Fraction E (2 g.) was dissolved in 200 ml. of anhydrous ether and intermittently shaken with 25 ml. of a saturated aqueous solution of sodium benzoate for 18 hr. The layers were separated, the ether layer evaporated to dryness, and the residue recrystallized three times from absolute ethanol to give N,N-dibenzoylbenzylamine, m.p. 109–110°; Mumm, Hesse and Volquartz[26] report 108°. When mixed with the starting amide, m.p. 105.5–106.5°, the m.p. was 80–100°.

α-p-Dimethylbenzyl Chloride.—The products from the von Braun reactions of N-α,*p*-dimethylacetamide, propionamide and benzamide were identical (infrared spectra). The following b.p. data were obtained: 65° (2.5 mm.), 67° (3.5 mm.), 65–70° (4.5 mm.), 88–90° (12.5 mm.); $n^{22}D$ 1.5250, $n^{25}D$ 1.5240.

Anal. Calcd. for $C_9H_{11}Cl$: C, 69.91; H, 7.17; Cl, 22.93. Found: C, 70.04; H, 7.25; Cl, 22.66.

In the propionamide reaction *p*-methylstyrene, b.p. 60–61° (12.5 mm.), $n^{22}D$ 1.5394, dibromide m.p. 44.5–45.5° (reported[27] b.p. 81°) (41 mm.), $n^{20}D$ 1.5420, dibromide m.p. 44.0–44.5°) was isolated.

α-Cyclopentylbenzyl Chloride.—The products from the von Braun reactions of N-α-cyclopentylbenzylacetamide and benzamide were identical (infrared spectra). The following b.p. data were obtained; 103–104° (2.5 mm.), 112–114° (4 mm.), $n^{26}D$ 1.5380.

Anal. Calcd. for $C_{12}H_{15}Cl$: C, 74.01; H, 7.77; Cl, 18.21. Found: C, 74.12; H, 7.73; Cl, 18.31.

The structure of this chloride was confirmed in the following manner. A 1.40-g. (0.007 mole) sample was dissolved in 30 ml. of a 50% aqueous solution of triethanolamine and then heated on the steam-bath for 48 hr. The resulting solution was extracted with benzene and the benzene extracts were washed twice with 10% hydrochloric acid and once with water, dried and evaporated in an air stream on the steam-bath leaving 1.0 g. of slightly yellow oil. The oil was dissolved in 2.5 ml. of glacial acetic acid, and this solution was added with shaking to a cooled mixture of 0.7 g. (0.007 mole) of chromic oxide in 2.5 ml. of 80% acetic acid. After standing at room temperature for 48 hr., the reaction mixture was poured into 10 ml. of ice-water and extracted with benzene. The benzene extract was washed twice with 10% sodium bicarbonate solution and once with water, dried and evaporated on the steam-bath. The residual oil possessed an infrared spectrum identical with that of authentic phenylcyclopentyl ketone,[28] and the 2,4-dinitrophenylhydrozone melted at 142.0–143.5°, reported[29] 144.5–145.5°.

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[26] O. Mumm, H. Hesse and H. Volquartz, *Ber.*, **48**, 379 (1915).

[27] L. H. Schwartzman and B. B. Corson, *J. Am. Chem. Soc.*, **78**, 322 (1956).

[28] P. A. Smith, D. R. Baer and S. N. Ege, *ibid.*, **76**, 4564 (1954).

[29] D. V. Nightingale and M. Maienthal, *ibid.*, **72**, 4823 (1950).

[CONTRIBUTION FROM SHELL DEVELOPMENT CO., EMERYVILLE, CALIF.]

Copper Salt-catalyzed Reaction of Butenes with Peresters[1a]

BY JAY K. KOCHI[1b]

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The mechanism of the copper salt-catalyzed reactions of peresters has been studied. The role of copper salts in these free radical reactions is described by a series of one-electron oxidation–reduction steps: first, the oxidation of cuprous ion by perester to alkoxy radical and cupric carboxylate; and second, reduction of the cupric salt by a free radical generated by the chain transfer reaction between the alkoxy radical and an hydrogen donor compound. With butenes, butenyl radical intermediates are shown to equilibrate to produce a mixture of α-methallyl and crotyl esters independent of the reactant normal butene isomer. The effect of solvent and foreign nucleophiles is examined. The nature of the oxidation of allylic radicals by cupric species is elaborated.

Introduction

The copper salt-catalyzed reactions of peroxides and hydrogen donor substrates have been extensively described by Kharasch and co-workers.[2,3] The reaction can be delineated in its most general form as

$$XOOY + RH \xrightarrow{Cu^I} ROX + HOY \qquad (1)$$

Peroxides which have been employed include benzoyl peroxide, *t*-butyl peracetate and perbenzoate, *t*-butyl hydroperoxide, di-*t*-butyl peroxide and related compounds. The hydrogen donor substrates include olefins, ethers, aldehydes, aralkanes and generally compounds possessing hydrogen atoms labile to free radical abstraction processes.

