did not occur during isolation and purification of the binary mixtures of alcohols was established by isolation of alcohol mixtures of known composition (75.1%, 51.1% and 29.3% II) from synthetic quenched reaction mixtures. The observed compositions were 73.7%, 50.3% and 27.9% II. Isolation of an alcohol mixture containing 1.57 atom % ^{18}O excess[23] by this procedure gave alcohol having 1.55 atom % ^{18}O excess. Thus the isolation does not result in change of the ^{18}O content. The results of a typical experiment are summarized in Table IV.

[CONTRIBUTION FROM EMERYVILLE RESEARCH CENTER, SHELL DEVELOPMENT CO., EMERYVILLE, CALIF., AND DEPARTMENT OF CHEMISTRY, CASE INSTITUTE OF TECHNOLOGY, CLEVELAND 6, O.]

Addition of Peroxides to Conjugated Olefins Catalyzed by Copper Salts[1]

BY JAY K. KOCHI

RECEIVED FEBRUARY 7, 1962

t-Butyl peracetate and perbenzoate react with conjugated olefins under catalysis by copper salts to form adducts containing one or more olefin units. From butadiene, *t*-butoxybutenyl derivatives are formed which are the same as those derived from *t*-butyl hypochlorite or *t*-butyl hydroperoxide and ferrous sulfate. It is demonstrated that these *t*-butyl peresters and copper salts form *t*-butoxy radicals as intermediates, which add to butadiene to produce *t*-butoxybutenyl radicals. The similarity in the oxidation by cupric salts of *t*-butoxybutenyl radicals and butenyl radicals from butenes examined earlier is discussed. The mechanistic implications of the oxidation of allylic radicals by an electron transfer process or a ligand transfer process is further amplified. The reaction of *t*-butyl hydroperoxide and copper salts is also postulated to form *t*-butoxy radical intermediates, and no evidence for the formation of *t*-butylperoxy radicals from this system is presently at hand.

Introduction

The copper salt-catalyzed reactions of *t*-butyl peresters and benzoyl peroxide with simple olefins, represented by the normal butenes, have been studied.[2,3] The difference in behaviors between these two peroxides was attributed to the initiating radical produced from each: *t*-butoxy from *t*-butyl perester and benzoyloxy from benzoyl peroxide. Although the former radicals reacted with simple olefins primarily by allylic hydrogen abstraction,

$$t\text{-BuO}_3\text{CR} + \text{Cu}^{\text{I}} \longrightarrow t\text{-BuO}\cdot + \text{Cu}^{\text{II}}\text{O}_2\text{CR} \quad (1)$$

$$(\text{C}_6\text{H}_5\text{CO}_2)_2 + \text{Cu}^{\text{I}} \longrightarrow \text{C}_6\text{H}_5\text{CO}_2\cdot + \text{Cu}^{\text{II}}\text{O}_2\text{CC}_6\text{H}_5 \quad (2)$$

benzoyloxy radicals reacted by an addition process. Kharasch and co-workers[4] have studied the behavior of *t*-butoxy radicals toward such receptive dienes as butadiene and found that addition at the terminal positions to produce allylic radicals was the predominant reaction. Similar considerations

$$t\text{-BuO}\cdot + \text{C}_4\text{H}_6 \longrightarrow \underset{\text{I}}{t\text{-BuO—CH}_2\text{—CH}\overset{-}{\cdots}\text{CH}\overset{-}{\cdots}\text{CH}_2\cdot} \quad (3)$$

apply to benzoyloxy radicals. If *t*-butoxy radicals are formed from the catalyzed reactions of *t*-butyl peresters in the presence of butadiene, such allylic *adduct* radicals as I will result. The reaction of these allylic radicals with cupric salts should be governed by the same considerations as the simple butenyl radicals II derived from butenes by a hydrogen abstraction reaction described earlier.[2]

$$t\text{-BuO}\cdot + \text{C}_4\text{H}_8 \longrightarrow t\text{-BuOH} + \underset{\text{II}}{\text{CH}_3\text{—CH}\overset{-}{\cdots}\text{CH}\overset{-}{\cdots}\text{CH}_2\cdot} \quad (4)$$

The reactions are

$$\text{C}_4\text{H}_7\cdot + \text{Cu}^{\text{II}}\text{O}_2\text{CR} \longrightarrow \text{C}_4\text{H}_7\text{O}_2\text{CR} + \text{Cu}^{\text{I}} \quad (5)$$

and analogously

$$t\text{-BuOC}_4\text{H}_6\cdot + \text{Cu}^{\text{II}}\text{O}_2\text{CR} \longrightarrow \underset{\text{III}}{t\text{-BuOC}_4\text{H}_6\text{O}_2\text{CR}} + \text{Cu}^{\text{I}}\text{, etc.} \quad (6)$$

The reaction between peresters and such conjugated olefins as butadiene, isoprene and styrene was investigated in the presence of copper salts to explore the behavior of these allylic radicals. The reactions of butoxybutenyl radical I postulated as an intermediate from butadiene and *t*-butyl peresters with the aid of copper salts were compared with those adduct radicals prepared unambiguously from known sources of *t*-butoxy radicals, such as *t*-butyl hypochlorite and *t*-butyl hydroperoxide and ferrous salts. Butadiene is also an effective trap for *t*-butylperoxy radicals,[5] and it was employed with *t*-butyl hydroperoxide and copper salts to attempt to obtain evidence for the formation of *t*-butylperoxy intermediates.[6]

The stoichiometry of the addition of peresters to butadiene catalyzed by copper salts is given by eq. 7.

$$t\text{-BuOO}_2\text{CR} + \text{C}_4\text{H}_6 \xrightarrow{\text{Cu}^{\text{I}}} t\text{-BuOC}_4\text{H}_6\text{O}_2\text{CR} \quad (7)$$

Results

Conjugated Olefins and Peresters.—Butadiene (1 mole) and *t*-butyl peracetate (0.25 mole) reacted readily in benzene solution (100 ml.) with catalytic amounts of cuprous bromide (1.4 meq.) to produce acetic acid (8–10%), *t*-butyl alcohol (approximately 5%) and 90–92% ester. A minor amount of polymeric butadiene (approximately 10 g.) was also produced. Distillation of the ester mixture yielded two fractions corresponding to a 1:1 (40–50%) and a 2:1 (25–30%) adduct of butadiene and *t*-butyl peracetate, in addition to higher boiling adducts which were not identified. The 1:1 adducts consisted of two isomers, 4-*t*-butoxy-3-acetoxybutene-1(V, R = CH_3) and 4-

---

[1] Presented in part before the Petroleum section of the Gordon Research Conference, Colby Jr. College, New London, N. H., June, 1961. Part III, Peroxide Reactions Catalyzed by Copper Salts.

[2] J. K. Kochi, *J. Am. Chem. Soc*, **83**, 3162 (1961); **84**, 774 (1962).

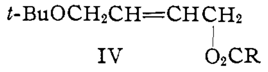
[3] J. K. Kochi, *ibid.*, **84**, 1572 (1962).

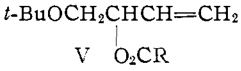
[4] M. S. Kharasch, F. Arimoto and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951); D. H. Volman and W. M. Graven, *J. Am. Chem. Soc.*, **75**, 3111 (1953).

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

[6] J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).

t-butoxy-1-acetoxybutene-2 (IV, R = CH_3). The 2:1 adducts were a mixture of the four possible isomers of acetoxy-*t*-butoxyoctadienes VI. They were not identified further.


$t\text{-BuOCH}_2\text{CH}{=}\text{CH}\underset{\text{O}_2\text{CR}}{\underset{|}{\text{CH}_2}}$
IV

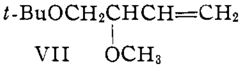

$t\text{-BuOCH}_2\underset{\text{O}_2\text{CR}}{\underset{|}{\text{CH}}}\text{CH}{=}\text{CH}_2$
V

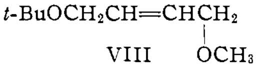
$t\text{-BuOC}_4\text{H}_6\text{C}_4\text{H}_6\text{OAc}$
VI

In the presence of excess cupric ion, the formation of 2:1 and higher adducts of butadiene and perester was drastically curbed. Thus, a homogeneous reaction consisting of butadiene (1.0 mole), *t*-butyl peracetate (0.27 mole), cuprous chloride (2 meq.) and cupric acetate (10 meq.) in 100 ml. of acetonitrile yielded a light yellow solution containing only cuprous salts. There was isolated a 70–75% yield of a mixture of 1:1 adducts and 10–15% of 2:1 adducts. A similar reaction in 50% v. acetic acid–benzene solution consisted of butadiene (1.0 mole), *t*-butyl peracetate (0.27 mole), cuprous chloride (2 meq.) and cupric acetate (10 meq.). The reaction mixture after heating appeared dark green which indicated that cupric acetate was still present. Distillation yielded only a mixture of 1:1 adducts in 90–95% yield. In neither system was a significant amount (<0.5 g.) of polymeric butadiene formed.

