tion of 2-mercaptobenzophenone; principal infrared bands were at 3.97 and 6.00 μ. The disulfide melted at 167–168.5° (lit.[19] 167–168°).

2-Mercaptobenzhydrol was prepared by the lithium borohydride reduction of 2-mercaptobenzophenone in 1,2-dimethoxyethane, followed by chromatography over alumina. The product was an oil; principal infrared bands were at 2.99, 3.30, 3.50, and 3.93 μ; n.m.r. showed (CCl_4) – δ 3.2, 5.8, and 7.1 in approximate ratio 2:1:9.

Anal. Calcd. for $C_{13}H_{12}OS$: C, 72.19; H, 5.59; S, 14.82. Found: C, 72.46; H, 5.63; S, 14.85.

α-Deuterio-2-mercaptobenzhydrol was prepared by the lithium aluminum deuteride reduction of mercaptobenzophenone in ether, and purified by chromatography over alumina; principal infrared bands were at 2.94, 3.25, 3.90, and 4.65 μ.

Anal. Calcd. for $C_{13}H_{11}DOS$: D, 8.33 atom % excess. Found: 5.15 atom % excess.

Isolation of Products.—Reaction of 0.01 *M* Hantzsch compound with 0.01 *M* 2-mercaptobenzophenone for 4 hr. at 69° in 70% aqueous ethanol in a sealed tube, evacuated to a pressure of 0.7 mm. gave a 90% yield of 2,6-dimethyl-3,5-dicarboethoxypyridine and a 79% yield of 2-mercaptobenzhydrol. The corresponding reaction, run for 16 hr. in a mixture of 70% CH_3OD and 30% D_2O, yielded IV together with α-deuterio-2-mercaptobenzhydrol which was identical (infrared and n.m.r.) with authentic material. Reduction using 4-deuterio Hantzsch compound yielded 2-mercaptobenzhydrol, which was purified by chromatography on Florisil. It showed no deuterium in infrared, and analysis for deuterium showed 0.00 atom % excess deuterium. (Deuterium analyses were by J. Nemeth, Urbana, Ill.)

Methods.—Reductions were followed by measuring the disappearance of the ultraviolet absorbance of the dihydropyridines, which show a broad absorption band between 340 and 370 mμ. This band is absent in the corresponding pyridine, and usually absent in the other reactants or products. For more concentrated solutions, the shoulder of the band (up to 430 mμ) was used, or a sample was withdrawn and diluted for ultraviolet measurement. Anaerobiasis was established either by multiple degassing on the vacuum line or more conveniently by scrubbing the solution with prepurified nitrogen in a special cuvette[20] equipped with gas-bubbling tube and a ground joint designed to hold a slight pressure of nitrogen.

The "pH" values reported for 70% ethanol are those measured for the various buffers in water, increased by 1.5 pH units. This procedure approximately compensates for the change in meter reading for 0.001 *M* HCl between water and 70% ethanol.

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[20] Designed by I. Fridovich.

Studies on the Mechanism of the Reaction of Peroxides and Alkenes with Copper Salts*,[1]

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Pertinent new information regarding the mechanism of the reactions of peroxides, particularly *t*-butyl peresters, with alkenes catalyzed by copper salts has accumulated in the last several years. The various mechanisms which have been proposed for these reactions since their discovery by Kharasch and his co-workers are reviewed critically. The original assertion that the substitution occurs without migration of the double bond is no longer tenable and mechanisms which have been invoked on this basis must be modified. The mechanism which involves free alkyl and alkenyl radicals as intermediates and copper salts in an oxidation–reduction capacity is elaborated. The essential unity between these perester types of substitution reactions and the catalyzed decomposition of peroxides is stressed. For example, octenyl acetates can be generated from octene-1 and *t*-butyl perester and they consist of the same isomeric mixture as that produced from valeryl peroxide and butadiene. The oxidation of allylic radicals by cupric salts is examined further. The conclusion that the high specificity in the oxidation of octenyl and related radicals by cupric salts arises from an interaction between the incipient carbonium ion and the copper(I) species is further delineated.

Since the discovery of the metal salt promoted reactions of peroxides with organic substrates,[2] there have been a number of additional examples of its synthetic utility.[3,4] Of the variety of hydrogen donors which have been treated with peroxides under these conditions, alkenes probably represent the one class about which the most serious investigations have revolved. No doubt information regarding the mode of substitution in alkenes would also aid in the understanding of the reactions of other substrates. Since the original review of the reaction was written,[5] other mechanisms have been proposed and recent reviews[6,7] have failed to clarify the vital steps in the reaction. We have felt that a common mechanism is applicable to *all* reactions of peroxides with copper salts, and the plethora of mechanisms serve only to obscure the basic aspects of these reactions. In this report we wish to review the pertinent available information regarding the mechanism of this interesting reaction and to present further studies concerning the common features of the perester reaction with reactions of peroxides generally with metal salts.

As described originally the perester reaction, applicable mainly to *t*-butyl peracetate or benzoate, with alkenes is given by reaction 1. Of the three necessary

$$(CH_3)_3CO_3CCH_3 + RH \xrightarrow{CuX_n} (CH_3)_3COH + RO_2CCH_3 \qquad (1)$$

components of the reaction, copper salt, perester, and alkene, only the copper salt and peroxide are required for the more general reaction involving the catalytic decomposition of peroxides.[5,8] Common intermediates are involved in both reactions (*vide infra*), and

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* Submitted in honor of Professor Louis F. Fieser by J. K. K.

[1] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

[2] (a) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **23**, 324, 325 (1958); (b) M. S. Kharasch and G. Sosnovsky, *J. Am. Chem. Soc.*, **80**, 756 (1958).

[3] (a) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 72 (1959); (b) M. S. Kharasch and A. Fono, *ibid.*, **24**, 606 (1959); (c) M. S. Kharasch and G. Sosnovsky, *Tetrahedron*, **3**, 97, 105 (1958); (d) M. S. Kharasch, G. Sosnovsky, and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959); (e) G. Sosnovsky and N. C. Yang, *J. Org. Chem.*, **25**, 899 (1960).

[4] (a) S. O. Lawesson and C. Berglund, *Arkiv Kemi*, **16**, 287 (1960); **17**, 393, 441, 421, 465, 475 (1961); (b) S. O. Lawesson, *et al.*, *Acta Chem. Scand.*, **15**, 36, 249, 260 (1961).

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

[6] G. Sosnovsky and S. O. Lawesson, *Angew. Chem., Intern. Ed. Engl.*, **3**, 269 (1964).

[7] G. Berglund and S. O. Lawesson, *Arkiv Kemi*, **20**, 225 (1963).

[8] (a) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963); (b) S. Goldschmidt, H. Späth, and L. Beer, *Ann.*, **649**, 1 (1962).

for this reason the role of each component can be discussed in common.

Catalysis by Copper(I) Salts.—Metal salts profoundly affect the rate as well as products of decomposition of a variety of organic peroxides. For example, Kharasch and Fono[2a] showed that the complexion of the reaction and the yields of products obtained in the thermal decomposition of peroxides with hydrogen donors such as octene-1 and cumene was quite different from those conducted in the presence of catalytic amounts of copper salts.

In such commonly employed solvents as benzene, the reaction is not apparently different whether cupric acetate or cuprous chloride or bromide is employed. At the temperatures at which the reaction is generally conducted (70–90°), these salts are initially insoluble. An induction period is observed, moreover, even with the soluble cupric 2-ethylhexanoate salts.[5] The length of the induction period is decreased with increasing temperature and removed by the addition of cuprous salts in homogeneous solution (acetonitrile). Furthermore, the addition of halogens, bromine or chlorine, lengthens the induction period proportionally to their concentration and in accord with their ability to oxidize copper(I) salts.[8a] Oxygen has been reported to retard the perester reaction.[9] Inhibition by halogen and retardation by oxygen is attributed mainly to oxidation of the copper(I) species.[5,9,10]

High temperatures (80–90°) need only be employed in the perester reactions if soluble copper(II) or insoluble copper(I) salts are used, since the thermal decomposition of the peroxide must then be the means to supply copper(I) salts in solution[5] (*vide infra*). The reaction can also be carried out at low temperatures (30–40°) by a rather inefficient photochemical means[11] or reducing agents such as zinc, zinc–copper couple, hydrogen-reduced copper, or hydroxylamine, which are all capable of converting copper(II) to copper(I).

When copper(I) is used to initiate the reaction it is not a true catalyst since it is consumed during the course of the reaction.[8a,12] The chain length (moles of peroxide decomposed per equivalent of cuprous salt) increases with cupric salt concentration and reaches a value of approximately 30 at 0.1 *M* cupric salt at 50° with octene-1 in glacial acetic acid. The chain length is also related to the activity of the substrate, being larger for cyclohexene than octene-1. Barnard and Yang[13] in a kinetic study found that the rate increased rapidly at low catalyst concentration but slowly at high copper concentration. Though they interpret their results in terms of a termolecular process involving copper salt, perester, and alkene on the basis of the aforementioned results, we attribute this change in rate to increasing chain lengths at higher copper concentrations. Walling and Zavitsas[9] arrive at a similar conclusion.