The mechanism originally[2] postulated for this versatile reaction involves a termolecular complex of substrate, peroxide and copper salt. Subsequently, Denney, *et al.*,[4] have presented corroborative evidence for this mechanism. An important part of this mechanism is its ability to account for the *non-rearrangement* of olefinic bonds during substitution. Thus, Kharasch and Sosnovsky and Yang[2b] reported that octene-1 with *t*-butyl perbenzoate yielded exclusively 3-benzoxyoctene-1. Denney, *et al.*,[4] also reported non-rearrangements in the cases of allylbenzene and propenylbenzene with *t*-butyl peresters. Some earlier work[2] with benzoyl peroxide, however, showed appreciable amounts of rearrangement products.

Studies[5] on the reactions of free radicals and metal ions demonstrated the facile oxidation–reduction reactions between free radicals and metal ions. With copper salts these reactions are described by the generalized equations[5a]

$$R\cdot + Cu^{II} \xrightarrow{SH} RS + Cu^I + H^+ \qquad (2)$$

$$R\cdot + Cu^{II} \longrightarrow \text{olefin} + Cu \;\, + H^+ \qquad (3)$$

SH is a protic solvent

In particular, allylic radicals were oxidized by cupric salts to a *mixture* of two isomeric allylic

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[1] (a) Presented, in part, before the Petroleum section of the Gordon Research Conference at Colby College, N. H., June 14, 1961. (b) Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio.

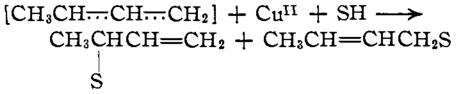
[2] M. Kharasch, *et al.*, (a) *J. Am. Chem. Soc.*, **80**, 756 (1958); (b) **81**, 5819 (1959); (c) *J. Org. Chem.*, **23**, 324 (1958); (d) **24**, 72, 606, (1959).

[3] (a) G. Sosnovsky and N. Yang, *J. Org. Chem.*, **25**, 899 (1960); (b) G. Sosnovsky, *ibid.*, **25**, 874 (1960); **26**, 281 (1961).

[4] D. Denney, *et al.*, *Tetrahedron Letters*, **No. 15**, 19 (1959).

[5] (a) H. De La Mare, J. Kochi and F. Rust, *J. Am. Chem. Soc.*, **83**, 2013 (1961); (b) J. Kochi, *ibid.*, **78**, 4815 (1956); **79**, 2942 (1957); (c) J. Kumamoto, H. De La Mare and F. Rust, *ibid.*, **82**, 1935 (1960); (d) E. Collinson, F. S. Dainton, D. R. Smith, G. J. Trudel and S. Tazuké, *Faraday Soc. Dis.*, **29**, 188 (1960); (e) R. M. Haines and W. A. Waters, *J. Chem. Soc.*, 4256 (1955); (f) C. Bamford, A. Jenkins and R. Johnston, *Nature*, **177**, 992 (1956).

products. No stereoselectivity was indicated in these reactions between isomeric allylic radical reactants and cupric salts. The reaction involving butenyl radicals was given by the equation



$$[CH_3CH\cdots CH\cdots CH_2] + Cu^{II} + SH \longrightarrow \underset{\textstyle S}{CH_3\underset{|}{C}HCH{=}CH_2} + CH_3CH{=}CHCH_2S + Cu^{I} + H^{+}$$

The mechanism of the copper salt-catalyzed peroxide reactions can be explained if these copper salt-free radical oxidation–reduction reactions are invoked, together with other conventional free radical processes. The steps (4), (5), (6) would be included

$$X\text{-}O\text{-}O\text{-}Y + Cu^{I} \longrightarrow XOCu^{II} + YO\cdot \quad (4)$$

$$YO\cdot + RH \longrightarrow YOH + R\cdot \quad (5)$$

$$R\cdot + XOCu^{II} \longrightarrow ROX + Cu^{I} \text{ etc.} \quad (6)$$

Since allylic radical intermediates from olefin substrates (RH = olefin), formed in reaction 5 and oxidized by cupric salt in 6, are not consonant with the earlier observations[2,4] of the non-rearrangement of olefinic bonds, the copper salt-catalyzed reaction of peresters and olefins was reinvestigated. The isomeric normal butene isomers were chosen as olefin hydrogen donors to facilitate accurate and unequivocal analysis of the well-characterized reaction products.