In toluene solvent, similar results were obtained. From a charge containing *t*-butyl peracetate (0.25 mole), butadiene (1.0 mole) and cuprous bromide (1.4 meq.) in 80 ml. of toluene, an over-all yield of 92% esters, 8% acetic acid and 7% *t*-butyl alcohol was formed. The ester components on distillation afforded the 1:1 adducts in 51% yield. No benzyl acetate was formed.

In methanol solution (75 ml.), butadiene (1.0 mole) and *t*-butyl peracetate (0.26 mole) reacted catalytically (CuBr, 1.4 meq.) to produce a colorless homogeneous solution which analysed for a complex mixture of products among which were methyl acetate (20%), acetic acid (27%), formaldehyde (11% per mole or 22% per equivalent), *t*-butoxyacetoxybutenes (35%), *t*-butoxymethoxybutenes (27%) and small amounts (0.9 g.) of polybutadienes. The yield of *t*-butoxyacetoxyoctadienes was approximately 20%. The *t*-butoxybutenyl acetate fraction consisted of 4-*t*-butoxy-3-acetoxybutene-1 (82%) and the 1,4-isomeric adduct (18%). The ether mixture was constituted of 73% 4-*t*-butoxy-3-methoxybutene-1 (VII) and 27% 4-*t*-butoxy-1-methoxybutene-2 (VIII).


$t\text{-BuOCH}_2\underset{\text{OCH}_3}{\underset{|}{\text{CH}}}\text{CH}{=}\text{CH}_2$
VII


$t\text{-BuOCH}_2\text{CH}{=}\text{CH}\underset{\text{OCH}_3}{\underset{|}{\text{CH}_2}}$
VIII

The ratio of 1:1 acetates (IV and V) to 1:1 ethers (VII and VIII) was 1.61, with the former predominating.

When excess cupric acetate was charged, the blue-green color of the final solution indicated the continued presence of cupric salts. Under these conditions the 2:1 and higher butadiene–perester telomers were not formed. The yields of *t*-butoxybutenyl methyl ethers and acetates formed in solutions of various compositions are given in Table I.

TABLE I

METHYL ETHERS AND ACETATES FROM BUTADIENE AND PERESTERS IN METHANOL–ACETIC ACID SOLUTIONS[a]

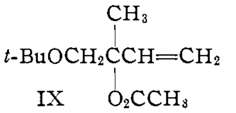
Run	*t*-Butyl perester	Methanol, ml.	Acetic acid, ml.	1:1 acetate,[b] %	1:1 ether,[b] %	Ester,[c] %
57	Acetate	100	0	31 (84)	36 (74)	39
53	Acetate	80	20	33 (83)	33 (72)	40
54	Acetate	50	50	40 (84)	25 (72)	48
67	Benzoate	85	15	17[d] (85)	40 (75)	51
58	Benzoate	50	50	29[e] (82)	27 (73)	49
59	Benzoate	0	100	89[f] (83)	0 . .	98

[a] In solutions containing butadiene (1.0 mole), cuprous chloride (2.0 meq.), cupric acetate (7.5 meq.) and *t*-butyl perester (0.23 mole). [b] Total yields of adducts by G.L.C.: in parentheses, yield of 1,2-adduct; remainder 1,4-isomer. [c] Ester values by saponification procedure; does not include methyl acetate. [d] In addition to 51% benzoic acid and 18% 1:1 benzoate ester adducts isolated. [e] 70% benzoic acid and 9% benzoates isolated. [f] 77% benzoic acid and 8% benzoates isolated.

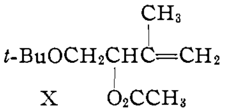
The distribution of the isomeric 1:1 adducts, 4-*t*-butoxy-3-acetoxybutene-1 and 4-*t*-butoxy-1-acetoxybutene-2, in the product mixture was insensitive to solvent variation, although the over-all yields of the 1:1 adducts varied considerably. Thus, the percentage of the major isomer, 4-*t*-butoxy-3-acetoxybutene-1, constituted in the 1:1 adduct mixtures was 79–83% in benzene, 84% in toluene, 82–85% in methanol, 82% in acetonitrile and 81% in 50% v. acetic acid–benzene.

t-Butyl perbenzoate reacted with butadiene in benzene solution to form a colorless solution consisting of 85% yield of mixed esters, 13% benzoic acid and 14% *t*-butyl alcohol. The mixed esters were fractionated into a 1:1 adduct mixture of *t*-butoxybenzoxybutenes (60–65%), 2:1 adducts, benzoxy-*t*-butoxyoctadienes (15–20%) and higher molecular weight esters (5–10%). The 1:1 adduct mixture consisted primarily of the 1,2-adduct 4-*t*-butoxy-3-benzoxybutene-1 (approximately 80% by distillation). As shown in Table I, *t*-butyl perbenzoate and butadiene in acetic acid solution with excess cupric acetate yielded a green-blue solution from which a mixture of 1:1 adduct acetates and benzoates could be isolated in 85% and 8% yields, respectively. In mixed methanol and acetic acid solutions, *t*-butoxybutenyl methyl ethers were formed in addition to the acetates and benzoates. The compositions of the acetate and methyl ether mixtures were the same as those obtained from *t*-butyl peracetate under similar conditions. When excess cupric acetate was employed, no high molecular weight adducts were formed.

Under slightly different conditions isoprene and *t*-butyl perbenzoate reacted with cuprous bromide catalyst to yield 81% of a mixture of 1:1 adducts. The structures corresponded to the four possible isomeric *t*-butoxybenzoxypentenes similar to the butadiene adducts. The infrared spectra indicated that the main constituents of the mixture of isomers were the 1,2- and 4,3-adducts IX and X. There were formed only small amounts of higher adducts (<5%) and no polymeric isoprene.



$t\text{-BuOCH}_2\overset{\text{CH}_3}{\underset{\text{O}_2\text{CCH}_3}{\text{C}}}\text{CH=CH}_2$ IX

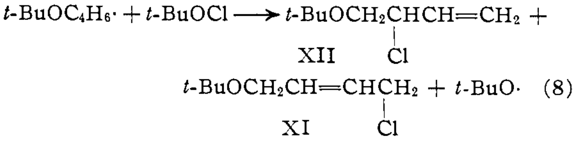


$t\text{-BuOCH}_2\underset{\text{O}_2\text{CCH}_3}{\text{CH}}\overset{\text{CH}_3}{\text{C}}\text{=CH}_2$ X

The reaction of styrene and *t*-butyl perbenzoate in benzene solution with copper salt catalyst led to a complete polymerization of styrene. No pure ester product could be isolated. In addition to telomers containing *t*-butoxy and benzoxy groups, there was isolated a 62% yield of benzoic acid. Even in the presence of excess cupric salt complete reaction of styrene resulted. Thus *t*-butyl peracetate (0.5 mole) and styrene (1.0 mole) in acetonitrile solvent containing excess cupric acetate (0.05 mole) and cuprous chloride (0.003 mole) yielded no discrete compound. Although no solid polystyrene was formed, the relatively low telomers of styrene and *t*-butyl peracetate were the main products.

Butadiene and *t*-Butyl Hydroperoxide.—A solution of butadiene (0.75 mole), *t*-butyl hydroperoxide (0.15 mole) and cupric acetate (3.0 meq.) in 25% v. acetic acid in benzene reacted to form a blue-green solution containing 80–85% yield of esters (by titration). Analysis by G.L.C. and isolation by distillation indicated a 50–55% yield of a mixture of *t*-butoxybutenyl acetates. The composition of this mixture was the same as that obtained under equivalent conditions from *t*-butyl peracetate or perbenzoate (in acetic acid): 79–83% 4-*t*-butoxy-3-acetoxybutene-1 and 17–21% 4-*t*-butoxy-1-acetoxybutene-2. A similar reaction in solution containing 25% v. acetic acid and 25% v. methanol in benzene afforded a 42% yield of 1:1 *t*-butoxybutenyl acetates which consisted of 81% 1,2-adduct. A reaction in 25% v. acetic acid in methanol yielded similar results. These reactions were carefully distilled *in vacuo* to attempt isolation of *t*-butylperoxy adducts such as *t*-butylperoxybutenyl acetates. However, no evidence could be found for their formation.

Butadiene and *t*-Butyl Hypochlorite.—*t*-Butyl hypochlorite has been shown[7] to chlorinate active hydrogen donor compounds through a radical chain reaction which involves *t*-butoxy radical intermediates. With olefins, allylic chlorides are the predominant products. Allylic intermediates I are also formed from the addition of *t*-butoxy radicals to conjugated dienes such as butadiene (reaction 3). A solution of butadiene and *t*-butyl hypochlorite in benzene or carbon tetrachloride reacted readily under actinic irradiation to form two isomeric 1:1 adducts XI and XII in 70–80% yields, in addition to small amounts of *t*-butyl alcohol (10–15%) and acetone (5%). The chloroether mixture was mainly the primary chloride XI (74%) with smaller amounts of 1,2-adduct XII (26%).



$$t\text{-BuOC}_4\text{H}_6\cdot + t\text{-BuOCl} \longrightarrow \underset{\text{XII}}{t\text{-BuOCH}_2\underset{\text{Cl}}{\text{CH}}\text{CH=CH}_2} + \underset{\text{XI}}{t\text{-BuOCH}_2\text{CH=CH}\underset{\text{Cl}}{\text{CH}_2}} + t\text{-BuO}\cdot \qquad (8)$$

The *t*-butoxybutenyl chloride (XI) was reduced with lithium aluminum hydride in tetrahydrofuran solvent to *t*-butyl crotyl ether. Catalytic hydrogenation of the crotyl ether yielded *t*-butyl *n*-butyl ether.