The Effect of the Structure of the Peroxide.—*t*-Butyl peresters are converted to *t*-butyl alcohol and alkenyl esters by copper salts and alkenes.[3d] Little carbon dioxide is liberated, and methane and acetone are formed in minor amounts. The latter products, in addition to methyl esters, increase in the presence of substrates of low reactivity and are the only identified products in benzene. This side reaction becomes the dominant reaction with the higher homologs such as *t*-amyl and *t*-heptyl peresters. Whereas *t*-butyl peracetate is slowly decomposed by copper salts in the absence of alkenes or other substrates, *t*-amyl peracetate is readily decomposed according to reaction 2.[5] Moreover, these peresters function poorly in the intermolecular substitution reactions.

$$CH_3CH_2C(CH_3)_2O_3CCH_3 \xrightarrow{CuX_n} CH_2{=}CH_2 + (CH_3)_2CO + CH_3CO_2H \quad (2)$$

Alkyl hydroperoxides can also be employed in the perester reaction.[3a] Thus, *t*-butyl and α-cumyl hydroperoxides in acetic acid react with alkenes catalytically to produce alkenyl acetates.[9,14,15] Alkyl hydroperoxides

$$C_6H_5C(CH_3)_2OOH + RH + HOAc \xrightarrow{CuX_n} C_6H_5C(CH_3)_2OH + ROAc + H_2O \quad (3)$$

with longer side chains are catalytically decomposed to alkene, ketone, and water, and are inefficient in the

$$CH_3CH_2C(CH_3)_2OOH \xrightarrow{CuX_n} CH_2{=}CH_2 + (CH_3)_2CO + H_2O \quad (4)$$

intermolecular reaction. A similar dichotomy is apparent among the dialkyl peroxides, di-*t*-butyl peroxide[3b,16] on one hand and the higher homologs on the other.[5]

Diacyl peroxides have not been employed generally as reagents for the copper-catalyzed intermolecular reactions. Benzoyl peroxide reacts with alkenes by two simultaneous processes involving substitution (similar to the reaction of peresters) and addition of the benzoyloxy moiety followed by elimination.[17] Diacetyl per-

$$(C_6H_5CO_2)_2 + RH \xrightarrow{CuX_n} RO_2CC_6H_5 + C_6H_5CO_2H \quad (5)$$

oxide behaves in a similar manner to afford addition products of methyl, such as pentenes from butenes in addition to substitution products, crotyl and α-methallyl acetates. Both of these diacyl peroxides are unique in their intermolecular reactions with alkenes, since the higher homologs of acetyl peroxide are catalytically decomposed by copper salts.[8] For example, *n*-valeryl peroxide in a variety of solvents is easily decomposed to butene-1, valeric acid, and carbon dioxide according to reaction 6. Their effectiveness in substitution reactions in the presence of added alkenes is limited.

$$(CH_3CH_2CH_2CH_2CO_2)_2 \xrightarrow{CuX_n} CH_3CH_2CH{=}CH_2 + CH_3CH_2CH_2CH_2CO_2H + CO_2 \quad (6)$$

The reaction of *t*-butyl peracetate with cyclohexene in benzene has been reported to be first order in peroxide.[13] A similar dependence on peroxide is followed in acetic acid and acetonitrile.[9] A kinetic study of the

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[9] C. Walling and A. A. Zavitsas, *J. Am. Chem. Soc.*, **85**, 2084 (1963).

[10] J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 1508 (1965).

[11] G. Sosnovsky, *J. Org. Chem.*, **28**, 2934 (1963). Sosnovsky[6] postulates that light directly affects the lability of the peroxide by photolyzing a complex between reactants. The low quantum yields observed qualitatively indicate that such is not the case, but the inefficient photochemical production of radicals [or equivalently, Cu(I)].

[12] J. K. Kochi and R. V. Subramanian, to be published.

[13] P. W. C. Barnard and N. C. Yang, *Chem. Ind.* (London), **39**, 1573 (1961).

[14] (a) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 2785 (1962); (b) *ibid.*, **84**, 3271 (1962).

[15] This differs from the original report[3a] which indicated cumene and *t*-butyl hydroperoxide in acetic acid yielded only peroxide and no acetates with copper salts. See also ref. 5.

[16] J. R. Shelton and A. Champ, *J. Org. Chem.*, **28**, 1393 (1963).

[17] J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1572 (1962).

decomposition of aliphatic acyl peroxides with metal salts is in progress.[12]

Substitution in Alkenes.—The reaction of peresters with alkenes in the presence of copper salts does not proceed by a simple direct substitution on the allylic carbon–hydrogen bond as initially reported.[2b,3d] Extensive equilibration of the alkenyl moiety is generally the rule.[18] However, 1-alkenes yield mainly 3-substituted 1-alkenes as the major product and equilibration cannot be detected easily by the use only of the terminal olefinic isomer.[2b,3d] Thus, butene-1 and *cis*- and *trans*-butene-2 react with *t*-butyl peracetate under a variety of conditions to yield the same mixture of isomeric butenyl acetates, 85–95% α-methallyl and 5–15% crotyl acetates.[18] Trimethylethylene and tetramethylethylene afford the extensively rearranged products, 2-methyl-3-benzoyloxybutene-1 and 2,3-dimethyl-3-benzoyloxybutene-1 (78%), respectively, with *t*-butyl perbenzoate.[19] The original report of the selectivity of the reaction with octene-1 has been shown to be incorrect,[9] although it has been erroneously perpetuated (*vide infra*).[20] The subsequent investigation which substantiated the original claim, by using an allylbenzene–propenylbenzene isomeric pair,[21] has been since retracted.[19]

The equilibration of the allylic moiety during the course of the reaction has been demonstrated. Optically active Δ^1-*p*-menthene reacted with *t*-butyl peracetate and cupric trimethylhexanoate as shown by Denney, *et al.*,[19] to afford a mixture of menthenyl acetates which on subsequent hydrolysis and oxidation yielded inactive 2-methyl-5-isopropylcyclohexen-2-one. More direct evidence for allylic equilibration was obtained by Goering and Mayer[22] from studies with bicyclo[3.2.1]octene-2, which yields a symmetrical alkenyl moiety. Optically active alkene (α^{25}D −80.4°) was converted by *t*-butyl perbenzoate and cuprous bromide in benzene to totally inactive bicyclo[3.2.1]-oct-3-enyl benzoate. In all cases the stability of the products to isomerization under conditions of the reaction was established.

Beside substitution *via* an equilibrated alkenyl moiety, certain peroxides like benzoyl peroxide react with alkenes by a second mode. Addition to the double bond followed by loss of a β-hydrogen generates products similar to those obtained from an equilibrated alkenyl group. Esters derived from the addition route are benzoates derived from the peroxide, and distinguished from esters by the latter route by withstanding metathesis with protic solvents (acetic acid).[17]

In general, the rate of peroxide decomposition by copper salt is less a function of the concentration of alkene as it is of its structure. The dependence on alkene concentration is not simple. It becomes half-order when excess cyclohexene is employed; the kinetic implications have been discussed.[9]

Mechanism of the Reactions.—Several mechanisms have been postulated for these reactions. A rigorous kinetic support is desired for any mechanism proposed. However, the multitude of side reactions, most of them minor but nonetheless important, has prevented a complete treatment.[9] For the most part, mechanisms have been presented on the basis of product analysis, in one form or another. Largely based on the lack of rearrangement during substitution, a termolecular mechanism involving alkene, perester, and copper salt was proposed.[6] Other modifications included alkene, *t*-butoxy radical, and copper salt in the transition state in several configurations.[20,21] The absence of an equilibrated alkenyl moiety has not been established; thus, the need for such complex mechanisms has evaporated. Moreover, the applicability of these mechanisms to substrates other than simple 1-alkenes is highly limited, and in view of the tenuous experimental evidence used in their support we consider these mechanisms unlikely.[7,23]

A chain mechanism[3d,24] has also been proposed for the perester reaction and invokes the copper salt in an oxidation–reduction capacity.[25] In protic solvents

$$(CH_3)_3CO_3CCH_3 + Cu(I) \longrightarrow (CH_3)_3CO\cdot + Cu(II)O_2CCH_3 \quad (7)$$

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \quad (8)$$

$$R\cdot + Cu(II)O_2CCH_3 \longrightarrow RO_2CCH_3 + Cu(I) \text{ etc.} \quad (9)$$

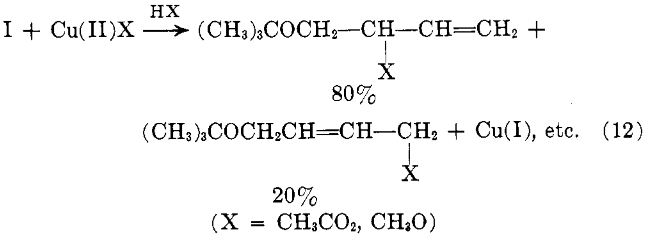
HX, the copper species are equilibrated.[5] Chain ter-

$$Cu(II)O_2CCH_3 + HX \rightleftharpoons Cu(II)X + CH_3CO_2H \quad (10)$$

mination can occur by a variety of reactions including the oxidation of copper(I) by oxy radicals,[17,26a] oxygen,[9] or methyl radicals.[26b] The latter is formed by the well-established fragmentation reaction of *t*-butoxy radicals. Dimerization and disproportionation of radicals are also potential modes of termination.

t-Butoxy radicals as intermediates (eq. 8) in these catalyzed decompositions have been trapped with butadiene in excellent yields.[14] Norbornadiene in many respects resembles conjugated dienes in its susceptibility to free-radical addition.[27] Story[28] has elegantly demonstrated that *t*-butoxynorbornadiene is formed from norbornadiene and *t*-butyl perester with copper salts by addition of *t*-butoxy radical followed by oxidation. 7-Benzoyloxynorbornadiene is formed from benzoyl peroxide by a similar route.[29]

$$(CH_3)_3CO\cdot + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \underset{\text{I}}{(CH_3)_3COCH_2CH{\cdots}CH{\cdots}CH_2} \quad (11)$$



$$\text{I} + Cu(II)X \xrightarrow{HX} \underset{80\%}{(CH_3)_3COCH_2{-}\underset{X}{\underset{|}{CH}}{-}CH{=}CH_2} + \underset{20\%}{(CH_3)_3COCH_2CH{=}CH{-}\underset{X}{\underset{|}{CH_2}}} + Cu(I), \text{ etc.} \quad (12)$$

$$(X = CH_3CO_2,\ CH_3O)$$

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[18] J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 774 (1962).