Results

Reaction of *t*-Butyl Perbenzoate with the Isomeric Butenes and Cuprous Salt in Benzene.—Butene-1 (0.7 mole) and *t*-butyl perbenzoate (0.2 mole) in the presence of catalytic amounts of cuprous bromide (200 mg.) in benzene react readily at 80–90° to form a mixture of butenyl benzoates in 70–80% yield, which was analyzed by gas-liquid chromatography (g.l.c.) and the esters isolated by distillation. The infrared spectra and g.l.c. characteristics were compared with authentic specimens. The mixture of butenyl benzoates consisted of 86–90% 3-benzoxybutene-1 and 14–10-% crotyl benzoate. In a similar manner butene-2 (55% *cis* and 45% *trans*) yielded a mixture of butenyl benzoates in 75% yield which consisted of 3-benzoxybutene-1 (87–89%) and crotyl benzoate (13–11%). Experiments were repeated at least in duplicate to check reproducibility. The results are shown in Table I (see Experimental). In all runs butene-1 yielded the same mixture (87–91% 3-benzoxybutene-1 and 13–9% crotyl benzoate) of isomeric butenyl benzoates.

The high yield of the secondary isomer is not due to the rearrangement of the primary crotyl benzoate. When crotyl benzoate is charged into a reaction of pentene-1 and *t*-butyl perbenzoate in benzene it is recovered unchanged. The isomeric 3-benzoxybutene-1 could not be detected by g.l.c. Under these conditions the pentenyl benzoates are formed in 68% yield and are distributed between 3-benzoxypentene-1 (88%) and 1-benzoxypentene-2 (12%).

The olefins also did not suffer allylic rearrangement. The unreacted olefin was recovered from the reaction mixture and was examined by g.l.c. Recovered butene-1 was not contaminated with the isomeric 2-butenes. Similarly, examination of the recovered butene-2 isomeric mixture indicated the complete absence of butene-1.

The isomeric 2-butenes were also examined separately in their reaction with *t*-butyl perbenzoate in benzene solution. They yielded the same mixture of butenyl benzoates in the same over-all yields (72% from *cis*, 71% from *trans*). The ester fraction consisted of 3-benzoxybutene-1 (90–94% from *cis* and 85–87% from *trans*) and crotyl benzoate (~8% and ~13%, respectively). Examination of the unreacted butene-2, however, indicated that *cis–trans* isomerization had occurred. The ester-free *trans*-butene-2 recovered from the reaction mixture indicated the presence of 5–8% *cis* isomer. No butene-1 was found. Similarly, the ester-free *cis*-butene-2 after recovery from the reaction mixture consisted of a mixture of 55–65% *cis* and 45–35% *trans* isomers. In a blank experiment under more drastic conditions pure *cis*-butene-2 was charged with a mixture of cupric and cuprous bromide in benzene solution containing ethyl acetate and heated for 50 hours at 90–100°. Less than 0.5% of *cis* was isomerized to *trans*-butene. No butene-1 was found. Similarly, with pentene-1 no rearrangement to pentene-2 was observed. Further blank experiments charged with *t*-butyl perester and *cis*-butene-2 (8–10-fold excess) in benzene and heated for 60 hr. at 98° produced 3–4% *trans* isomer.

The reaction, however, catalyzed by cuprous chloride showed less than 3% *cis–trans* isomerization of the olefin. The gross relative reactivity of *cis*- and *trans*-butene-2 was measured using a four-fold excess of the olefin mixture. In benzene and acetic acid solvents *cis*-butene-2 was consumed 1.3–1.4 times faster than *trans*-butene-2. This compares with a *cis*/*trans* relative rate for the chlorination of butene-2 with *t*-butyl hypochlorite of 1.33 in benzene at 25° and 1.38 in carbon tetrachloride.[6]

Effect of Solvent.—The effect of solvent variation on the reaction of the isomeric butenes with *t*-butyl perbenzoate was examined. Butene-1 and *t*-butyl perbenzoate in acetonitrile yielded a mixture of butenyl benzoates in 74% yield. It consisted of 91% 3-benzoxybutene-1 and 9% crotyl benzoate.

In anhydrous *t*-butyl alcohol, *trans*-butene-2 and *t*-butyl perbenzoate gave the butenyl benzoates in 77% yield. The mixture consisted of 91% 3-benzoxybutene-1 and 9% crotyl benzoate.

A reaction consisting of *t*-butyl perbenzoate and *trans*-butene-2 in a solution of 83% v. *t*-butyl alcohol–water yielded 57% butenyl benzoates and 8% butenols. The butenyl benzoate mixture consisted of 87% 3-benzoxybutene-1 and 13% crotyl benzoate. Similarly, the butenol fraction consisted of 83% butene-1-ol-3 and 17% crotyl alcohol.