Butadiene and *t*-Butyl Hydroperoxide–Ferrous Sulfate.—*t*-Butoxy radicals can also be produced from the oxidation–reduction reaction of ferrous ion and *t*-butyl hydroperoxide.[8] In the presence of butadiene the alkoxy radicals add to yield the butoxybutenyl radicals I. An alternative mode

$$t\text{-BuO}_2\text{H} + \text{Fe}^{\text{II}} \longrightarrow t\text{-BuO}\cdot + \text{Fe}^{\text{III}}\text{OH} \qquad (9)$$

of chain termination employs metal halides, particularly cupric and ferric salts.[9] The chloro-*t*-butoxybutene mixture produced in 55% yield

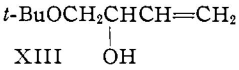
$$t\text{-BuOC}_3\text{H}_6\cdot + \text{CuCl}_2 \longrightarrow t\text{-BuOC}_4\text{H}_6\text{Cl} + \text{CuCl} \qquad (10)$$

from the reaction of butadiene and *t*-butyl hydroperoxide in the presence of ferrous and cupric chlorides in aqueous methanol solution at 0° had the same composition (65% XI and 35% XII) as the mixture produced from *t*-butyl hypochlorite under different reaction conditions. In addition, *t*-butyl alcohol (approximately 30%) and formaldehyde (approximately 20%) were formed.

In the absence of chloride ion, the intermediate butoxybutenyl radicals I suffer oxidation by cupric ions to yield solvolytic products.[10] Thus, *t*-butyl hydroperoxide and butadiene react (11) with ferrous and cupric sulfate in aqueous methanol solution at 0° to yield 60–65% of the two isomeric *t*-butoxymethoxybutenes VII and VIII and minor amounts (3–5%) of the corresponding

$$t\text{-BuOC}_4\text{H}_6\cdot + \text{Cu}^{\text{II}}(\text{CH}_3\text{OH}) \longrightarrow t\text{-BuOC}_4\text{H}_6\text{OCH}_3 + \text{Cu}^{\text{I}} + \text{H}^+ \qquad (11)$$

alcohols XIII and XIV. The diether mixture



$t\text{-BuOCH}_2\underset{\text{OH}}{\text{CH}}\text{CH=CH}_2$ XIII

$t\text{-BuOCH}_2\text{CH=CHCH}_2\text{OH}$ XIV

consisted of 72% secondary methyl ether VII and 28% primary methyl ether VIII. This was the same mixture as that obtained from the diether fraction from the copper-catalyzed reaction of *t*-butyl peracetate or perbenzoate and butadiene in methanol cited earlier.

Competition experiments were conducted in methanol–acetic acid solutions. The reaction of *t*-butyl hydroperoxide (0.26 mole), butadiene (1.5 moles), cupric acetate (50 meq.) and ferrous sulfate (0.10 eq.) in 350 ml. of 15% v. acetic acid in methanol at 0° yielded 58% *t*-butoxybutenyl methyl ether and only 5% *t*-butoxybutenyl acetates. In 50% v. acetic acid in methanol, a 63% yield of methyl ether and 8% yield of acetate was formed. The reaction in glacial acetic acid was slow due to the insolubility of the metal salts; however, the addition of water (10%) increased the rate sufficiently so that mixtures of *t*-butoxy-

---

(7) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960); F. D. Greene, *ibid.*, **81**, 2688 (1959); D. B. Denney and W. F. Beach, *J. Org. Chem.*, **24**, 108 (1959).

(8) A. Tobolsky and R. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 95 ff.

(9) (a) J. K. Kochi, *J. Am. Chem. Soc.*, **78**, 4815 (1956); **79**, 2942 (1957); (b) E. Collinson and F. Dainton, *Nature*, **177**, 1224 (1956); (c) C. Bamford, A. Jenkins and R. Johnston, *Proc. Royal Soc.* (*London*), **A239**, 214 (1957); (d) J. Kumamoto, H. De La Mare and F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960).

(10) H. De La Mare, J. Kochi and F. Rust, *J. Am. Chem. Soc.*, **83**, 2013 (1961); to be published.

butenyl acetates and alcohols were formed in 20 and 8% yields, respectively, after several hours. The *t*-butoxybutenyl methyl ether mixture formed under these conditions consisted mainly of the 1,2-isomer (74–76%).

Silver-ion Assisted Solvolysis of *t*-Butoxybutenyl Chlorides.—The methanolysis of primary *t*-butoxybutenyl chloride XI with silver trifluoroacetate in methanol yielded the methyl ethers in 70% yield. The unrearranged ether VIII (78%) predominated over the secondary methyl ether VII (22%). A mixture of chlorides consisting mainly of the secondary allylic isomer XII (72%) on similar treatment yielded a mixture of methyl ethers consisting of 46% unrearranged VII and 54% rearranged primary methyl ether VIII. These results are similar to the results of Young, Sharman and Winstein[11a] for the silver-ion assisted hydrolysis of butenyl chlorides. The small amounts of *t*-butoxytrifluoroacetoxybutenes formed were not analyzed.

The acetolysis of the primary chloride XI in glacial acetic acid with silver acetate yielded *t*-butoxybutenyl acetates in 82% yield. This mixture consisted of 38% rearranged acetate V and 62% unrearranged isomer IV. In the 33% v. acetic acid–acetonitrile solution the primary chloride XI yielded with silver trifluoroacetate a 40% yield of butenyl acetates consisting of 18% rearranged acetate V and 82% primary acetate IV. Alternatively the 1,2-adduct XII in 33% v. acetic acid–benzene yielded a 45% yield of acetates consisting of approximately a 60:40 mixture of IV and V, respectively. The trifluoroacetate products were not analyzed. Finally, the reaction of primary chloride XI with potassium acetate in glacial acetic acid yielded 80–90% of unrearranged acetate IV.

The competition between silver-ion assisted methanolysis and acetolysis was examined in a homogeneous solution consisting of 50% v. methanol, 25% v. acetic acid and 25% v. acetonitrile. The primary chloride yielded a butenyl methyl ether mixture (40%) and a butenyl acetate mixture (1–2%). The ether mixture consisted of 11% unrearranged secondary methyl ether VII and 89% unrearranged ether VIII; the acetate fraction consisted of approximately 50% of each isomer. Under the solvolytic conditions employed for the studies above, no rearrangement of the products was evident, since in blank runs in acetic acid it was demonstrated that 4-*t*-butoxy-3-acetoxybutene-1 (the more labile isomer) did not isomerize to the 1,4-isomer with silver acetate. It is concluded from these studies that the mixture of *t*-butoxybutenyl products derived from the solvolysis of the *t*-butoxybutenyl chlorides consists of approximately 25–40% (depending on the reactant chloride[11b]) of the 1,2-isomer.

These results are similar to those obtained earlier from the silver ion-assisted solvolysis of α-methallyl and crotyl chlorides.[2,11] Thus, it appears that when butenyl carbonium ions are formed as intermediates in solvolytic reactions such as these, the solvation of the ion by a kinetically controlled process yields approximately equal amounts of α-methallyl and crotyl isomers. Analogously, the *t*-butoxybutenyl carbonium ion affords on solvation slightly greater yields of the primary derivatives (IV and VIII) than the secondary isomers. The relative yields of primary and secondary allylic products obtained from solvolytic reactions involving carbonium ions as intermediates are in contradistinction to the formation of predominantly secondary allylic products from the oxidation of allylic radicals by cupric salts.

Discussion

The copper salt-catalyzed reaction of *t*-butyl peresters with conjugated dienes such as butadiene can be represented by eq. 6. This is contrasted to reactions 12 of simple olefins such as butene.[1]

$$t\text{-BuOO}_2\text{CR} + \text{C}_4\text{H}_8 \xrightarrow{\text{Cu}^{\text{I}}} \text{C}_4\text{H}_7\text{O}_2\text{CR} + t\text{-BuOH} \quad (12)$$

In both cases, the reactions can be formulated to occur *via* similar steps: (a) the formation of *t*-butoxy radicals by reaction 1 of cuprous salt with *t*-butyl perester, (b) the chain transfer reaction to produce allylic radicals by addition (3) to butadiene or hydrogen abstraction from butene (4) and followed by (c) the oxidation–reduction reaction of the allylic radicals (I or II) with cupric salt to yield substituted butenes.