[19] D. Z. Denney, A. Appelbaum, and D. B. Denney, *ibid.*, **84**, 4969 (1962).

[20] A. L. J. Beckwith and G. W. Evans, *Proc. Chem. Soc.*, 63 (1962).

[21] D. B. Denney, D. Z. Denney, and G. Feig, *Tetrahedron Letters*, 19 (1959).

[22] H. L. Goering and V. Mayer, *J. Am. Chem. Soc.*, **86**, 3753 (1964).

[23] B. Cross and G. H. Whitham, *J. Chem. Soc.*, 1650 (1961).

[24] J. K. Kochi, *J. Am. Chem. Soc.*, **83**, 3162 (1961).

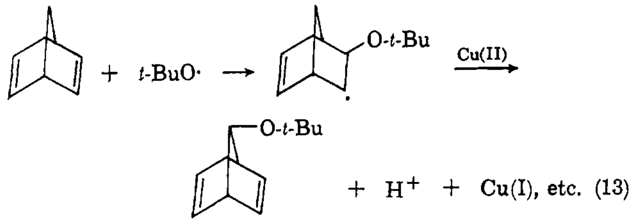
[25] H. E. DeLaMare, J. K. Kochi, and F. F. Rust, *ibid.*, **83**, 2013 (1961); **85**, 1437 (1963).

[26] (a) J. K. Kochi and P. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965). (b) Unlike other alkyl radicals, methyl is oxidized rather slowly by cupric carboxylates. Methane may arise from *reduction* of methyl radicals by cuprous salts in addition to hydrogen abstraction processes.

[27] S. J. Cristol and D. I. Davies, *ibid.*, **29**, 1282 (1964); D. J. Trecker and J. P. Henry, *J. Am. Chem. Soc.*, **85**, 3205 (1963).

[28] P. R. Story, *Tetrahedron Letters*, 401 (1962).

[29] H. Tanida and T. Tsuji, *Chem. Ind.* (London), 211 (1963).



(13)

t-Butoxy radicals generated from peresters and copper salts show the same selectivity pattern in intermolecular competitive chain-transfer reactions as those produced photolytically from *t*-butyl hypochlorite.[9,18,30] The minor extent of addition[18] to alkenes is

$$\begin{tikzcd}
(CH_3)_3CO_3CCH_3 + Cu(I) \arrow[dr] & & (CH_3)_3COH + R_1\cdot \quad (14) \\
& (CH_3)_3CO\cdot \arrow[ur, "R_1H"] \arrow[dr, "R_2H"'] & \\
(CH_3)_3COCl + h\nu \arrow[ur] & & (CH_3)_3COH + R_2\cdot \quad (15)
\end{tikzcd}$$

also the same with *t*-butoxy radicals generated from both sources.[31] The interaction[3d] of *t*-butoxy radicals with copper salts during the chain transfer step (8) is, therefore, unimportant.

The absence of substitution reactions between alkenes and homologous *t*-alkyl peracetates can be readily accounted for by the rapid fragmentation of alkoxy radicals formed as intermediates to ketone and alkyl radicals, particularly when the latter is ethyl or higher alkyl radicals.[32] Alkyl radicals (with the exception of methyl) react rapidly with copper(II) and chain transfer with alkene is minor.[5] 2-Methyl-2-hexyl peracetate yields an alkoxy radical II which undergoes two competitive unimolecular reactions, fragmentation (18) and intramolecular hydrogen transfer (19). Both of the resultant radicals are oxidized by copper(II) to regenerate copper(I) and butene-1 and a mixture of 2-methylhexenols.[8a] Intramolecular hydrogen transfer (eq. 19) has been established as a facile and general reaction of alkoxy radicals.[32a,b,33]

$$CH_3CH_2C(CH_3)_2O\cdot \longrightarrow CH_3COCH_3 + CH_3CH_2\cdot \quad (16)$$

$$CH_3CH_2\cdot + Cu(II) \longrightarrow CH_2{=}CH_2 + H^+ + Cu(I), \text{ etc.} \quad (17)$$

$$\begin{tikzcd}
& CH_3CH_2CH_2CH_2\cdot + CH_3COCH_3 \quad (18) \\
CH_3CH_2CH_2CH_2C(CH_3)_2O\cdot \arrow[ur] \arrow[dr] & \\
& CH_3\underset{\cdot}{C}HCH_2CH_2C(CH_3)_2OH \quad (19)
\end{tikzcd}$$

The extension of this simple mechanism to the catalyzed decomposition of many classes of peroxides, to perform intermolecular substitution reactions as well as decomposition, can be made with little difficulty. In each case the primary step involves a one-electron reduction of the peroxide by copper(I). Di-*t*-butyl peroxide yields *t*-butoxy radicals (eq. 20) which can carry out hydrogen transfer reactions (8)[3b,16] like those derived from *t*-butyl peracetate (eq. 7). The higher homologous dialkyl peroxides yield alkoxy radicals which fragment too rapidly (eq. 16, 18) to be involved in chain transfer with alkene. Instead they are catalytically decomposed to alcohol, ketone, and alkene in equimolar amounts.[5]

$$(CH_3)_3COOC(CH_3)_3 + Cu(I) \longrightarrow (CH_3)_3CO\cdot + Cu(II)OC(CH_3)_3 \quad (20)$$

Alkyl hydroperoxides initially yield alkoxy radicals (eq. 21) by reduction with copper(I) or iron(II), and these have been trapped with butadiene, especially *t*-butoxy radical.[14] It has also been involved in chain-transfer reactions with alkenes.[3a,9] The higher homologs generate alkoxy radicals such as II which evince the same multiplicity of behavior as those generated from peresters.[8a] The selectivity of oxy radicals generated from *t*-butyl hydroperoxide is slightly different from those generated from *t*-butyl hypochlorite.[9] It is possible that some *t*-butylperoxy radicals also serve as chain-transfer agents, and may be formed by oxidation of *t*-butyl hydroperoxide by copper(II)[5] or hydrogen transfer from *t*-butyl hydroperoxide.[9]

$$CH_3CH_2CH_2CH_2C(CH_3)_2OOH + Cu(I) \longrightarrow \underset{\text{II}}{CH_3CH_2CH_2CH_2C(CH_3)O\cdot} + Cu(OH)^+ \quad (21)$$

Diacyl peroxides produce acyloxy radicals on reduction with Cu(I). Benzoyloxy radicals so generated from benzoyl peroxide have been trapped with butenes[17] and norbornadiene.[29] The aliphatic analogs are quite unstable and decarboxylate too rapidly to be trapped by conventional means. Szwarc[34] has estimated a reaction such as 25 to be exothermic by 15–20 kcal./mole.

$$(CH_3CH_2CH_2CH_2CO_2)_2 + Cu(I) \longrightarrow CH_3CH_2CH_2CH_2CO_2\cdot + Cu(II)O_2CCH_2CH_2CH_2CH_3 \quad (22)$$

$$\left.\begin{array}{l} C_6H_5CO_2\cdot + \\ CH_2{=}CHCH_2CH_3 \end{array}\right\} \begin{array}{ll} \nearrow C_6H_5CO_2CH_2{-}\dot{C}HCH_2CH_3 & (23) \\ \searrow C_6H_5CO_2H + CH_2\cdots CH\cdots CHCH_3 & (24) \end{array}$$

$$CH_3CH_2CH_2CH_2CO_2\cdot \longrightarrow CH_3CH_2CH_2CH_2\cdot + CO_2 \quad (25)$$

There is no doubt that oxy radicals, whether they be alkoxy or acyloxy radicals, are formed as intermediates in the reaction of peroxides with copper salts. The efficiency with which they carry out intermolecular chain-transfer reaction is less dependent on their origin than their structure. Among the alkoxy radicals, the *t*-butoxy and α-cumyloxy, and, among the acyloxy, the aroyloxy radicals are the most suited to perform this task since their rates of unimolecular cleavage are relatively slow.[35] *t*-Amyloxy and the higher homologs together with the aliphatic acyloxy, particularly the latter, fragment to alkyl radicals and ketone or carbon dioxide too rapidly to ensure sufficient intermolecular substitution reactions. Oxy radicals are not particularly reactive in hydrogen transfer reactions[30,36] and a substrate for substitution reactions must be selected with this in mind.[5] Among such substrates, alkenes are suited because of the lability of the hydrogen

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[30] C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

[31] C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

[32] (a) F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963); (b) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593, 1597 (1963); (c) J. K. Kochi, *ibid.*, **84**, 1193 (1962).

[33] M. Akhtar and D. H. Barton, *ibid.*, **83**, 2213 (1961).

[34] M. Szwarc, "Peroxide Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 153.

[35] In the gas phase the difference between the activation energy for cleavage of *t*-butoxy and other aliphatic *t*-alkoxy radicals has been estimated to be approximately 8 kcal./mole (private communication, Dr. G. R. McMillan).

[36] C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960); A. L. Williams, E. A. Oberright, and J. W. Brooks, *ibid.*, **78**, 1190 (1956); J. H. Raley, F. F. Rust, and W. E. Vaughan, *ibid.*, **70**, 1336 (1948).

located in the allylic position. The allylic radicals produced in the chain-transfer reaction are completely equilibrated since no optical activity was retained when either dextrorotatory Δ^1-p-menthene[19] or levorotatory bicyclo[3.2.1]octene-2[22] was converted with t-butyl perester to the alkenyl esters. The question of complex formation with alkene, perester, and copper salt so often raised[3d,6,7] is entirely unnecessary.