The butenol mixture did not arise *via* hydrolysis of the butenyl benzoates. If crotyl benzoate is charged into a reaction of pentene-1 and *t*-butyl perbenzoate in 83% v. *t*-butyl alcohol–water, it is recovered unchanged. Neither the rearrangement product, 3-benzoxybutene-1, nor the hydrolysis

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[6] C. Walling, B. Jacknow and W. Thaler, Abstracts, American Chemical Society Meeting, Sept., 1959, Atlantic City, N. J., p. 59-P.

product, crotyl alcohol (nor buten-1-ol-3), could be found. There is formed in 41% yield a mixture of pentenyl benzoates consisting of 90% 3-benzoxypentene-1 and 10% 1-benzoxypentene-2. The pentenol fractions were not examined.

The reaction of *trans*-butene-2 and *t*-butyl perbenzoate in glacial acetic acid gave a mixture of esters in 60% yield. The mixture consisted of the isomeric butenyl acetates (77%) and butenyl benzoates (23%). The distribution of the isomers in the acetate fraction was 89% 3-acetoxybutene-1 and 11% crotyl acetate. The butenyl benzoates consisted of 90% 3-benzoxybutene-1 and 10% crotyl benzoate.

Under the reaction conditions the benzoates do not undergo exchange with acetic acid to form the butenyl acetates. A charge of crotyl benzoate in a mixture of pentene-1 and *t*-butyl perbenzoate in glacial acetic acid was converted to less than 1% crotyl acetate. No 3-acetoxybutene-1 was found. The products are the pentenyl acetates formed in 67% yield and pentenyl benzoates formed in 5% yield. The pentenyl acetate mixture consisted of 91% 3-acetoxypentene-1 and 9% crotyl acetate. The pentenyl benzoate fraction consisted of 91% 3-benzoxybutene-1 and 9% crotyl benzoate. The ratio of *t*-butyl alcohol to 3-acetoxypentene-1 was 1.50 which indicated a 72% yield of the pentenyl acetates.

Reaction of Butene with *t*-Butyl Peracetate and Cuprous Salts.—*cis*-Butene-2 and *t*-butyl peracetate were allowed to react in benzene solution to yield a mixture of butenyl acetates in 84% yield. The mixture consisted of 90% 3-acetoxybutene-1 and 10% crotyl acetate. They were compared with authentic samples. The isomeric butenyl acetates and *t*-butyl alcohol were analyzed by g.l.c. The ratio of *t*-butyl alcohol to butenyl acetates was found to be 1.16 which indicated a 86% yield of acetates based on *t*-butyl alcohol formed. This is in excellent agreement with the 84% yield determined titrimetrically. The stoichiometry of the reaction is, thus

$$C_4H_8 + CH_3CO_2Bu\text{-}t \xrightarrow{Cu^I} C_4H_7O_2CCH_3 + t\text{-BuOH} \quad (7)$$

trans-Butene-2 and *t*-butyl peracetate reacted in 83% v. *t*-butyl alcohol–water to yield a mixture of butenyl acetates (48%) and butenols (10%). The butenyl acetate mixture consisted of 85% 3-acetoxybutene-1 and 15% crotyl acetate. Similarly, the butenol mixture was found to consist of 81% buten-1-ol-3 and 19% crotyl alcohol.

Butene-1 and *t*-butyl peracetate were allowed to react in absolute methanol to yield a mixture of butenyl methyl ethers (11%) and esters (82%). The butenyl methyl ether mixture was compared with authentic samples prepared from the reactions of crotyl chloride and 3-chlorobutene-1 with sodium methoxide. The composition of the mixture corresponded to 87% 3-methoxybutene-1 and 13% crotyl methyl ether. The ester components were identified as methyl acetate (43%) and the isomeric butenyl acetates (57%). The over-all butenyl acetate yields were 43% (based on peroxide) distributed between 3-acetoxybutene-1 (94%) and crotyl acetate (6%). Other experiments with *cis*-butene-2 yielded similar results. Thus, 9% butenyl methyl ethers and 51% butenyl acetates were formed. The butenyl ether mixture was composed of approximately 90% 3-methoxybutene-1. The butenyl acetate fraction was 97% 3-acetoxybutene-1 and 3% crotyl acetate.

The reactions in methanol, *tert*-butyl alcohol, acetonitrile and acetic acid solvents were completely homogeneous. Those in benzene and *n*-hexane were partially heterogeneous even at the low levels of copper salts charged. In the former solvents, the addition of extra cupric acetate (~3 mole %) caused a slight increase in the percentage of α-methallyl acetate (~95–98%) in the butenyl acetate mixture.