The formation of *t*-butoxy radicals as intermediates in the reaction of *t*-butyl peresters with copper salts is demonstrated by the fact that the same or related products are obtained from these systems as from *t*-butyl hypochlorite[7] or *t*-butyl hydroperoxide and ferrous salts.[4] Indeed, the structures of all the 1:1 adducts are related (*via* the *t*-butoxybutenyl radical I) to the adducts of *t*-butyl hypochlorite and butadiene: first by reduction to *t*-butyl *n*-butyl ether and secondly by acetolysis to *t*-butoxybutenyl acetates and methanolysis to the corresponding methyl ethers. These experiments conclusively eliminate the alternative possibility of acyloxy radicals as intermediates from the reduction of peresters by cuprous salt (*e.g.*, reaction 13) instead of *t*-butoxy radicals (reaction 1). If acyloxy radicals were intermediates the predominant product would be 4-acyloxy-3-*t*-butoxybutene-1. In addition, carbon dioxide would be an important product, especially with *t*-butyl peracetate.

$$t\text{-BuO}_3\text{CR} + \text{Cu}^{\text{I}} \longrightarrow \text{RCO}_2\cdot + t\text{-BuOCu}^{\text{II}} \quad (13)$$

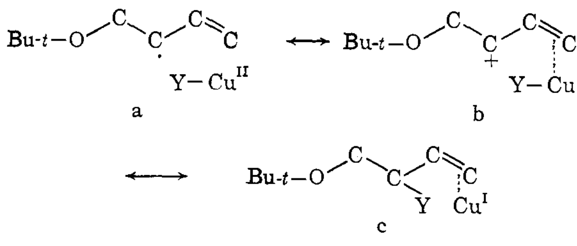
The oxidation of the intermediate *t*-butoxybutenyl radical I by cupric salts such as acetate, benzoate and methoxide is analogous to the oxidation of the simple butenyl radical II. With both radicals the termination reaction leads to a predominance of the secondary ester, although it is slightly more important with butenyl radical than with the *t*-butoxy analog. Thus, from *t*-butoxybutenyl radical, the 1,2-adduct 4-*t*-butoxy-3-acyloxybutene-1 is formed in 78–83% yields relative to the isomeric 1,4-adduct. From butenyl radicals 3-acyloxybutene-1 constitutes 85–95% of the butenyl ester mixture. Similarly, the *t*-butoxybutenyl methyl ethers from butadiene in methanol consist mainly of the 1,2-adduct (72–75%) and the butenyl methyl ethers from the

---

[11] (a) W. G. Young, S. Sharman and S. Winstein, *J. Am. Chem. Soc.*, **82**, 1376 (1960); (b) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

normal butenes consist mainly of the α-methallyl isomer (85%). In both reactions the distribution between the two isomers (1,2- and 1,4-adducts from butadiene and α-methallyl and crotyl isomers from butenes) is quite insensitive to the solvents employed, which can be varied from benzene, methanol, acetonitrile to acetic acid. This predominance of the more highly substituted allylic secondary isomer is unique in non-stereospecific reactions which involve the equilibrated allylic moieties.[2] If either free radical or carbonium ion processes were involved in the substitution step, it would be expected that the primary allylic isomer (4-*t*-butoxy-1-acyloxybutene-2 from butadiene and crotyl ester from butene) would constitute *at least* 50% of the isomeric fractions.[2]

The observed specificity and insensitivity to solvent has led to the postulate that the oxidation of allylic radicals by cupric salts is subject to ligand transfer and to electron transfer control.[2] The degree to which each contributes is a function of the free radical, metal ion and ligand. With oxyanions such as acetate, benzoate and methoxide, the transition state XV is largely characterized by the oxidation of the free radical to a carbonium ion (XVb). The role of copper in this mechanism for the oxidation–reduction reaction is to transfer an electron as well as the ligand and to coördinate with the carbon–carbon π-bond of the allylic radical.



XV

The relatively higher yields of primary products (1,4-adducts) from *t*-butoxybutenyl radicals compared to the butenyl radicals (crotyl products) can be rationalized, if the steric effect of the *t*-butoxy group and the stabilization of the incipient carbonium ion by an ether grouping in the α-position is considered. The higher yields of the 1,4-isomer among methyl ethers (~30%) compared to the esters (~20%) lend support to the importance of the latter factor since it is expected that the electron transfer contribution in the transition state is more important with ether substitution than ester substitution. If such were the case the transition state of the substitution would resemble a carbonium ion (electron transfer) process more than a purely ligand transfer process. Factors such as these may be important in considering the contribution of each resonance form in the transition state for the oxidation of a particular free radical by a metal salt.[10,12]

The oxidation of *t*-butoxybutenyl radicals from *t*-butyl peresters and butadiene in mixed methanol and acetic acid solutions has indicated that acetate and benzoate are transferred from cupric salt to the free radical in preference to methoxide. For example the *t*-butoxybutenyl radical intermediate 1 reacted with cupric acetate in methanol solvent to be partitioned approximately 57% to acetate ester and 43% to methyl ether. In each product mixture the secondary isomer predominated, 82% 4-*t*-butoxy-3-acetoxybutene-1 and 73% 4-*t*-butoxy-3-methoxybutene-1. The latter product was also formed in the same (72%) isomeric proportion from the reaction of *t*-butyl hydroperoxide and butadiene in aqueous methanol solution and the ferrous–cupric sulfate couple. With butenyl radicals from butenes studied earlier the partitioning of the butenyl moiety between acetate ester and methyl ether (approximately 4:1) with cupric acetate was not as great as that observed with the *t*-butoxybutenyl radical (approximately 2:1). This may be due in part to the greater role played by carbonium ion processes with *t*-butoxybutenyl radicals in comparison to butenyl radicals (*vide supra*).[10] Acetate is completely interchangeable with benzoate derived from *t*-butyl perbenzoate in acetic acid. These observations, however, are not paralleled by *t*-butoxybutenyl radicals derived from *t*-butyl hydroperoxide and ferrous salt at 0°. In the latter system the methyl ethers are the preferred products even in the presence of gross amounts of acetic acid. We tentatively attribute this apparent inconsistency in the behavior of *t*-butoxybutenyl radicals in intermolecular competitive reactions to the different temperatures at which the reactions were carried out. At present little is known regarding the equilibrium constants of the exchange reactions of cupric salts.[2]

Although the oxidations of *t*-butoxybutenyl and butenyl radicals by cupric salts such as acetate, benzoate and methoxide can be characterized as proceeding *via* transition states in which the radical moiety has attained an appreciable amount of carbonium ion character (electron transfer), the same is not true if chloride and bromide ligands are present. Thus, the distribution of products obtained from these allylic radicals and cupric chloride is not the same as those obtained with oxyanions under essentially the same conditions. For example, *t*-butoxybutenyl radical with cupric chloride yields mainly the 1,4-adduct 4-*t*-butoxy-1-chlorobutene-2, whereas with cupric acetate it yields mainly the 1,2-adduct, 4-*t*-butoxy-3-acetoxybutene-1. The distribution between the two isomeric *t*-butoxychlorobutenes obtained from butadiene, *t*-butyl hydroperoxide, ferrous and cupric chloride (65% 1,4 and 35% 1,2) is fortuitously similar[13] to that obtained from the free radical addition of *t*-butyl hypochlorite to butadiene

---

(12) J. Kochi and F. Rust, to be published.

(13) The predominance of the 1,4-adduct may be attributable to the rearrangement of the less stable 1,2-isomer by cuprous chloride.[14] Under the mild and dilute reaction conditions this possibility appears unlikely. It would be expected that accompanying the catalytic rearrangement there would be a simultaneous solvolysis. We could not isolate, however, any solvolytic product corresponding to those found by De La Mare, *et al.*, *viz.*, the *t*-butoxybutenyl methyl ethers. Moreover, 4-*t*-butoxy-3-chlorobutene-1 charged into the reaction was recovered unchanged. The equilibrium mixture of the related dichlorobutenes consists of about 35% 1,2- and 65% 1,4-adduct.[14,15]

(14) G. Hearne and D. LaFrance, U. S. Patent 2,446,476; P. Kurtz, *et al.*, *Ann.*, **631**, 21 (1960); M. Farlow, U. S. Patent 2,518,608.

(15) O. Nicodemus and W. Schmidt, U. S. Patent 2,242,084.

(74% 1,4 and 26% 1,2). This observation, together with evidence previously cited,[6,9,10,12] has been used to describe the oxidation of free radicals by metal salts such as cupric chloride, bromide and thiocyanate, as a ligand transfer process. The transition state for the ligand transfer process differs from that of the electron transfer process mainly in the relative contribution of the carbonium ion and the free radical forms.[2,3,6,10,12] In the ligand transfer process, the carbonium ion contribution is minimal, whereas in electron transfer processes it lends an important part to the driving force of the oxidation. The converse is applicable to the role played by free radical forms. The attainment of carbonium ion character in the transition state is associated with the conversion of the copper from the cupric to the cuprous valence. The importance of the coördination of copper with the π-bond of the allylic radical during the oxidation step postulated earlier is consistent with the electron transfer process. Since the driving force for ligand transfer is associated with the free radical character (*e.g.*, XVa) of the transition state, it is expected that the reaction would take the course approaching that of other radical chain reactions (*e.g.*, conversion of butenyl radicals to crotyl derivatives mainly), and that coördination of the π-bond with copper in the transition state is minimal. A similar discussion can be based on Hammond's postulate[16] if it is assumed that oxidations by ligand transfer are more exothermic than those by electron transfer.