Carbon-centered radicals can thus be formed from peroxides by hydrogen abstraction from an alkene by an oxy-radical intermediate *or* fragmentation of the oxy radical itself. In either case, the majority of carbon radicals formed by these routes is easily oxidized by copper(II)[25,37] to regenerate copper(I) (*e.g.*, eq. 9, 12, 16, 25, etc.) and so sustain a catalytic process. The degree to which a catalytic reaction (*vide supra*) is not obtained reflects in large part the inefficiency of alkyl- or alkenyl-radical production. If alkyl or alkenyl radicals are efficiently produced by the fragmentation of oxy radicals, no hydrogen donor is required for a catalytic reaction of relatively long chain length. Active substrates are required in those cases (t-butyl and benzoyl peroxides) which depend on the chain-transfer reaction, and, if such is not available, higher temperatures required for the thermolysis of the peroxide are needed to sustain a metal salt reaction. Alkyl radicals generally cannot be effectively generated by the latter route owing to the selectivity of oxy radicals, and in many cases alkanes can be employed as solvent.

The distinction between the catalyzed perester-type substitution reactions on one hand, and the catalyzed decompositions of peroxides on the other, has been arbitrary and unnecessary.[6] More properly, the classification should be based on the nature of the oxy-radical intermediate and the facility with which it abstracts a labile hydrogen as opposed to its propensity to dissociate. For these reasons we stress the essential unity between both types of catalyzed reactions: the alkene-dependent perester-type reactions of t-butyl, cumyl, and aroyl peroxides, and the decomposition of peroxides essentially independent of alkenes and other donor substrates.

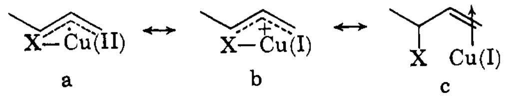
Oxidation of Alkyl and Alkenyl Radicals by Cu(II).— The ease of oxidation of alkyl radicals with copper(II) has been compared with intramolecular chain transfer,[38] hydrogen transfer with reactive donors,[12] polymerization,[14,39] rearrangement,[8a,9,40] and ligand transfer.[10] Studies have indicated that oxidation of n-butyl radicals by copper acetate in acetic acid is at least 10^5 times faster than hydrogen abstraction from phenylacetaldehyde, chloroform, or dichloroacetic acid. In nonaqueous solvents, cupric acetate exists largely as a dimer and the rate of oxidation is one-half order in cupric acetate.[12]

The nature of the products obtained also depends on the step involving oxidation of the alkyl, alkenyl, or similar radicals by copper(II). The oxidation of simple alkyl radicals by cupric salts generally yields alkenes by loss of a β-hydrogen.[8,25] The transition state of this reaction has considerable carbonium-ion character. High yields of alkenes are obtained even in protic solvents such as acetic acid and no skeletal rearrangement of isobutyl or n-butyl radicals has been observed. *sec*-Butyl radicals are oxidized to a mixture of butene-1 and *cis*- and *trans*-butene-2 approximating a statistical distribution. Extensive rearrangement occurs during oxidation of neopentyl and related radicals.[8a,9] The isomeric cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl radicals are oxidized in acetic acid to a mixture of the C_4H_7 acetates reminiscent of the homoallylic carbonium ions.[40] Alkyl radicals with α substituents, such as a halogen, cyano, or carbonyl group, are less rapidly oxidized[39,41] than alkyl or alkenyl radicals. The pattern of carbonium-ion behavior in these oxidations can be discussed in terms of an electron-transfer process and suggests that carbonium ions less solvated than those conventionally obtained from solvolytic or deaminative processes are involved.[8a] The degree to which copper is bonded to the alkyl moiety in the transition state has not yet been ascertained beyond this description.

$$CH_3CH_2CH_2CH_2\cdot + Cu(II) \longrightarrow CH_3CH_2CH{=}CH_2 + Cu(I) + H^+ \qquad (26)$$

$$R\cdot + Cu(II) \longrightarrow R^+ + Cu(I) \qquad (27)$$

There is more evidence for such an interaction between allylic radicals and copper salts. The behavior of terminal allylic radicals such as t-BuOCH$_2$CH$\overset{\cdots}{-}$CH$\overset{\cdots}{-}$CH$_2$, CH$_3$CH$\overset{\cdots}{-}$CH$\overset{\cdots}{-}$CH$_2$, and CH$_3$(CH$_2$)$_4$CH$\overset{\cdots}{-}$CH$\overset{\cdots}{-}$CH$_2$ during oxidation[14,18] did not conform to expectations based on earlier studies of butenyl cations by Winstein and Young. Allylic carbonium ions formed by the silver ion assisted acetolysis of either α-methylallyl chloride or crotyl chloride was partitioned approximately equally between α-methallyl acetate and crotyl acetate. The predominant formation of the secondary α-methallyl isomer from butenes and the analogous isomers from other 1-alkenes under a variety of conditions is not in accord with the solvolytic experiments. The modification of the properties of an allylic carbonium ion by copper(I) formed within its locus was used to explain the unique oxidation of allylic radicals by copper(II). The transition state for such a transformation in valence-bond terminology consists of electron-transfer (b) and ligand-transfer (c) components, as given in III.[14,18a] The ability of copper to mediate the fate of the incipient carbonium ion lies in its ability as copper(I) to coordinate with the double bond.[42] The importance of such coordination is supported by studies of copper complexes with phenanthroline or bipyridine as ligands capable of synergic bonding (d-π^*) with copper.[14b] The resultant attenuation of the ability of copper(I) to coordinate with the double bond is manifested as a change in the isomer ratio toward the value obtained by solvolytic methods. We considered the latter as an electron-transfer reaction. Walling and Zavitsas[9] differ with this interpretation and prefer to consider the oxidation of allylic radicals with cupric acetate to be "primarily electron-transfer



III

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[37] There is no evidence that oxy radicals are oxidized by cupric salts.

[38] J. K. Kochi and R. D. Gilliom, *J. Am. Chem. Soc.*, **86**, 5251 (1964).

[39] J. K. Kochi and F. F. Rust, *ibid.*, **84**, 3945 (1962).

[40] J. K. Kochi and H. E. Mains, to be published.

[41] J. K. Kochi and D. M. Mog, *J. Am. Chem. Soc.*, **87**, 522 (1965).

[42] J. Chatt in "Cationic Polymerization and Related Complexes," P. H. Plesch, Ed., Heffer, Cambridge, 1953, p. 40, for a general reference.

TABLE I

FORMATION OF OCTENYL ACETATES FROM OCTENE-1 AND 1,3-BUTADIENE BY REACTIONS OF PEROXIDES WITH COPPER SALTS

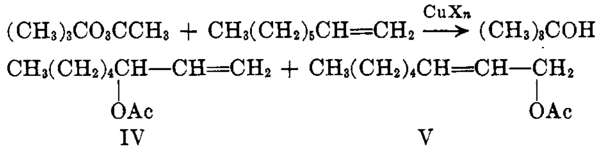
Solvent (vol. %)	Peroxide	Copper salt	Alkene	Temp., °C.	Octenyl acetate total, %	3-Acetoxy-octene-1,[a] %	1-Acetoxy-octene-2,[a] %
C_6H_5Cl[b] (100)	$(CH_3)_3CO_3CCH_3$	Cu(I)Cl	Octene-1	70	89	87	13
C_6H_5Cl[b] (100)	$(CH_3)_3CO_3CCH_3$	Cu(II)OAc$_2$	Octene-1	70	. .	89	11
Octene-1 (100)	$(CH_3)_3CO_3CCH_3$	Cu(II)OAc$_2$	Octene-1	80	75	86	14
Octene-1 (85), HOAc (15)	$(CH_3)_3CO_3CPh$	Cu(II)OAc$_2$	Octene-1	80	79	87	13
C_6H_5 (80), HOAc (20)	$(CH_3)_3CO_3CCH_3$	Cu(II)OAc$_2$	Octene-1	80	81	88	12
Octene-1[c] (95), CH_3CN (5)	$(CH_3)_3CO_3CCH_3$	Cu(II)Oct$_2$	Octene-1	50	52	84	16
Octene-1[c] (90), CH_3CN (10)	$(CH_3)_3CO_3CCH_3$	Cu(II)Oct$_2$	Octene-1	23	47	82	18
HOAc (100)	$(CH_3)_3CO_3CCH_3$	Cu(II)Ac$_2$	Octene-1	75	84	87	13
HOAc (100)	$[CH_3(CH_2)_3CO_2]_2$	Cu(II)OAc$_2$	Butadiene	50	71	90	10
HOAc (100)	$[CH_3(CH_2)_3CO_2]_2$	Cu(II)OAc$_2$ Cu(I)Cl	Butadiene	26	84	88	12

[a] Composition in the octenyl acetate fraction. [b] See ref. 9. [c] With added zinc or copper metal.

reactions giving products approaching free carbonium ions." Electron transfer has been stated to be a significant driving force in the oxidation of allylic radicals by cupric acetate.[43] However, free carbonium ions uninfluenced by copper salts are not intermediates which lead to product, and we prefer to attribute the selective formation of the secondary allylic isomer to a *component* of ligand transfer in the transition state for product formation.