Discussion

Butene–*t*-Butyl Perester Reactions.—The pattern of results indicates that within a few per cent. the compositions of the products obtained were quite independent of the reactant olefin. In those reactive solvents such as water, methanol and acetic acid, mixtures of pairs of butenyl derivatives are formed, in which the ratios of primary to secondary isomers are approximately the same, Thus, the pairs of acetates, benzoates, ethers and alcohols are all formed with the α-methallyl isomer predominant (approximately 85–95%). This distribution also was extended into the series derived from pentene-1. Moreover, the effect of solvents on these reactions was found to be surprisingly small. The yields of esters in acetonitrile, *tert*-butyl alcohol, *tert*-butyl alcohol/water, and acetic acid were approximately the same as those obtained in benzene. The distribution of products into secondary and primary isomers was also relatively unaffected by solvent.

In the protic solvents the degree of solvent intervention is related to the acid strength. Thus, acetic acid as solvent yields primarily acetates (not through interchange of the ester or perester). Methanol, water, and to a much lesser degree *t*-butyl alcohol are less effective (*e.g.*, the ratio of ether to ester was 4 to 66 at high methanol concentration).

Any mechanism postulated for this reaction must account for the following observations: (a) catalysis by cuprous salt, (b) the similarity of products and yields obtained from the three isomeric normal butenes, (c) the relatively high ratio of α-methallyl relative to crotyl derivatives, (d) the minor role played by the solvent, (e) the high yields of esters obtained in protic solvents such as methanol and water in relation to ethers and alcohols, and (f) the acetates produced from reactions of perbenzoates in acetic acid.

With these considerations in mind the copper-catalyzed peroxide reaction is postulated to proceed as shown

$$RCO_2OBu\text{-}t + Cu^I \xrightarrow{I} RCO_2Cu^{II} + t\text{-BuO}\cdot \quad (8)$$

$$t\text{-BuO}\cdot + C_4H_8 \xrightarrow{II} t\text{-BuOH} + C_4H_7\cdot \quad (9)$$

$$C_4H_7\cdot + Cu^{II}\ O_2CR \xrightarrow{III} C_4H_7O_2CR + Cu^I \text{ etc.} \quad (10)$$

Step I.—The cuprous-catalyzed decomposition of peroxides has ample analogies. The complete realm of reactions involving hydroperoxides and reduced metal ions such as Fe^{II}, V^{III}, Ti^{III}, etc., has been extensively documented.[7] In each case the reaction proceeds *via* an electron transfer from the metal to the peroxide link. Catalysis of the decomposition of disubstituted peroxides by

$$ROOH + M^{+n} \longrightarrow RO\cdot + M(OH)^{+n} \quad (11)$$

metal ions is less well-known.[8] The analogous reaction between *t*-butyl perester and cuprous ion would be

$$RCO_2OR' + Cu^{I} \longrightarrow RCO_2Cu^{II} + R'O\cdot \quad (12)$$

This cleavage is preferred to the alternative path (13) on energetic grounds

$$RCO_2OR' + Cu^{I} \longrightarrow RCO_2\cdot + R'OCu^{II} \quad (13)$$

With benzoyl peroxide, however, the production of benzoxy radicals is unavoidable.[9]

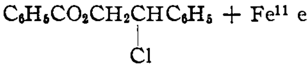
$$(C_6H_5CO_2)_2 + Cu^{I} \longrightarrow C_6H_5CO_2Cu^{II} + C_6H_5CO_2\cdot \quad (14)$$

The latter reaction was observed earlier[10] in the facile peroxide addition to styrene in the presence of ferric(ous) chloride.[11b]

$$(C_6H_5CO_2)_2 + Fe^{II} \longrightarrow C_6H_5CO_2Fe^{III} + C_6H_5CO_2\cdot \quad (15)$$

$$C_6H_5CO_2\cdot + C_6H_5CH{=}CH_2 \longrightarrow C_6H_5CO_2CH_2\underset{\cdot}{C}HC_6H_5$$

$$C_6H_5CO_2CH_2\underset{\cdot}{C}HC_6H_5 + Fe^{III}Cl_3 \longrightarrow$$



$$C_6H_5CO_2CH_2\underset{\substack{|\\ Cl}}{C}HC_6H_5 + Fe^{II} \text{ etc.}$$

The catalysis of perester decomposition by cuprous ion is easily observed with *t*-amyl perbenzoate. In benzene solution containing 0.2 g. of cuprous bromide, *t*-amyl perbenzoate is completely decomposed at 80° in 3 hours. In the absence of cuprous bromide the half-life for decomposition of the related *t*-butyl perbenzoate is 18 hours at 100° [11a]; the former decomposition proceeds[11b] with the production of an equivalent of gas comprised predominantly of ethylene with small amounts of ethane. Similar results are obtained with di-*t*-amyl peroxide.[11b]

$$C_6H_5CO_2Am\text{-}t + Cu^{I} \longrightarrow C_6H_5CO_2Cu^{II} + t\text{-}AmO\cdot \quad (16)$$

$$CH_3CH_2(CH_3)_2CO\cdot \longrightarrow CH_3COCH_3 + CH_3CH_2\cdot$$

$$CH_3CH_2\cdot + Cu^{II}O_2CC_6H_5 \longrightarrow CH_2{=}CH_2 + C_6H_5COOH + Cu^{I} \text{ etc.}$$