The oxidation of the *t*-butoxybutenyl radical by cupric salts to form 1:1 adducts competes with a propagation reaction to form telomers with several butadiene units (reactions such as 14 and 15). However, these competing radical chain

$$t\text{-BuOC}_4\text{H}_6\cdot + n\text{C}_4\text{H}_6 \longrightarrow t\text{-BuO(C}_4\text{H}_6)\cdot_{n+1} \qquad (14)$$

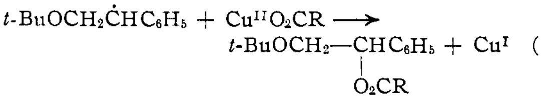
$$t\text{-BuO(C}_4\text{H}_6)\cdot_{n+1} + \text{Cu}^{\text{II}}\text{O}_2\text{CR} \longrightarrow \text{Cu}^{\text{I}} + t\text{-BuO(C}_4\text{H}_6)_{n+1}\text{-O}_2\text{CR} \qquad (15)$$

reactions can be completely eliminated by increasing the cupric salt concentration. Since in this system only carbon radicals are oxidized by cupric salts, it is possible to control the reaction to produce only 1:1 butadiene–perester adducts.

With styrene monomer, the propagation step 17 is fast relative to the termination step 18 and 1:1 adducts with peracetate are not formed even under conditions employing excess cupric salt. However,

$$t\text{-BuO}\cdot + \text{C}_6\text{H}_5\text{CH}{=}\text{CH}_2 \longrightarrow t\text{-BuOCH}_2\underset{\cdot}{\text{C}}\text{HC}_6\text{H}_5 \qquad (16)$$

$$t\text{-BuOCH}_2\dot{\text{C}}\text{HC}_6\text{H}_5 + n\text{C}_6\text{H}_5\text{CH}{=}\text{CH}_2 \longrightarrow t\text{-BuO(CH}_2\text{CHC}_6\text{H}_5)\cdot_{n+1} \qquad (17)$$


(18)

$$t\text{-BuOCH}_2\dot{\text{C}}\text{HC}_6\text{H}_5 + \text{Cu}^{\text{II}}\text{O}_2\text{CR} \longrightarrow t\text{-BuOCH}_2\text{—}\underset{\displaystyle \text{O}_2\text{CR}}{\underset{|}{\text{CHC}_6\text{H}_5}} + \text{Cu}^{\text{I}} \qquad (18)$$

in a slightly different system which employs ferric chloride as a terminating agent, it is possible to prevent telomer formation.[17] Thus, benzoyl peroxide reacts with styrene in the presence of equivalent amounts of ferric chloride to form the 1:1 adduct, 2-benzoxy-1-chloroethylbenzene, in good yield.[9a]

In methanol solvent the high yields of 2:1 butadiene–perester adducts formed relative to 1:1 adducts indicate that the chain transfer step 19 involving methanol does not complete too effectively with the polymerization step 14 for allylic radicals. The formaldehyde obtained, thus, must arise *via* the attack of *t*-butoxy radicals on methanol (20), followed by reaction 21.

$$t\text{-BuOC}_4\text{H}_6\cdot + \text{CH}_3\text{OH} \longrightarrow t\text{-BuOC}_4\text{H}_7 + \cdot\text{CH}_2\text{OH} \qquad (19)$$

$$t\text{-BuO}\cdot + \text{CH}_3\text{OH} \longrightarrow t\text{-BuOH} + \cdot\text{CH}_2\text{OH} \qquad (20)$$

$$\cdot\text{CH}_2\text{OH} + \text{Cu}^{\text{II}} \longrightarrow \text{CH}_2\text{O} + \text{Cu}^{\text{I}} + \text{H}^+ \qquad (21)$$

Since polymerization reactions (14) are important in the reactions with conjugated dienes, the effect of cupric salt concentration on the yield of 1:1 adducts is much more significant than it is with the formation of butenyl esters from butene substrates.[2,3]

t-Butyl Hydroperoxide and Copper Salts.—Earlier Kharasch and Fono[18] reported that olefins reacted with *t*-butyl hydroperoxide to produce substituted *t*-butyl peroxides. There are several routes by which these peroxides can arise,[6] of which one involves the formation of *t*-butylperoxy radicals by the oxidation of *t*-butyl hydroperoxide. If such peroxy radicals are intermediates they will be trapped by butadiene as *t*-butylperoxybutenyl radicals.[5] We could find no evidence for the formation of such adducts in acetic acid and methanol solutions. Instead a 50% yield of a mixture of *t*-butoxybutenyl acetates were formed which had the same composition of 1,2- and 1,4-adducts as those obtained from *t*-butyl peresters and butadiene. This leads us to postulate tentatively that *t*-butylperoxy radicals are not intermediates in the reaction of *t*-butyl hydroperoxides and copper salts. The mechanism of this reaction appears to be similar to that of peresters in that *t*-butoxy radicals are the reactive intermediates.[19] The initial reaction is postulated to be[6]

$$t\text{-BuO}_2\text{H} + \text{Cu}^{\text{I}} \longrightarrow t\text{-BuO}\cdot + \text{Cu(OH)}^{\text{II}} \text{ etc.} \qquad (23)$$

---

(16) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(17) The different reactivities of various alkyl radicals toward cupric salts in oxidation-reduction reactions are general phenomena. The distinction among alkyl radicals shown by cupric halides in ligand transfer reactions is not great. Although quantitative data are not yet available, it is shown qualitatively that electron donor and electron acceptor radicals react with equal facility with cupric halides.[12] In electron transfer reactions, however, cupric salts (sulfate, perchlorate, carboxylate, etc.) show enhanced discrimination toward these radicals.[10] The difference between ligand transfer reactions and electron transfer reactions is attributable in part to the degree of carbonium ion character in the transition state of the oxidation-reduction reactions.[2,10,12]

(18) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **23**, 324 (1958); **24**, 72 (1959).

(19) These conclusions should be accepted with certain reservations for the following reasons. The material balances in these reactions are poor and the best yields of 1:1 adducts obtained was 50%. Although water and *t*-butyl alcohol were formed, they were not quantitatively determined. (However, neither oxygen nor high molecular weight products were in evidence.) There is a possibility that *t*-butyl hydroperoxide in acetic acid produces *t*-butyl peracetate. Furthermore, it is possible that *t*-butylperoxy compounds are formed, but are catalytically destroyed. If this were true, oxidation products of butadiene should be observed. The decomposition of dialkyl peroxides by cuprous salts is, however, slow at these temperatures.[3,6]

Peroxy radicals may be intermediates in systems which are inert to free radicals. The formation of oxygen under these conditions was observed by Kharasch and Fono[18] and is compatible with peroxy radicals as intermediates. In the presence of compounds reactive to free radicals, no or little oxygen is formed and our studies indicate that peroxy radicals are not intermediates. We do not consider this duality to be satisfactory and will investigate the problem further.

Experimental

Materials.—*t*-Butyl peracetate: Lucidol Corp., 75% in benzene; redistilled before use; b.p. 28–30° (5 mm.), $n^{25}_{\rm D}$ 1.4027. *t*-Butyl perbenzoate: Lucidol Corp., used as such. *t*-Butyl hypochlorite: Prepared according to the procedure of Teeter and Bell.[20] *t*-Butyl hydroperoxide: Lucidol Corp. (68%) redistilled before use; m.p. 3–4°, b.p. 37–38° (16 mm.), (96–97% by titration). Butadiene: Matheson Company, C.P. grade, distilled from cylinder. Isoprene: Phillips Petroleum Co., polymerization grade. Styrene: Eastman Kodak Co. white label, redistilled before use. Cupric chloride, $CuCl_2 \cdot 2H_2O$: Baker analyzed reagent dehydrated at 100° *in vacuo*. Cupric sulfate, $CuSO_4 \cdot 5H_2O$: Baker analyzed reagent. Cuprous bromide: Amend Drug and Chemical Co., C.P. grade. Cupric Acetate, $Cu(OAc)_2 \cdot H_2O$: Baker analyzed reagent. Silver acetate, AgOAc: Baker and Adamson. Silver trifluoroacetate, $AgO_2C_2F_3$: Kindly supplied by Dr. H. V. Holler; prepared from silver oxide and trifluoroacetic acid.

