hydroperoxide.**—Heating 1.0 ml. of peroxide and 0.1 g. of cupric 2-ethylhexoate in a sealed tube for 48 hr. at 70° and 100 hr. at 120° led to complete decomposition. (Reaction was incomplete at 70°, and initial heating to 120° led to detonation.) Gas-liquid chromatographic analysis showed the products: 100% acetone, 30% neopentane, 55% neopentyl alcohol, 10% 2-methyl-2-butene and a trace (1–2%) of 2-methyl-1-butene. Products were identified by retention time, and the 2-methyl-2-butene was further identified by collection and infrared spectrum. A similar reaction using 0.75 ml. of peroxide, 1 ml. of acetic acid, 3 ml. of *o*-dichlorobenzene and a trace of cupric 2-ethylhexoate gave neopentane, acetone, neopentyl acetate, neopentyl alcohol and a little 2-methyl-2-butene. The neopentyl acetate was further identified by infrared and n.m.r. spectra after collection. A similar reaction without acetic acid gave neopentane, acetone, neopentyl alcohol and a little 2-methyl-2-butene.