Step II.—The abstraction of hydrogen from donor substrates by *t*-butoxy radicals is well-known.[12] All substrates found[1–3,13,14] reactive to the copper *t*-butyl perester reactions are those also labile to *t*-butoxy radicals. Moreover, those systems such as styrene and butadiene[12] which readily add *t*-butoxy radicals yield[11b] telomers *via* the process

$$RCO_2OBu\text{-}t + Cu^{I} \longrightarrow RCO_2Cu^{II} + t\text{-}BuO\cdot \quad (17)$$

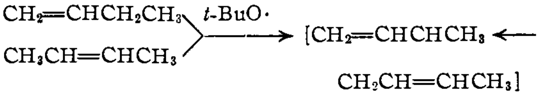
$$t\text{-}BuO\cdot + C_4H_6 \longrightarrow t\text{-}BuO\text{-}C_4H_6\cdot$$

$$t\text{-}BuO\text{-}C_4H_6\cdot + nC_4H_6 \longrightarrow t\text{-}BuO\text{-}(C_4H_6)_{n+1}\cdot$$

$$t\text{-}BuO\text{-}(C_4H_6)_{n+1}\cdot + Cu^{II}\,O_2CR \longrightarrow t\text{-}BuO\text{-}(C_4H_6)_{n+1}O_2CR + Cu^{I}$$

$$n = 0,1\ldots$$

With butenes abstraction of allylic hydrogens (the ones most labile to *t*-butoxy radicals) results in the same allylic radical from any of the normal isomers.



$$\left.\begin{array}{l} CH_2{=}CHCH_2CH_3 \\ CH_3CH{=}CHCH_3 \end{array}\right\rangle \xrightarrow{t\text{-}BuO\cdot} [CH_2{=}CHCHCH_3 \longleftrightarrow CH_2CH{=}CHCH_3] \quad (9)$$

The relative reactivity of *cis*- and *trans*-butene-2 toward *t*-butoxy radical produced in the perester reaction (1.3–1.4) is of the same order of magnitude as that produced in the radical chain chlorination with *t*-butyl hypochlorite (1.33–1.38) and it appears to be solvent insensitive. If a small difference in activation energy for the two isomers in the chain transfer step 9 is assumed, the approximately equal values obtained for the relative reactivity in the two systems is not fortuitous. The chain transfer steps in both the copper salt-catalyzed perester and photoinitiated *t*-butyl hypochlorite reactions thus proceed through the same intermediates.[15]

The *cis–trans* isomerization of butene-2 in these reactions is ascribable to bromine atoms since neither cuprous chloride nor cupric acetate catalyzed this rearrangement. The bromine atom-catalyzed *cis–trans* isomerization of olefins is well-documented,[12] and is postulated to occur *via* an addition–elimination mechanism. The extensive

$$Br\cdot + cis\text{-}C_4H_8 \rightleftarrows BrC_4H_8\cdot \rightleftarrows Br\cdot + trans\text{-}C_4H_8 \quad (18)$$

isomerization in the presence of catalytic amounes of bromide salts indicates the relatively long kinetic chain length[16] for the steps 18, even in the presence of cupric salts which compete for the intermediate bromoalkyl radicals.

Step III.—The distribution of products into 3-substituted butene-1 and 1-substituted butene-2 is nearly independent of the substituent. Thus, in each pair of isomeric butenyl products formed (acetoxy, benzoxy, methoxy and hydroxy substituted butenes) the mixture consists predominantly (85–95%) of the 3-substituted butene-1. This preponderance of the secondary isomer is unusual in allylic substitution reactions.

Typical SN1 reactions involving an incipient allylic carbonium ion yield mixtures of products which consist approximately of equal amounts of each allylic isomer.[17] Our studies have corroborated some earlier work[17] on the silver-ion assisted acetolysis of 3-chlorobutene-1 in glacial acetic acid.

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[7] A. Tobolsky and R. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

[8] See, *e.g.*, B. Davis, T. Halsall and A. Hands, *Proc. Chem. Soc.*, 83 (1961).