***t*-Butyl Hypochlorite with Butadiene.**—To a 1-liter round-bottom flask with a magnetic stirrer and immersed in a large battery jar filled with an ice–water slurry was added 400 ml. of carbon tetrachloride, 150 ml. of butadiene and 21 g. of freshly redistilled *t*-butyl hypochlorite. Oxygen-free nitrogen was flushed over the yellow solution for 15 minutes. The irradiation was conducted with a 200-watt frosted light bulb placed directly into the stirred ice slurry. The reaction became colorless in approximately 0.5 hour. The reaction mixture was distilled *in vacuo* to remove the butadiene, carbon tetrachloride, acetone and *t*-butyl alcohol. The carbon tetrachloride solution was weighed and analyzed for total hydroxyl value (nitrite method). The titrated yield of *t*-butyl alcohol was 0.025 equiv. (~13%). The acetone was estimated to be formed in approximately 5%. The combined yield of chloro-*t*-butoxybutenes was 22.2 g. (71.5%). The distillation of the chloro-*t*-butoxybutenes yielded 4.3 g. (13.5%) of 3-chloro-4-*t*-butoxybutene-1 (b.p. 50–55° (10 mm.), $n^{25}_{\rm D}$ 1.4372) and 17.7 g. (55%) of 1-chloro-4-*t*-butoxybutene-2 (b.p. 69–72° (10 mm.), $n^{25}_{\rm D}$ 1.4526). *Anal.* Calcd. for $C_8H_{15}OCl$: C, 59.1; H, 9.30; Cl, 21.8; bromine number, 98. Found (3-chloro-4-*t*-butoxybutene-1): C, 59.0; H, 9.1; Cl, 21.5; bromine number, 97. Found (1-chloro-4-*t*-butoxybutene-2): C, 59.1; H, 9.3; Cl, 21.5; bromine number, 99. The two isomeric chlorobutenyl *t*-butyl ethers were cleanly separated by G.L.C. in a 5-foot diethylene glycol succinate–Chromosorb W at 115° (4-*t*-butoxy-3-chlorobutene-1, 5.6′; 4-*t*-butoxy-1-chlorobutene-2, 17.0′). In general, it was found that of two allylic butene isomers, the terminally unsaturated derivative emerged faster. The structural assignments of the two isomers were made on the basis of their infrared spectra. The spectra differ significantly only in the fingerprint region (10–14 μ). The lower boiling isomer has absorption bands at 10.15(s), 10.8(s), (11.3, 11.5), 12.7(s) and 14.15(s) while the higher boiling isomer absorbs at 10.38(s), (11.2, 11.5), 12.8(w), 13.3(w) and 14.7-(s) μ. The doublet at 10.2 and 10.8 is characteristic of the vinyl group and the absorption band at 10.3 is characteristic of a *trans*-butene structure. In addition to the compounds given above, there was formed 2.1 g. of an unidentified compound(s) boiling at 135–138° (760 mm.). The infrared spectrum indicates that they are unsaturated and do not appear to possess other functional groups; there are prominent bands at 3.5(s), 6.1(m), 7.0(m), 8.8(w), 10.1(m), 11.0(s) and 13.7(s) μ. They were not characterized further (*vide infra*).

If the irradiation is carried out at 20°, essentially the same results are obtained. The yield of *t*-butyl alcohol is 9%, and the combined yield of chloroethers is 74.5% and the distribution between the 1,2-adduct and 1,4-adduct is not significantly changed. If the ratio of butadiene to hypochlorite, however, is reduced, the yield of *t*-butyl alcohol becomes significant. A reaction consisting of 21 g. of *t*-butyl hypochlorite, 33 ml. of butadiene and 400 ml. of carbon tetrachloride at 0° yields 29% *t*-butyl alcohol and 58% of chloroethers. In benzene solution (400 ml.), *t*-butyl hypochlorite (130 g.) and butadiene (130 g.) reacted at 10° in 1 hour to yield 73 g. of mixed *t*-butoxychlorobutene isomers. The crude reaction mixture analyzed by G.L.C. was found to contain 25% 4-*t*-butoxy-3-chlorobutene-1 and 75% 4-*t*-butoxy-1-chlorobutene-2. Distillation yielded 2 cuts: b.p. 45–62° (10 mm.), $n^{25}_{\rm D}$ 1.4381–1.4398, 16 g.; and b.p. 65–70° (10 mm.), $n^{25}_{\rm D}$ 1.4499–1.4532, 55 g.

4-*t*-Butoxy-1-chlorobutene-1 (22.7 g.) in 25 ml. of tetrahydrofuran was added dropwise (over 0.5 hour) to a refluxing suspension of 5.3 g. of lithium aluminum hydride in 150 ml. of purified tetrahydrofuran. The mixture was refluxed for an additional hour, cooled and carefully poured into an ice-water slurry. The mixture was diluted with *n*-pentane and carefully treated with chilled, dilute sulfuric acid. The pentane extract was immediately washed with saturated $NaHCO_3$ and dried over K_2CO_3. Distillation yielded 15 g. of colorless material boiling at 129–130° (760 mm.), $n^{25}_{\rm D}$ 1.4117. *Anal.* Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58; bromine no., 125. Found: C, 74.3, 74.4; H, 12.5, 12.4; bromine no., 122, 123.

t-Butyl crotyl ether (2 g.) was hydrogenated at atmospheric pressure and room temperature with platinum catalyst in ethyl acetate solution. Filtration followed by distillation yielded 1.7 g. of material boiling at 121° (760 mm.). The infrared spectrum was the same as an authentic sample of *t*-butyl *n*-butyl ether prepared by the method of Norris and Rigby.[21]

***t*-Butyl Hydroperoxide with Butadiene and Cupric Chloride.**—In 200 ml. of methanol was dissolved 54 g. of butadiene, 17 g. of cupric chloride ($CuCl_2 \cdot 2H_2O$) and 25 ml. of concentrated hydrochloric acid. To the stirred solution at 0° was added simultaneously a solution of 60 g. of ferrous chloride in 80 ml. of water and 30 g. of *t*-butyl hydroperoxide in 50 ml. of methanol. The solution became brown but remained homogeneous. After stirring an additional half hour, it was poured into 1 liter of water and extracted twice with chloroform. The chloroform extract after washing with water and drying with sodium sulfate on distillation yielded 23.9 g. (49%) of the mixture of chloro-*t*-butoxybutenes. It was shown by distillation and comparison of the infrared spectrum of the crude material that this mixture of isomeric chloro-*t*-butoxybutenes had the same distribution of isomers as that obtained from the reaction of *t*-butyl hypochlorite and butadiene described earlier. Less than 5% *t*-butoxybutenyl methyl ethers was formed in these reactions (*vide infra*). The main side reaction appeared to be oxidation of methanol solvent to formaldehyde, presumably by *t*-butoxy radical attack. When authentic 4-*t*-butoxy-3-chlorobutene-1 was charged into the reaction, it was recovered unchanged. There was, thus, no rearrangement of the chlorobutenes under these reaction conditions. In addition, the compounds described earlier in the *t*-butyl hypochlorite reaction were also formed in these reactions with *t*-butyl hydroperoxide under quite different conditions. The infrared spectra of these compounds are the same as those described earlier. The residual material is less than 0.5 g.

***t*-Butyl Hydroperoxide with Butadiene and Cupric Sulfate.**—The procedure of DeLaMare, *et al.*,[10] was repeated using 50 g. of 97% *t*-butyl hydroperoxide, 200 g. of butadiene, 600 ml. of methanol and a solution of 100 g. of ferrous sulfate and 40 g. of cupric sulfate in 400 ml. of water. The reaction was stirred at 0° for 2 hours and worked up in the usual manner; G.L.C. of the crude pentane extract indicated the 4-*t*-butoxy-3-methoxybutene-1 isomer (72%) to predominate over the 4-*t*-butoxy-1-methoxybutene-2 (28%). Distillation of the reaction mixture yielded two fractions: b.p. 97–105° (100 mm.), $n^{25}_{\rm D}$ 1.4142–1.4157, 43 g.; and b.p. 115–122° (100 mm.), $n^{25}_{\rm D}$ 1.4240–4262, 9 g. The infrared spectra of the two fractions were the same as those obtained by DeLaMare. They were cleanly separated by G.L.C. on a 5-foot diethylene glycol succinate–Chromosorb W column at 115° (4-*t*-butoxy-3-methoxybutene-1, 3.9′; 4-*t*-butoxy-1-methoxybutene-2, 11.8′). *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.4; H, 11.5; bromine number, 101. Found (4-*t*-butoxy-3-methoxybutene-1): C, 68.2; H, 11.4; bromine number, 101. Found (4-*t*-butoxy-1-methoxybutene-2): C, 68.1; H, 11.4; bromine number, 100. The infrared spectrum of 4-*t*-butoxy-3-methoxybutene showed distinguishing bands at 10.05(m), 10.8(s), 11.30(s), 11.8(w) and 13.3(m)μ; and 4-*t*-butoxy-1-methoxybutene-2: 10.30(s), 11.9(w), 11.35(w) and 13.4(w)μ.

Silver-ion Assisted Solvolysis.—The butoxychlorobutene isomers obtained pure from the reaction of *t*-butyl hypochlorite and butadiene were solvolyzed in acetic acid, methanol and combinations of these solvents with benzene and

---

[20] H. Teeter and E. Bell, *Org. Syntheses*, **32**, 20 (1952).