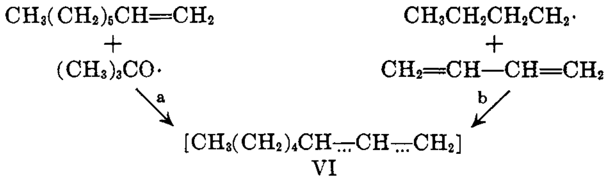
Results and Discussion

In addition to the aforementioned results, the common feature between the perester reaction and the decomposition of peroxides is supported by the isolation of the same products from both reactions. Octene-1 reacts with *t*-butyl peracetate or benzoate in acetic acid solutions to yield (Table I) a mixture of octenyl acetates (IV and V).[3d,9,20] The same mixture of octenyl acetates is obtained from *n*-valeryl peroxide and butadiene. Butene-1 is also produced in minor amounts (20–40%)


$$(CH_3)_3CO_3CCH_3 + CH_3(CH_2)_5CH{=}CH_2 \xrightarrow{CuX_n} (CH_3)_3COH + \underset{\substack{|\\ OAc\\ IV}}{CH_3(CH_2)_4CH}{-}CH{=}CH_2 + CH_3(CH_2)_4CH{=}CH{-}\underset{\substack{|\\ OAc\\ V}}{CH_2} \quad (28)$$

in the latter reaction (*vide supra*, eq. 6). Octenyl radical VI is an intermediate in both reactions; in the former it arises from octene-1 (30a) by abstraction (eq. 7, 8), whereas in the latter it derives from butadiene (30b) by addition (eq. 22, 25).

$$(CH_3CH_2CH_2CH_2CO_2)_2 + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[HOAc]{CuX_n} CH_3CH_2CH_2CH_2CO_2H + CO_2 + IV + V \quad (29)$$



(30)

The isomer distribution between 3-acetoxyoctene-1 (IV) and 1-acetoxyoctene-2 (V) obtained under a given set of experimental conditions is highly reproducible (±2%) and quite independent of the total yield of octenyl esters over a wide range and irrespective of reactants. We take this to indicate that they arise directly from a common intermediate, and it is the partitioning of the octenyl radical VI during oxidation by Cu(II) salts which determines this distribution. This ratio can qualitatively be of diagnostic value to help ascertain the changes in the transition state of the oxidation brought about by variations in the Cu(II) oxidant and the medium.

TABLE II

EFFECT OF SOLVENT ON THE COMPOSITION OF THE OCTENYL ACETATE FRACTION[a]

Solvent (vol. %)[b]	Temp., °C.	Dielectric constant[c] (temp.)	Total octenyl acetate, %	3-Acetoxyoctene-1,[d] %	1-Acetoxyoctene-2,[d] %
Ethyl acetate (75)	50	6.02 (25°)	58	86	14
Nitromethane (75)	50	36.7 (25°)	28	89	11
Tetramethylene sulfone (75)	40	44 (30°)	57	90	10
Tetramethylene sulfone (25)	40		64	89	11
Acetonitrile (75)	50	36.7 (25°)	76	80	20
Acetonitrile (25)	50		73	74	26
N,N-Dimethylformamide (75)	50	36.7 (25°)	34	91	9
N,N-Dimethylformamide (25)	40		55	83	17
Formic acid (99)	25	58 (16°)	61[e]	80[e]	20[e]
Acetic acid (100)	40	6.2 (25°)	78	88	12
Diethyl ether (25)	40	4.23 (25°)	62	88	12
Dioxane (25)	40	2.21 (25°)	. . .	89	11
Water (40)	40	78.5 (25°)	49	78	22
			21[f]	85[f]	15[f]
Water (10)	40		71	79	21
Benzene (60)	40		67	85	15
Acetonitrile (15)					
Pyridine (5)	50	12.3 (25°)	40	66	34
2,6-Lutidine (5)	50		63	68	32
2,4,6-Collidine (5)	50		30	65	30

[a] In solutions containing valeryl peroxide (0.125 *M*), cupric acetate (0.005 *M*), and 1 atm. of butadiene. [b] Remainder composed of acetic acid. [c] Dielectric constant of the pure solvent only. A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards, Circular No. 514, U. S. Government Printing Office, Washington, D. C., 1951; R. L. Burwell and C. H. Langford, *J. Am. Chem. Soc.*, **82**, 1503 (1960); F. E. Critchfield, *et al.*, *ibid.*, **75**, 1991 (1953). [d] Composition of the octenyl acetate fraction. [e] Formates. [f] Alcohols.

Effect of Solvents.—The relatively high temperatures required for the perester reaction in the absence of Zn or Cu as initiator makes a detailed study of the influence of temperature and solvents on the reaction inconvenient. Since equivalent results are obtained from valeryl peroxide and butadiene, we chose this sys-

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[43] See ref. 14a (p. 2789) and 14b (p. 3275).

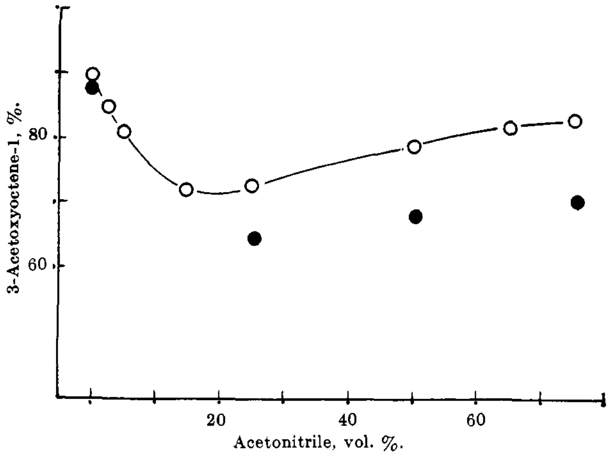

Figure 1.—Effect of acetonitrile in acetic acid solutions on the composition of the octenyl acetate mixture: O, 40°; ●, 25°.

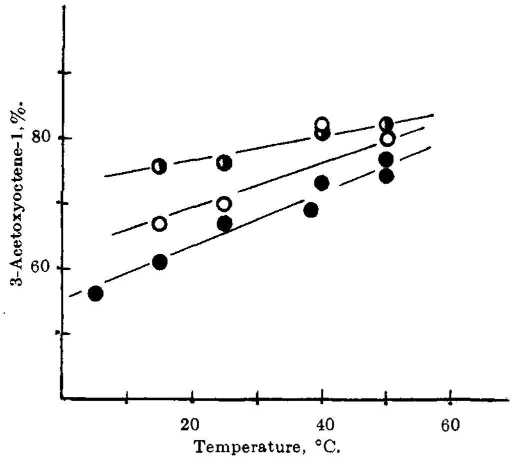

Figure 2.—Effect of temperature on the composition of the octenyl acetate mixture in acetonitrile–acetic acid solutions: ◑, 5 vol. % acetonitrile; ●, 25 vol. % acetonitrile; O, 75 vol. % acetonitrile.

tem for further study. In Table I is given the isomer ratios of IV and V in different solvents and peroxides. In every case the octenyl acetate mixture consists of approximately 85–90% of the secondary isomer IV.[9,18a] These changes in reaction conditions include solvent variation from chlorobenzene, benzene, octene-1, to acetic acid at several temperatures including initiation with zinc and copper metal. Cupric acetate or 2-ethylhexanoate was in every case the metal salt involved and the same results were obtained irrespective of whether the system consisted of octene-1 and *t*-butyl peracetate or butadiene and valeryl peroxide. The isomer ratio is quite independent of a wide variety of solvents listed in Table II, with the exception of pyridine and related compounds. At low concentration of these bases, *there is a noticeable change in isomer distribution.* A change in the nature of the copper species is also apparent from the alteration in color from green to blue. Taken as a whole there is no apparent correlation between the isomer distribution and the dielectric constant ("dissociating power") of the medium. Neither is there any relationship between the isomer ratio and the solvent "ionizing power" as measured by the Grunwald–Winstein m*Y* treatment applied to the solvolysis of a neophyl tosylate.[44]

Effect of Ligands.—The effects of stronger nitrogen ligands are listed in Table III; in these cases the ligands were present in stoichiometric amounts. Oxygen-type ligands such as acetylacetonate and hexafluoroacetylacetonate have a minor but real effect. On the basis of these experiments we conclude that the *isomer distribution is not determined by solvents so much as it is by the nature of the catalytic metal species.*

TABLE III

EFFECT OF CUPRIC SALTS ON THE ISOMER DISTRIBUTION[a]

Solvent (vol. %)	Copper salt	Temp., °C.	Total octenyl acetates, %	3-Acetoxyoctene-1,[b] %	1-Acetoxyoctene-1,[b] %
HOAc (100)	Acetylacetonate	50	78	75	25
HOAc (25), C_6H_6 (75)	Acetylacetonate	50	73	78	22
HOAc (25), C_6H_6 (75)[c]	Acetylacetonate	50	. .	58	42
HOAc (25), C_6H_6 (75)	Hexafluoroacetylacetonate	50	44	77	23
HOAc (100)	2,2′-Bipyridine[d]	50	86	42	58
HOAc (100)	2,2′-Biquinoline[e]	50	. .	57	43
HOAc (60), CH_3CN (40)	1,10-Phenanthroline[e]	50	30	53	47

[a] In solutions containing valeryl peroxide (0.125 *M*), cupric acetate (0.005 *M*), and 1 atm. of butadiene. [b] Composition in octenyl acetate fraction. [c] Contains 10% pyridine, 65% benzene, and 25% acetic acid. [d] 1:1 complex. [e] 3:1 complex.

Acetonitrile solutions are unique among all solvents examined (with the exception of pyridine) in their ability to affect the isomer distribution. The effect is subtle and not completely understood. Figure 1 illustrates the manner in which the isomer distribution is altered by changes in concentration of acetonitrile in solutions with acetic acid at 40°. The fall in selectivity between zero and 25 vol. % acetonitrile is rather unique with this solvent. The increase between 25 vol. % and higher concentrations is also duplicated by nitromethane (*i.e.*, a ternary solution of acetonitrile, acetic acid, and nitromethane). The minimum of this plot, *i.e.*, the point of least selectivity between the two isomeric octenyl acetates, corresponds to a solution consisting of approximately 25 vol. % acetonitrile. Moreover, the isomer distribution obtained in this solution varies considerably with temperature, as shown in Figure 2. The extrapolated value at 80° is approximately 90% 3-acetoxyoctene-1 (IV) or that value found from other studies (*vide supra*). The temperature variation in the isomer ratio is less marked at higher and lower concentrations of acetonitrile.