[9] The reaction of benzoyl peroxide and olefins in the presence of copper salts will be published subsequently.

[10] J. Kochi, *J. Am. Chem. Soc.*, **79**, 2942 (1957).

[11] (a) D. Doehnert and A. Mageli, *Modern Plastics*, **36**, 142 (1959); A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3408 (1951); (b) J. Kochi, to be published.

[12] C. Walling, "Free Radicals in Solution," J. Wiley and Sons, Inc., New York, N. Y., 1957.

[13] S. Lawesson and C. Berglund, *Tetrahedron Letters*, **No. 2**, 4 (1960); *Angew. Chem.*, **73**, 67 (1961).

[14] P. Story, *J. Am. Chem. Soc.*, **82**, 2085 (1960); *J. Org. Chem.*, **26**, 287 (1961).

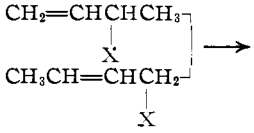
[15] The possibility of a copper-*t*-butoxy radical complex intermediate similar to the metal ion–alkyl radical complexes postulated earlier cannot be entirely discounted. Studies of the modes of decomposition of highly substituted alkoxy radicals in the presence of metal ions indicate that the formation of oxy radical–metal ion complexes are unlikely[11b] (J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **83**, 2017 (1961)).

[16] C. Walling, private communication.

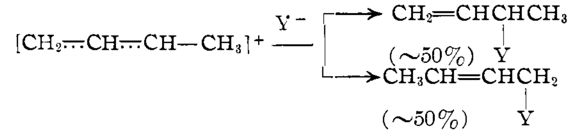
[17] R. DeWolfe and W. Young, *Chem. Revs.*, **56**, 753 (1956).

This system produces a mixture of 3-acetoxybutene-1 (48%) and crotyl acetate (52%). Similarly, the isomeric crotyl chloride under the same conditions yields 3-acetoxybutene-1 (46%) and crotyl acetate (54%) in approximately the same relative yields. The acetolysis of butenyl benzoates and acetates (exchange) is also catalyzed by cuprous ion. In 50% v. glacial acetic acid–acetonitrile the rate of acetolysis of the α-methallyl ester is faster than the crotyl isomer by several-fold. With α-methallyl benzoate the products are α-methallyl acetate (60–70%) and crotyl acetate (30–40%). Crotyl benzoate yields α-methallyl and crotyl esters in approximately equal amounts.

The nitrous acid deamination of the isomeric butenylamines yields[17] similar results. In these cases it has been postulated that the resonance-stabilized butenyl carbonium ion is an intermediate.

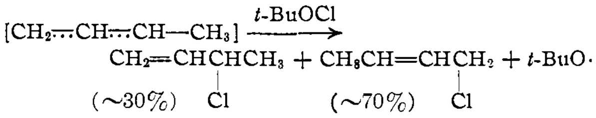


$$\left.\begin{array}{l} CH_2{=}CHCH(X)CH_3 \\ CH_3CH{=}CHCH_2X \end{array}\right\} \longrightarrow$$



$$[CH_2\cdots CH\cdots CH-CH_3]^+ \xrightarrow{Y^-} \begin{cases} CH_2{=}CHCH(Y)CH_3 \quad (\sim 50\%) \\ CH_3CH{=}CHCH_2Y \quad (\sim 50\%) \end{cases}$$

In a typical free radical substitution reaction involving a butenyl radical the distribution of products favors the crotyl isomer. Thus at low temperatures the isomeric butenes react with *t*-butyl hypochlorite to yield predominantly crotyl chloride.[6]

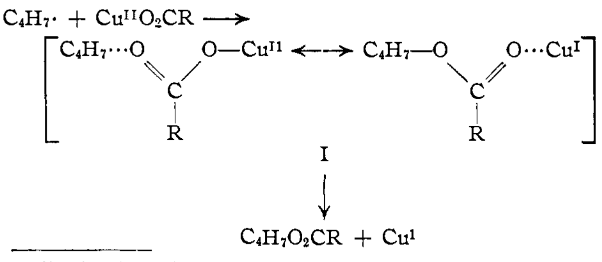


$$[CH_2\cdots CH\cdots CH-CH_3] \xrightarrow{t\text{-BuOCl}} \underset{(\sim 30\%)}{CH_2{=}CHCH(Cl)CH_3} + \underset{(\sim 70\%)}{CH_3CH{=}CHCH_2Cl} + t\text{-BuO}\cdot$$

In another free radical reaction $BrCCl_3$ adds to butadiene to form 1,4- and 1,2-adducts in 65–85% and 15–35% yields, respectively.[18] Cristol[19] has reported that the free radical addition of thiols to dienes proceeds predominantly in the 1,4-manner.