[21] J. Norris and G. Rigby, *J. Am. Chem. Soc.*, **54**, 2096 (1932).

acetonitrile. The procedure was to add the chloride to a solution of the silver salt. Silver trifluoroacetate in general was more soluble than silver acetate in these solvents. The solvolysis of 4-*t*-butoxy-1-chlorobutene-2 in silver acetate–acetic acid at 50–60° for 4 hours was less than 20% complete. However, heating at 100° for 2 hours led to complete reaction. There was formed in 82% yield a mixture consisting of 62% 4-*t*-butoxy-1-acetoxybutene-2 and 38% 4-*t*-butoxy-3-acetoxybutene-1. The former boiled at 42–47° (2 mm.), $n^{25}\mathrm{D}$ 1.4268, and the latter boiled at 55–59° (2 mm.), $n^{25}\mathrm{D}$ 1.4341–1.4358. The infrared spectra of these isomers differed mainly in the fingerprint region: 4-*t*-butoxy-3-acetoxybutene-1, 10.05(m), 10.7(m), 11.40(m) and 13.25(w)μ; 4-*t*-butoxy-1-acetoxybutene-2, 10.30(m), 10.8(w) and 11.40(w)μ. The G.L.C. of the isomers was also examined on a 5-foot diethylene glycol succinate–Chromosorb W column at 115° (4-*t*-butoxy-3-acetoxybutene-1, 5.1′; 4-*t*-butoxy-1-acetoxybutene-2, 19.0′. *Anal.* Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74; bromine number, 86, ester value, 0.537. Found (4-*t*-butoxy-3-acetoxybutene-1): C, 64.0; H, 9.5; bromine number, 83; ester value, 0.542. Found (4-*t*-butoxy-1-acetoxybutene-2): C, 64.1; H, 9.5; bromine number, 86; ester value, 0.536.

The methanolysis of 4-*t*-butoxy-1-chlorobutene-2 in a solution of silver trifluoroacetate in methanol at 25–30° for 16 hours yielded a mixture of *t*-butoxybutenyltrifluoroacetates and methyl ethers. The *t*-butoxybutenyl methyl ether fraction was constituted of 22% 4-*t*-butoxy-3-methoxybutene-1 and 78% allylic isomer. A mixture of *t*-butoxychlorobutenes rich in the 4-*t*-butoxy-1-chlorobutene isomer (72%) under similar conditions yielded the methyl ether mixture which was analyzed for 46% 4-*t*-butoxy-3-methoxybutene-1 and 54% 4-*t*-butoxy-1-methoxybutene-2.

In acetic acid solution, a significant proportion (40–60%) of the chlorobutene solvolyzed to the trifluoroacetate product. Thus, 4-*t*-butoxy-3-chlorobutene-1 (72% in mixture) yielded 50–60% *t*-butoxytrifluoroacetoxybutenes and 30% *t*-butoxyacetoxybutenes. The latter mixture analyzed for 50% of each isomer. Pure 4-*t*-butoxy-1-chlorobutene-2 under the same conditions yielded 40–50% trifluoroacetate and 40% acetate. The acetate fraction analyzed for 18% 4-*t*-butoxy-3-acetoxybutene-1 and 82% allylic isomer.

In a complex solution containing 50% v. methanol, 25% v. acetic acid and 25% v. acetonitrile, 4-*t*-butoxy-1-chlorobutene-2 undergoes reaction in the presence of silver trifluoroacetate to yield predominantly *t*-butoxy trifluoroacetoxybutenes (approximately 60%) and smaller amounts of *t*-butoxymethoxybutenes (approximately 30%) and *t*-butoxyacetoxybutenes (1%). The methyl ether mixture was analyzed for 11% *t*-butoxy-3-methoxybutene-1 and the remainder allylic ether. The mole ratio of total ether to ester was approximately 30–35.

A solution of 4-*t*-butoxy-1-chlorobutene-2 was heated with potassium acetate in glacial acetic acid at 90° for 20 hours. Approximately 70% underwent acetolysis to 4-*t*-butoxy-1-acetoxybutene-2 with small amounts (approximately 5–10%) of 3-acetoxy isomer.

Reaction of *t*-Butyl Peracetate with Butadiene.—The procedure was that described earlier.[2] A solution of 40 g. (80%) of *t*-butyl peracetate, 48 g. of butadiene and 100 ml. of benzene with 0.203 g. of cuprous bromide reacted at 80–85° for 30 hours. The crude reaction mixture was homogeneous and yellow indicating that the copper was present mainly in the cuprous state. There was an accompanying 5–7% decrease in the reaction volume. The unreacted butadiene was distilled and an aliquot of the residue titrated for acetic acid potentiometrically. It was also saponified to determine the total ester content. The mixture was then extracted with dilute HCl once and $NaHCO_3$ solution until neutral. After drying with Na_2SO_4, the mixture was distilled. In several representative reactions 8–10% acetic acid and 90–92% total esters were formed. The material balance represented by the acid and esters produced with the perester charged was within 1–2%. The esters were isolated by distillation at 2 mm. There was obtained 18.8 g. boiling at 48–57° of a fraction which was a mixture of the two isomeric *t*-butoxyacetoxybutenes IV and V. The mixture was the same as that obtained from the acetolysis of the *t*-butoxychlorobutenes obtained previously. There was also obtained a fraction boiling at 60–106° (22.2 g., $n^{25}\mathrm{D}$ 1.4451–1.4547) which was probably a mixture of *t*-butoxyacetoxyoctadienes. The infrared spectra and analysis were compatible with these structures. G.L.C. (5 foot DEGS/Chromosorb W) indicated at least three isomers were present. *Anal.* Calcd. for $C_{14}H_{24}O_3$: C, 70.0; H, 10.1; bromine number, 133; ester value (equiv./100 g.), 0.417. Found: C, 69.8; H, 10.0; bromine number, 131; ester value, 0.414. By distillation no evidence for the formation of *t*-butoxydodecatrienes could be found.

The reaction in methanol solution (75 ml.) was charged with 41.1 g. (80% benzene solution) of *t*-butyl peracetate, 47 g. of butadiene and 0.203 g. of cuprous bromide. The crude reaction mixture (colorless) analyzed for 0.044 equiv. carbonyl (formaldehyde), 0.070 equiv. (27%) acetic acid and 0.19 equiv. (73%) total ester. After workup, distillation yielded 0.08 equiv. (31%) of methyl acetate and 0.031 equiv. of formaldehyde (isolated as the methone derivative, m.p. 187–188°). The higher ester fraction (44%) consisted predominantly (approximately 70%) of the *t*-butoxyacetoxybutenes (82% 4-*t*-butoxy-3-acetoxybutene-1 and 18% 4-*t*-butoxy-1-acetoxybutene-2). In addition to the esters there was formed a mixture of *t*-butoxymethoxybutenes (72% 4-*t*-butoxy-3-methoxybutene-1 and 28% 4-*t*-butoxy-1-methoxybutene-2). The mole ratio of total *t*-butoxybutenyl acetates to ethers was 1.64. An insoluble precipitate (0.92 g.) of polybutadiene was isolated (C, 87.1; H, 10.9).

A homogeneous solution of butadiene (53 g.), redistilled *t*-butyl peracetate (35.8 g.), cuprous chloride (0.304 g.) and cupric acetate (2.007 g.) in 100 ml. of acetonitrile was heated 70–85° for 30 hours. An aliquot of the light yellow solution was analyzed for acetic acid (0.024 equiv.) and total ester (0.240 equiv.). Two hundred ml. of *n*-pentane was added and the mixture extracted several times with water and saturated $NaHCO_3$. After drying (Na_2SO_4) it was distilled (33 g. of 1:1 adduct boiling at 46–72° (2 mm.); 5.5 g. of 2:1 adduct boiling at 85–120° (2 mm.); and 2 g. of residue). A similar reaction in a solution of 50 ml. of acetic acid and 50 ml. of benzene yielded a dark green homogeneous solution which precipitated cupric acetate on cooling. Workup yielded a clean distilling product in two fractions: 85–88° (15 mm.) 1,2-adduct, 38 g.; 104–110° (12 mm.), 1,4-adduct, 7.8 g.; and approximately 0.5 g. of residue.

In each of the preceding cases, the ratio of 4-*t*-butoxy-3-acetoxybutene-1 to 4-*t*-butoxy-1-acetoxybutene-2 constituting the 1:1 adduct mixture was determined by the G.L.C. examination (5 foot, DEGS/Chromosorb W column at 115°) of the crude reaction mixture. In addition to these products there was formed a pair of compounds which boiled slightly higher (125–130° (2 mm.)) than 4-*t*-butoxy-1-acetoxybutene-2. These compounds though separated (15′) from 4-*t*-butoxy-1-acetoxybutene-2 (19′) were not cleanly resolved between themselves. They were present (approximately in equal amounts) in the reactions using benzene and toluene as solvents in approximately 10% yield. In the acetonitrile reaction they were formed in approximately 2% yield. In methanol and acetic acid (excess cupric salt) solvents no evidence for their formation was found. *Anal.* Found for undetermined compounds: C, 68.85, 68.98; H, 9.93, 9.93; ester value, 0.497; bromine number, 116.