Acetonitrile forms coordination complexes with cupric and cuprous salts. Complexes such as $\mathrm{Cu(CH_3CN)_4(BF_4)_2}$,[45] $\mathrm{Cu(CH_3CN)_4(ClO_4)_2}$,[45] $\mathrm{Cu(CH_3CN)_nCl_2}$,[45] $\mathrm{Cu(CH_3CN)_4BF_4}$,[46] $\mathrm{Cu(CH_3CN)_4ClO_4}$,[46] and $\mathrm{Cu(CH_3CN)_4NO_3}$[46] have been isolated. They are not so stable as the pyridine, bipyridyl, and phenanthroline complexes and do lose the coordinated acetonitrile ligands relatively easily. Thus, cupric acetate–acetonitrile complexes lose acetonitrile on standing in air. The

$$\mathrm{Cu(OAc)_2} + n\mathrm{CH_3CN} \rightleftarrows \mathrm{Cu(OAc)_2(CH_3CN)}_n \qquad (31)$$
$$(n = 2, 4)$$

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[44] S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 619 (1961).

[45] (a) B. J. Hathaway, D. G. Holah, and A. Underhill, *J. Chem. Soc.*, 2444 (1962); (b) R. J. Kern, *J. Inorg. Nucl. Chem.*, **25**, 5 (1963); (c) B. J. Hathaway and D. G. Holah, VIIth International Conference on Coordination Chemistry, Stockholm, 1962; Abstracts, p. 48.

[46] B. J. Hathaway, D. G. Holah, and I. D. Postlethwaite, *J. Chem. Soc.*, 3215 (1961).

TABLE IV

EFFECT OF NUCLEOPHILES ON THE PARTITIONING OF THE OCTENYL MOIETY[a]

Reactants			Products			
HX[b] (vol. %)	HOAc:HX, mole ratio	Salt (M)	3-AcO-octene-1,[c] %	3-X-octene-1,[d] %	$\frac{\text{Total } C_8H_{15}OAc}{\text{total } C_8H_{15}\text{–}X}$, mole ratio	Molar selectivity[e]
Formic acid (80)	0.13	0	~75	83	0.091	0.70
Formic acid (80)	0.13	0	~75	81	0.094	0.72
Formic acid (60)	0.44	0	~74	83	0.22	0.50
Formic acid (40)	0.99	0	79	82	0.35	0.36
Formic acid (20)	2.63	0	80	81	0.55	0.21
Formic acid (20)	2.63	LiOAc (0.61)	65	64	0.38	0.15
Formic acid (8)	7.57	0	85	84	1.26	0.17
Water (27)	0.81	LiOAc (1.24)	58	82	14.0	17.3
Water (27)	0.81	LiOAc (0.61)	60	82	9.5	11.7
Water (27)	0.81	LiOAc (0.31)	63	84	8.7	10.7
Water (27)	0.81	LiOAc (0.14)	66	84	5.9	7.3
Water (27)	0.81	$LiClO_4$ (0.40)	73	80	2.0	2.4
Water (27)	0.81	0	73	82	2.7	3.4
Water (16)	1.63	0	75	81	4.0	2.5
HOAc only	...	LiOAc (3.1)	53	..	77[f]	...
HOAc only	...	LiOAc (1.8)	54	..	79[f]	...
HOAc only	...	LiOAc (0.72)	59	..	74[f]	...
HOAc only	...	LiOAc (0.61)	62	..	79[f]	...
HOAc only	...	LiOAc (0.31)	64	..	81[f]	...
HOAc only	...	LiOAc (0.12)	70	..	80[f]	...
HOAc only	...	$LiClO_4$ (1.2)	74	..	79[f]	...
HOAc only	...	0	87	..	83[f]	...

[a] In acetic acid solutions at 25° containing valeryl peroxide (0.10 M), cupric acetate (0.008 M), and 1,3-butadiene (saturated at 1 atm.). [b] Remainder is acetic acid. [c] Composition of octenyl acetate fraction, remainder is 1-acetoxyoctene-2. [d] Composition of octenyl-X (formate or alcohol) fraction, remainder is 1-X-octene-2. [e] Column 6 divided by column 2. See text. [f] Total yield of octenyl acetates.

bonding between copper and the acetonitrile is probably related to the amine complexes. Acetonitrile shares with phenanthroline its ability to preclude multiple π bonding between copper and the weaker olefinic ligands; and oxidation of allylic radicals with such species is probably the same as those obtained with the phenanthroline and related complexes.[14b] Temperature dependence of the isomer ratio may be attributed to the shift in the equilibrium (31) at lower temperatures from left to right, such that the acetonitrile–copper complex is the effective oxidant at lower temperatures. In acetonitrile, however, the problem is complicated by an additional equilibrium[47] involving monomers and dimers (eq. 32). Kinetic studies have shown

$$2Cu(OAc)_2(CH_3CN)_2 \rightleftarrows [Cu_2(OAc)_4(CH_3CN)_2] + 2CH_3CN \quad (32)$$

that only the monomeric species is an oxidant.[12] The change in isomer ratio is not affected by this monomer–dimer equilibrium since water, dimethylformamide, and tetramethyl sulfone can effectively displace equilibrium (32) to the left.[47,48] Yet they have little effect on the isomer ratio (Table II).

A change in the oxidation potential of the copper(II) oxidant by coordination can affect the isomer distribution since the strongest complexes generally have the largest effect in decreasing the selectivity. The ligands in point are those which preferentially stabilize the copper(I) oxidation state at least in aqueous solutions.[49] The higher oxidation potentials of these complexes would lend greater driving force to an electron-transfer reaction. This effect alone cannot be used to explain the selectivity pattern. The oxidation potential of copper(II) is markedly enhanced in acetonitrile solutions from −0.089 v. *vs.* s.c.e. in water to 1.0 v. *vs.* s.c.e.[50] However, as shown in Figure 1, the 3-acetoxyoctene-1 isomer goes to a minimum at approximately 25 vol. % acetonitrile and *rises* with increasing acetonitrile concentration. The effect of water is to decrease selectivity, if at all.

Partitioning of the Allylic Moiety during Oxidation.—In formic acid the decomposition of valeryl peroxide with copper salts in the presence of butadiene affords a mixture of octenyl formates in good yields, with the 3-formyloxyoctene-1 again the predominant isomer (80%, Table II). In acetic–formic acid mixtures two pairs of octenyl acetates and formates are formed, as shown in Table IV. The composition of each isomeric fraction is relatively invariant with changes in the composition of the solvent. However, the total yield of octenyl formates relative to acetates is not simply related to the molar ratio of formic and acetic acids. The values for the molar selectivity listed in Table IV were calculated by dividing the molar ratios of total octenyl acetates to formates by the ratio of acetic to formic acid used as solvent, and represent the ease of acetate substitution relative to formate. It decreases with increasing acetic acid concentrations such that at high (92%) acetic acid concentrations, acetate is approximately a fourth less effective in trapping the octenyl moiety than it is at lower (20%) concentrations. This is further support for the hypothesis that a simple octenyl carbonium ion is not an intermediate

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(47) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(48) W. Schneider, *Helv. Chim. Acta*, **46**, 1842 (1963).

(49) (a) C. J. Hawkins and D. D. Perrin, *J. Chem. Soc.*, 1351 (1962); 2993 (1963); (b) S. Cabini, G. Moretti, and E. Serocco, *ibid.*, 88 (1962).

(50) (a) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870, 1825 (1957); (b) I. V. Nelson, R. C. Larson, and R. T. Iwamoto, *J. Inorg. Nucl. Chem.*, **22**, 279 (1961).

in the reactions. In these solutions the copper species exists predominantly as formatocopper(II) and acetatocopper(II) complexes (eq. 10, $X = O_2CH$), both dimeric and monomeric. Since formic acid is stronger than acetic acid, it is expected that the equilibrium (10) is in favor of the formatocopper(II) complex.[51] The changes in molar selectivity are associated with the variation of the equilibrium concentration of each carboxylatocopper(II) species with changes in solvent from largely acetic acid (dielectric constant, 6.2) to largely formic acid (dielectric constant, 58).

A similar change in molar selectivity is shown by acetic acid–water mixtures. The roles, however, are reversed in that with decreasing acetic acid concentration the molar selectivity of acetate decreases with respect to water. This is consistent with the notion that the stronger acetic acid is more highly complexed with the Cu(II) ion.[52]

The subsequent solvolysis of reaction products in such a strongly solvolyzing medium as formic acid is minor under these experimental conditions. Less than 10% of the 3-acetoxyoctene-1 is formolyzed in 5 hr., and after 20 hr. it is 40% converted to a mixture consisting of 48% 3-formyloxyoctene-1 and 52% 1-formyloxyoctene-2.[53] The formolysis is strongly catalyzed by perchloric acid and it yields an equilibrium mixture of octenyl formates consisting of 36% 3-formyloxyoctene-1 and 64% 1-formyloxyoctene-2.

The effect of lithium perchlorate as a neutral salt on the isomer distribution is minor, even at relatively high concentrations (Table IV). However, the common ion introduced as lithium acetate exerts a profound effect in suppressing 3-acetoxyoctene-1 (IV) relative to the isomeric 1-acetoxyoctene-2 (V). The effect levels off at concentrations greater than 0.7 *M* lithium acetate to a mixture consisting of 55% IV and 45% V, which is the same limiting composition obtained earlier with pyridine, phenanthroline, and acetonitrile. A similar effect is observed in formic–acetic acid mixtures. Lithium acetate does not cause isomerization of the octenyl acetates and the total yields of octenyl acetates are consistently high (Table IV) under these conditions. The effect is only slightly less pronounced in aqueous acetic acid solutions, but more importantly the composition of the octenol fraction is singularly unaffected by lithium acetate. The molar selectivity for acetate formation relative to alcohol increases monotonically with lithium acetate concentration (Table IV) even beyond 0.7 *M* and it decreases relative to formate.