Reaction of *t*-Butyl Perbenzoate with Butadiene.—A solution of 40 g. of *t*-butyl perbenzoate, 46 g. of butadiene and 100 ml. of benzene with 0.203 g. of cuprous bromide reacted at 75–85° for 24 hours in sealed tubes. The light yellow solution was distilled to remove the unreacted butadiene, and extracted to remove the benzoic acid (1.3 g). An aliquot of the resulting solution was saponified (total ester 0.175 equiv., 85%), dried (Na_2SO_4) and distilled to remove volatile materials and then vacuum distilled (1 mm.). It yielded 25 g. of 4-*t*-butoxy-3-benzoxybutene-1 boiling at 94–99° ($n^{25}\mathrm{D}$ 1.4943, bands at 10.05 and 10.85μ), 6 g. of 4-*t*-butoxy-1-benzoxybutene-2 boiling at 110–118° ($n^{25}\mathrm{D}$ 1.5061, band at 10.4μ) and 9 g. of a *t*-butoxybenzoxyoctadiene mixture boiling at 140–180°. *Anal.* Calcd. for $C_{15}H_{20}O_3$: C, 72.6; H, 8.13; bromine number, 64; ester value, 0.404. Found (low boiling isomer): C, 73.0; H, 8.1; bromine number, 67; ester value, 0.40. (High boiling isomer): C, 72.7; H, 8.0; bromine number, 60; ester value, 0.42. *Anal.* Calcd. for $C_{19}H_{26}O_3$: C, 75.5; H, 8.67; bromine number, 106; ester value, 0.331. Found: C, 75.7; H, 8.4; bromine number, 97; ester value, 0.34.

Reaction of *t*-Butyl Perbenzoate with Isoprene.—Isoprene reacted under slightly different conditions. A mixture of benzene (200 ml.), isoprene (75 ml.), 20.2 g. of *t*-butyl perbenzoate and 0.212 g. of cuprous bromide in a 3-neck round-bottom flask was maintained under pressure (200 m.) at 68–70° for 50 hr. As the reaction progressed, the cuprous bromide went into solution and the mixture became bluer. The blue reaction mixture was extracted with dilute HCl and $NaHCO_3$. Benzoic acid did not precipitate on acidification of the $NaHCO_3$ washes. Distillation yielded 18 g. of material boiling at 106–109° (1 mm.), $n^{25}D$ 1.4908–1.4893; 3.6 g. boiling at 113–125° (1 mm.), $n^{25}D$ 1.4932–1.5040; and 2.2 g. of undistilled residue ($n^{25}D$ 1.5172). The distilled fractions each analyzed for the 1:1 adduct *t*-butoxybenzoxypentene (*Anal.* Calcd.: C, 73.25; H, 8.45; ester value, 0.382; bromine no., 61. Found: C, 73.3, 73.3; H, 8.4, 8.3; ester value, 0.394, 0.394; bromine no., 59, 62). The undistilled residue (*Anal.* Found: C, 75.1; H, 8.3) was not polyisoprene since prominent carbonyl bands (5.79, 5.85μ) were present in the infrared spectrum. The infrared spectrum of the lower boiling isomer exhibited distinctive bands at 10.1(m), 10.85(ms), 11.3(ms) and 11.75(m)μ. It was probably a mixture of 4-*t*-butoxy-3-benzoxy-2-methylbutene-1 and 4-*t*-butoxy-3-benzoxy-3-methylbutene-1. The higher boiling component showed bands in the infrared spectrum at 10.6(m) and 11.2(m)μ and is probably a mixture containing the 1,4- and 4,1-adducts of *t*-butyl perbenzoate to isoprene.

Reaction of *t*-Butyl Perbenzoate with Styrene.—In an apparatus similar to the reaction with isoprene were charged 75 g. of *t*-butyl perbenzoate, 180 g. of styrene, 200 ml. of benzene and 0.403 g. of cuprous bromide. The reaction was heated at 85–95° for 30 hours. Benzoic acid (20.8 g.) was extracted from the crude reaction mixture. In addition, 142 g. of polystyrene was precipitated with methanol (*Anal.* Calcd. for C_8H_8: C, 92.26; H, 7.74. Found: C, 91.7; H, 7.7). Approximately 10 g. of viscous oil was also obtained.

A homogeneous mixture of 60 g. of *t*-butyl peracetate, 100 g. of styrene, 10 g. of cupric acetate and 0.3 g. of cuprous chloride in 200 g. of acetonitrile was allowed to react at 75–80° for 24 hours. Analysis indicated the presence of unreacted *t*-butyl peracetate. It was reheated for an additional 24 hours at 80°. The dark green solution was decanted from approximately 20 g. of viscous oil and washed with water, and $NaHCO_3$ after dilution with a mixture of *n*-pentane and ether. After drying and distillation of the solvent, the residue was an orange-colored viscous residue. Infrared analysis indicated the presence of benzoate and *t*-butoxy end groups.

Acknowledgment.—I wish to thank Mr. Fred Rodgers for valuable technical assistance and Dr. Paul Berrigan for helpful suggestions.

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

The Cyclopropenylcarbinyl Cation, a Non-classical Carbonium Ion

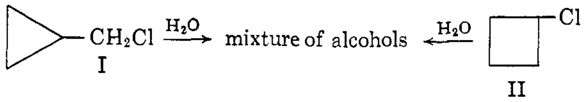
BY RONALD BRESLOW, JOYCE LOCKHART AND AUDREY SMALL

RECEIVED FEBRUARY 15, 1962

The solvolysis of diphenylcyclopropenylcarbinyl tosylate proceeds with ring expansion to diphenylcyclobutenyl cation. The rate of this process shows that a non-classical carbonium ion is involved; rate studies on *p*-anisylphenylcyclopropenylcarbinyl tosylate show that the double bond is not directly involved in the ionization, but that the process is analogous to that in the cyclopropane series, involving delocalization of a ring single bond. From the observation that neither the double bond nor the extra methoxyl group have an appreciable effect on the rate of solvolysis a transition state is deduced which resembles, both geometrically and stereoelectronically, the starting cyclopropenylcarbinyl system. This result is discussed in terms of other evidence on the structure of the bicyclobutonium ion. The expected effect of a methoxyl group on the rate as a function of the geometry of the transition state is treated by use of simple m.o. calculations.

Introduction

In recent years considerable attention has been devoted to the non-classical carbonium ions derived from cyclopropylcarbinyl derivatives. Roberts and Mazur[1] first showed that the solvolysis of cyclopropylcarbinyl chloride (I) is considerably faster than is that of β-methylallyl chloride, the cyclopropane ring being thus even more effective than a double bond in stabilizing the developing carbonium ion. They showed that cyclobutyl chloride (III) is also unexpectedly reactive, and that the same mixture of products is obtained from solvolysis of I or II.

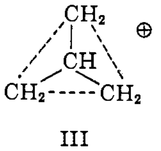


I

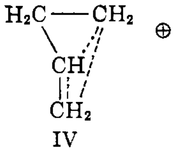
II

Shortly thereafter Bergstrom and Siegel[2] reported observations on the fast solvolysis of cyclopropylcarbinyl benzenesulfonate. To explain these high rates it was clear that transition states resembling non-classical carbonium ions must be invoked, and for a time[1,2] it was considered that a tricyclobutonium ion (III) might be the first intermediate in these solvolyses. However, subsequent studies[3-7] have demonstrated clearly that the incipient ionization of I involves the delocalization of electrons from the C_2–C_3 σ-bond, the intermediate in solvolysis being a bicyclobutonium ion (IV).

It has been found[4,8] that substituents on C-3 and C-4 have little effect on the rate of solvolysis, but that a methyl group on C-2 accelerates it fifty times.[6] Coupled with the evidence that the more stable open chain alcohol is formed to only a slight extent, this suggests that the bicyclobutonium ion has its charge distributed chiefly over C-1 and C-2. Furthermore, substituent effects[5-7] in the solvoly-



III



IV

---

[1] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509, 3542 (1951).

[2] C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145, 254 (1952).

(3) R. H. Mazur, *et al.*, *ibid.*, **81**, 4390 (1959).

(4) S. Borčić, M. Nikoletić and D. E. Sunko, *ibid.*, **84**, 1615 (1962), and earlier work.

(5) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959).

(6) E. Cox, M. Caserio, M. Silver and J. Roberts, *ibid.*, **83**, 2719 (1961); M. Silver, M. Caserio, H. Rice and J. Roberts, *ibid.*, **83**, 3671 (1961).

(7) R. A. Sneen and A. L. Baron, *ibid.*, **83**, 614 (1961).

(8) R. A. Sneen, K. M. Lewandowski, I. A. I. Taha and B. R. Smith, *ibid.*, **83**, 4843 (1961).