The effect of lithium acetate is not solely one of adding acetate as a base. A change in the extant Cu(II) species is apparent from a change in the color of the solution from green to blue, which we attribute to the formation of anionic acetatocopper(II) complexes VIIa. Whether such complexes as VIIa can behave in the same manner as those derived from the nitrogen-containing ligands discussed earlier forms an interesting speculation. If such were the case, the increase in molar selectivity with increasing acetate indicates that species such as VIIa are highly effective oxidants for allylic radicals.[54] An alternative explanation of the acetate effect is to consider a bimolecular attack of acetate ion on an octenyl–copper(II) complex. This would require that III, previously formulated as a transition state, be an intermediate with a sufficient lifetime to undergo bimolecular displacement.[55]

$$[Cu(OAc)_2]_2 + n\text{LiOAc} \rightleftarrows \underset{\text{VIIa}}{2Cu(OAc)_{2+n}{}^{-n}}\, n\text{Li}^+ \quad (n = 1,2,\ldots)$$

$$\underset{\text{III}}{[C_8H_{15}\cdot Cu(II)]} + OAc^- \longrightarrow \underset{\text{IV,V}}{C_8H_{15}OAc} + Cu(I)$$

The reaction in the presence of perchloric acid also yields a mixture of octenyl acetates whose composition tends toward an equimolar mixture of isomers with increasing acid concentration. However, the rearrangement of 3-acetoxyoctene-1 catalyzed by perchloric acid is significant under these conditions, and product analysis is insufficient to separate the oxidation step from the subsequent isomerization.

We feel that the accumulated evidence points to coordination between the incipient allylic carbonium ion and copper(I) in the transition state III as an important factor which helps to determine the manner in which the allylic moiety collapses to products. Only small differences in energy are required to account for the observed selectivity with simple copper salts. The formation of complex copper species, especially with nitrogen ligands discussed previously and to a lesser extent the acetylacetonate, acetate, and aquo ligands, may be sufficient to disrupt this interaction between the incipient allylic carbonium ion and copper. Alternatively, in such cases as 2-methylbutenyl and 2,3-dimethylbutenyl radicals studied by Denney, *et al.*,[19] the added stability of the methylated allylic carbonium ions may be sufficient for them to eschew entirely such aid from the copper species. The behavior of the latter radicals during oxidation is consistent with carbonium ions from solvolytic studies.[56]

Trapping Free Radicals with Butadiene.—The capture of butadiene by butyl radicals from valeryl per-

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[51] Mixed formato and acetato complexes are also undoubtedly formed. For purposes of discussion only the separate cases will be considered.

[52] A similar though not equivalent argument can be made about the relative ease of transfer of a ligand from a given Cu(II) complex (*e.g.*, formate > acetate > water). However, since the transition state III is postulated to embrace a significant component of electron transfer, this effect should be small.

[53] For a discussion of the mechanism of allylic solvolyses, see H. L. Goering, *et al.*, *J. Am. Chem. Soc.*, **86**, 1951 (1964); **85**, 965 (1963); and earlier papers.

[54] (a) This explanation is not without its attendant difficulties. If acetato ligands aid the stabilization of the Cu(I) oxidation state, the transition state for oxidation by species such as VIIa is largely electron transfer. In such a case one may expect the molar selectivity (*e.g.*, between acetate and formate) to approach 1 as acetate is added to the system; instead, it decreases from 0.21 to 0.15 (Table IV). To contradict this objection, however, the partitioning of the octenyl carbonium ion so formed may not be reflected by the molar ratio of nucleophiles (*i.e.*, selectivity $\simeq$ 1) if it is the octenyl carbonium ion–Cu(I) carboxylate ion pair which collapses to products prior to equilibration with solvent. In such a case the constitution of the Cu(II) species will determine the selectivity even in those instances where electron transfer is the mode of oxidation. (b) I. Lundqvist, *Acta Chem. Scand.* **18**, 1125, 1210 (1964). (c) The absorbance of the maximum at 700 mμ in the visible absorption spectra of cupric acetate in glacial acetic acid decreases progressively with the addition of lithium acetate and levels off at higher acetate concentrations. This change correlates well with the change in the composition of the octenyl acetate mixtures (Table IV) formed as products, and is attributable to the formation of the anionic complexes VIIa.

$$C_8H_{15}\cdot + Cu(O_2CR)_{2+n}{}^{-n} \longrightarrow [C_8H_{15}{}^+Cu(O_2CR)_{2+n}{}^{-n-1}] \longrightarrow \underset{\text{IV, V}}{C_8H_{15}O_2CR} + Cu(I)(O_2CR)_{1+n}{}^{-n}$$

[55] The less hindered terminal position of the octenyl moiety would be more susceptible to this kind of oxidative nucleophilic displacement, and one may expect an increase in the 1-acetoxyoctene-2 relative to the 3 isomer. However, the leveling off of the effect beyond 0.7 *M* lithium acetate is not easily explained by this mechanism.

[56] R. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

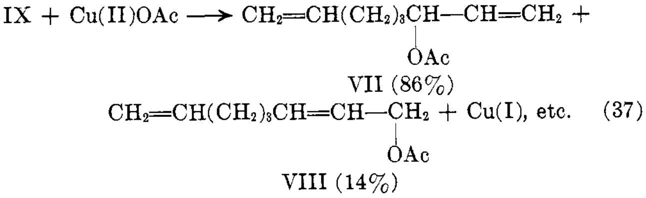
oxide (eq. 22, 25, and 30b) is an exceedingly efficient reaction. Considering the limited solubility of butadiene in acetic acid at 50°, the attainment of octenyl acetates in about 70% yields indicates that the addition of these radicals to butadiene (eq. 30b) is successfully competing with the facile oxidation by cupric salt (eq. 26). This phenomenon is further indicated by the formation of octadienyl acetates VII and VIII in approximately 30–40% yield (based on a 1:2 stoichiometry) from the catalyzed decomposition of allylacetyl peroxide in acetic acid with no added butadiene. In analogy with the previous scheme,[8a] the following reactions (33–37) can be invoked. In the presence of butadiene, these octadienyl acetates are formed in 85% yields (based on a 1:1 stoichiometry) at 15°.

$$(CH_2{=}CHCH_2CH_2CO_2)_2 + Cu(I) \longrightarrow CH_2{=}CHCH_2CH_2CO_2\cdot + Cu(II)O_2CC_4H_7 \qquad (33)$$

$$CH_2{=}CHCH_2CH_2CO_2\cdot \longrightarrow CH_2{=}CHCH_2CH_2\cdot + CO_2 \qquad (34)$$

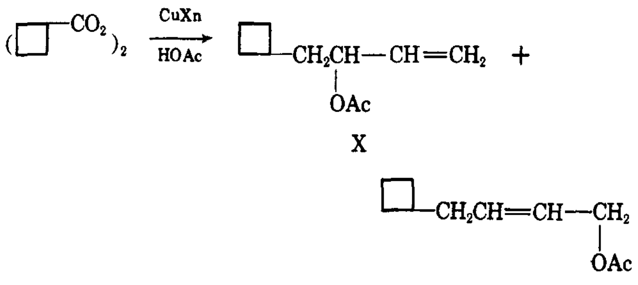
$$CH_2{=}CHCH_2CH_2\cdot + Cu(II)O_2CC_4H_7 \longrightarrow CH_2{=}CHCH{=}CH_2 + C_4H_7CO_2H + Cu(I), \text{etc.} \qquad (35)^{8a}$$

$$CH_2{=}CHCH_2CH_2\cdot + C_4H_6 \longrightarrow \underset{\text{IX}}{CH_2{=}CH(CH_2)_3CH{\cdots}CH{\cdots}CH_2} \qquad (36)$$



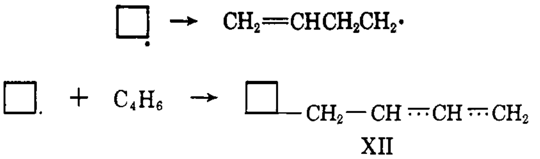
$$\text{IX} + Cu(II)OAc \longrightarrow \underset{\text{VII (86\%)}}{CH_2{=}CH(CH_2)_3\underset{\displaystyle OAc}{CH}{-}CH{=}CH_2} + \underset{\text{VIII (14\%)}}{CH_2{=}CH(CH_2)_3CH{=}CH{-}\underset{\displaystyle OAc}{CH_2}} + Cu(I), \text{etc.} \qquad (37)$$

Cyclobutanecarbonyl peroxide on decomposition with copper salts yields only small amounts (~5%) of addition products X and XI, related to those obtained from allylacetyl peroxide or valeryl peroxide and butadiene. The low yields of X and XI as adducts is attributed to the rather slow ring opening of cyclobutyl radicals followed by subsequent oxidation to butadiene.



X

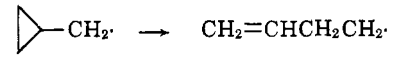
XI



XII

The addition of cyclobutyl radical to butadiene to form the allylic cyclobutylbutenyl radical XII is favored in the presence of added butadiene. In the latter instance, 78% yields of X and XI have been obtained (based on peroxide). The oxidation of the adduct radicals IX and XII to a mixture of isomeric allylic acetates is subject to the same effects of acetonitrile as those observed with the octenyl radical III as shown in Table V.

Cyclopropylacetyl peroxide reacts with cupric acetate to yield the same mixture of octadienyl acetates VII and VIII in 35–45% yields as that obtained from allylacetyl peroxide. Even at −8°, no evidence for a cyclopropyl or cyclobutyl adduct could be found. The isomerization of the cyclopropylcarbinyl radical is apparently too rapid to trap with butadiene under these conditions.



Experimental

Materials.—Octene-1,1,3-butadiene, and butene-1, Phillips Petroleum Co. pure grade, redistilled before use, were used. The sources for other materials were cupric acetate hydrate, $Cu(O_2CCH_3)_2\cdot 2H_2O$, Mallinckrodt analytical reagent; cupric 2-ethylhexanoate, Shepherd Chemical Co.; cuprous chloride and bromide, City Chemical Co.; cupric acetylacetonate, Pearsall Chemical Co.; phenanthroline, G. F. Smith Chemical Co.; biquinoline and bipyridine, Eastman Kodak Co.; hexafluoroacetone, Peninsular Chemical Co.; zinc, American Smelting and Refining Co.; zinc–copper couple prepared according to Schechter; and hydrogen-reduced copper from reduction of cuprous oxide.

t-Butyl peracetate, Lucidol Corp., was redistilled *in vacuo*, b.p. 25–26° (0.6 mm.). *n*-Valeryl peroxide was synthesized from valeryl chloride and hydrogen peroxide. Allylacetyl peroxide was prepared from allylacetyl chloride and hydrogen peroxide (allylacetic acid, Peninsular Chemical Co.).

Solvents were acetic acid, glacial, Du Pont reagent grade; acetonitrile, Matheson reagent or practical redistilled from phosphorus pentoxide. Other solvents were commercially available reagent grade pyridine, 2,6-lutidine, and γ-collidine, Eastman Kodak Co.; tetramethylene sulfone, Shell Development Co.

Perester Reaction.—A mixture of *t*-butyl peracetate (15 g.), 30 ml. of octene-1, and 100 ml. of benzene (thiophene free) was stirred with 1.83 g. of cupric 2-ethylhexanoate and 5 ml. of acetic acid for 12 hr. at 80°. The reaction was diluted with water and washed with dilute hydrochloric acid and water. It was analyzed by gas chromatography on a 9-ft. diethylene glycol succinate column at 165° (retention times: *n*-hexyl acetate, 10 min.; 3-acetoxyoctene-1, 13 min.; 1-acetoxyoctene-2, 24 min.) using *n*-hexyl acetate as an internal standard. After separation of the solvent, distillation yielded 14 g. of a mixture of octenyl acetates, b.p. 84–110° (12 mm.). It was hydrogenated over Adams catalyst to a mixture of 1- and 3-octyl acetates which was compared with authentic samples prepared from 1- and 3-octanols (K and K Laboratories) and acetic anhydride.

Reactions at lower temperatures with octene-1 were run with added zinc, zinc–copper couple, or hydrogen-reduced copper. Since the metals are insoluble, these reactions were conducted with vigorous stirring for approximately 30 hr. In general, yields of octenyl acetates obtained in reactions conducted with zinc were lower than those run at higher temperatures in the absence of metals. Zinc was consumed partially during the reaction and probably reacted with free radicals generated in solution since the peroxide itself does not react with zinc under these conditions. Neither do zinc nor zinc salts cause isomerization of the octenyl acetates. Isomer distributions determined by gas chromatography were generally reproducible to ±1.5%. Values reported in the tables were average values which were highly consistent from run to run.

Valeryl Peroxide and Butadiene.—Valeryl peroxide (1.50 g.) was added to a solution of cupric acetate (0.36 g.) in 20 ml. of acetic acid in a 50-ml. round-bottom ₸ 14/10 flask equipped with an 8-mm. side arm. The flask was connected to a gas buret *via* a three-way stopcock. Butadiene was passed through the solution with a capillary inserted in the side arm and the air was displaced from the system. Excess (100 cc.) butadiene was collected in the reservoir over mercury. In this way a butadiene atmosphere was maintained over the reaction at approximately 1 atm. pressure. No attempt was made to regulate the butadiene concentration in solution since the solubility of butadiene varies with solvents. The reactions at low temperatures were initiated

TABLE V

OXIDATION BY CUPRIC ACETATE OF BUTADIENE ADDUCTS WITH CYCLOBUTYL AND 3-BUTENYL RADICALS[a]

Peroxide	Solvent (vol. %)[b]	Cupric acetate, M	Temp., °C.	Total C_8 acetates,[c] %	1,2-Acetate[d] VII, X, %	1,4-Acetate[d] VIII, XI, %
Allylacetyl	HOAc (100)	0.009	57	40	86	14
Allylacetyl	HOAc (100)	0.05	57	30	86	14
Allylacetyl	HOAc (100)	0.011	50	35	84	16
Allylacetyl	HOAc (100)	0.011	25	34	83	17
Allylacetyl	HOAc (100)	0.011	0	37	82	18
Allylacetyl	HOAc[e] (100)	0.012	22	81	85	15
Allylacetyl	CH_3CN (63)	0.05	15	31	75	25
Allylacetyl	CH_3CN (50)	0.06	25	42	65	35
Allylacetyl	CH_3CN[e] (50)	0.06	15	85	59	41
Allylacetyl	CH_3CN (50)	0.06	1	41	57	43
Allylacetyl	HOAc[e,f] (90)	0.012	26	76	53	47
Cyclobutanecarbonyl	HOAc (100)	0.03	26	4	89	11
Cyclobutanecarbonyl	HOAc[e] (100)	0.016	26	74	83	17
Cyclobutanecarbonyl	CH_3CN[e] (50)	0.06	15	78	54	46
Cyclobutanecarbonyl	CH_3CN (60)	0.03	25	1	~60	40
Cyclobutanecarbonyl	CH_3CN (20)	0.03	15	4	~45	55
Cyclobutanecarbonyl	HOAc[e,f] (90)	0.012	26	69	42	58
Cyclopropylacetyl	HOAc (100)	0.05	26	47	88	12
Cyclopropylacetyl	CH_3CN (63)	0.05	2	35	60	40
Cyclopropylacetyl	CH_3CN (48)	0.06	−8 ± 0.5	34	53	47

[a] In solutions of 0.3 M peroxide, acetic acid, and acetonitrile. [b] Remainder is acetic acid. [c] Yield of adducts based on peroxide (1:2 stoichiometry). [d] Composition of isomeric C_8 acetate. [e] In butadiene atmosphere. Yields based on 1:1 stoichiometry. [f] Pyridine (10 vol. %).

with either cuprous chloride or acetate. No difference was noted between the cuprous salts. At low temperatures the chain length is about five and cuprous salt had to be added periodically to maintain reaction.[12]

The reaction mixture was generally clean and consisted of butene-1 and carbon dioxide as gases and valeric acid, 3-acetoxyoctene-1, and 1-acetoxyoctene-2 as the principal components. The latter were identified by trapping the peaks from the gas chromatograph and comparing the infrared spectrum with samples obtained from the octene-1 and perester reaction (acetate bands at 8.2 μ; 1-acetoxyoctene-2, *trans*-alkene band at 10.4 μ; 3-acetoxyoctene-1, vinyl group at 10.1 and 10.7 μ). The formation of butene-1 was the only apparent side reaction obtained when octenyl acetates were formed in this manner. It undoubtedly arises by the oxidation of n-butyl radicals[8a] by cupric salts in competition with its addition to butadiene. Optimum copper salt concentrations were not explored. Qualitatively, it was observed that, at high cupric salt concentrations, more butene-1 and less octenyl acetates were formed as expected by their mode of formation.

The addition of butyl radicals to butadiene is rapid under these conditions. Even when only 2 equiv. of butadiene was added to a reaction mixture under nitrogen, 30–40% yields of octenyl acetates (based on peroxide) were formed. Butadiene forms complexes with cuprous salts and it is possible that a cuprous-butadiene species is the reductant. If such is so, the high trapping efficiency of butadiene may be attributed to its "high concentration" in the vicinity of the butyl radical being formed. We are exploring the possibility of such germinate combinations further.

$$(C_4H_9CO_2)_2 + Cu(I)(C_4H_6) \longrightarrow \overline{C_4H_9\cdot + C_4H_6\cdot Cu(II)O_2CC_4H_9} + CO_2, \text{ etc.}$$

Allylacetyl Peroxide.—Allylacetyl peroxide (1.15 g.) was decomposed in 20 ml. of a deaerated solution of cupric acetate (0.009 M) in acetic acid at 57°. Hexane was added to the reaction mixture, which was then poured into water. The hexane extract, after washing with sodium bicarbonate and water, was dried with sodium sulfate. It was analyzed by gas chromatography on a diethylene glycol succinate column at 150° with 2-ethylhexyl acetate as an internal standard (retention times: 2-ethylhexyl acetate, 18 min.; 3-acetoxy-1,7-octadiene, 24 min.; 1-acetoxy-2,7-octadiene, 48 min.). Each octadienyl isomer was trapped and the infrared spectrum in the region between 10 and 11 μ showed that the isomer eluted earlier was VII (absorption at 10.1 and 10.8 μ), and the later one was VIII (complex band at ~10.1, 10.5, and 10.8 μ). Each isomer was hydrogenated at atmospheric pressure over Adams catalyst. The infrared spectra and gas chromatographic behavior showed that VII was converted to 3-octyl acetate and VIII to 1-octyl acetate. When VII was reduced with less than 2 equiv. of hydrogen, three new peaks were resolved on the gas chromatogram; the first and second peaks were 3-octyl acetate and 3-acetoxyoctene-1, respectively.

Cyclobutanecarbonyl Peroxide.—Cyclobutanecarbonyl peroxide was decomposed in the same manner as allylacetyl peroxide. The low-temperature reactions were initiated by either cuprous acetate or chloride. The cyclobutylbutenyl acetates were not isolated. The gas chromatographic behavior (on DEGS at 165°) was similar to the octadienyl acetates, being displaced further by approximately 5 min. The mixture was hydrogenated over Adams catalyst to a mixture of cyclobutylbutenyl acetates (g.l.c.); partial hydrogenation gave only two peaks. The infrared spectrum of X showed the characteristic acetate band at 8.2 μ and the vinyl doublet at 10.3 and 10.8 μ; the latter largely disappeared on hydrogenation. The spectrum of XI showed bands at 8.2 and 10.4 (*trans*-alkene) μ. The spectrum of the hydrogenation products of X and XI are similar.

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