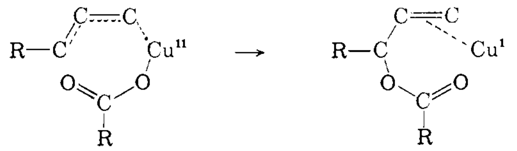
The high yields of 3-but-1-enyl derivatives from the copper-catalyzed peroxide reactions thus appear to be unique. To account for this selectivity several possibilities for step III can be considered.

(a) **Ligand Transfer.**—The carboxylate moiety is transferred directly from copper to the radical *via* a carboxylate bridge, in a process similar to the halide transfers.[20]



I

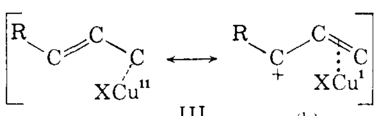
This mechanism has the attractive feature of predicting the minor effect of the solvent. To account for the preponderance of substitution at the secondary center, two possibilities can be considered: (i) cyclic process, in which an intermediate *complex* between butenyl radical and cupric species is formed.[15] Complex II is similar to the



II

recently described allyl cobalt carbonyl compounds[21a]; the driving force for substitution at the 3-position is the stabilizing effect of the cuprous–olefin interaction which is favored by a terminal rather than an internal double bond.[21b]

(ii) The alternative to the cyclic complex mechanism is one in which considerable carbonium ion character is developed in the *transition state* as in III



(a) III (b)

Under these conditions the stabilizing effect of the cuprous-olefin interaction would be maximized. In either (i) or (ii) product can arise intramolecularly by participation of ligand X (O_2CR, OR, OH, etc.).

(b) **Electron Transfer.**—It is also possible to postulate a simple electron transfer process for step III, in which an ion-pair IV is formed. Collapse of

$$C_4H_7\cdot + Cu^{II}O_2CR \longrightarrow \underset{IV}{\overline{C_4H_7{}^+\,Cu^IO_2CR}}$$

IV to ester[22] can occur directly or it is possible to exchange the ion-pair with solvent. With a simple allylic system it is difficult to see why the ion-

$$\overline{C_4H_7{}^+\,Cu^IO_2CR} + SH \longrightarrow C_4H_7S + Cu^I + HO_2CR$$

pair IV would exist long enough to exchange with solvent. However, if free radicals capable of yielding stable carbonium ions are formed, it is possible for such an exchange to occur. Triphenylmethyl and 7-norbornadienyl radicals may be such cases (see, however, footnote 29).

The essential difference between ligand transfer processes and electron transfer processes is one of timing or, stated alternatively, the amount of carbonium ion character in the transition state. The transition states for each can be formalized in this way

$R\cdots X\cdots M^{+n}$	$R^+\,X{-}M^{+n-1}$
Ligand transfer	Electron transfer

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[18] M. Kharasch, "Rapports et Discussions sur le Mecanisme de l'Oxydation," 8e Conseil International de Chimie Solvay, 1950, p. 186.

[19] S. Cristol, *et al.*, *J. Org. Chem.*, **26**, 365 (1961).

[20] J. Kochi, *J. Am. Chem. Soc.*, **78**, 4815 (1956); **79**, 2942 (1957); J. Kumamoto, H. De La Mare and F. Rust, *ibid.*, **82**, 1935 (1960).

[21] (a) R. Heck and G. D. Breslow, *ibid.*, **82**, 750 (1960); (b) J. Bailar, Editor, "Chemistry of Coördination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956, p. 487 ff.

[22] There are no direct model systems for the reactions of an unsolvated unsymmetrical allylic carbonium ion. In an electron transfer process the butenyl ion is produced in a milieu unaffected by solvent molecules. In such an ion reactions with nucleophilic species would occur primarily at the secondary center (*cf.* G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955); M. Silver, M. Caserio, H. Rice, J. Roberts, *ibid.*, **83**, 3671 (1961)).

The degree to which each of these two extreme cases in oxidation–reduction reactions participates in a particular metal system is dependent on the ligand being transferred as well as the ionization potential of the intermediate free radical.

With cupric salts and simple alkyl radicals, halides are transferred primarily by the ligand transfer process in which a minimum amount of carbonium ion character is developed in the transition state.[5a,5b,5c,11b] With resonance stabilized radicals even halides proceed via transition states with a high degree of ionic character.[11b]

In an electron transfer process a considerable amount of carbonium ion character is generated in the transition state. This mechanism is considered to be most important with radicals yielding resonance stabilized carbonium ions and cupric salts with poor ligand transfer properties (carboxylates, alkoxides, sulfate, perchlorate, etc.). These reactions can be formally considered to be solvolytic in character since products formed are those from carbonium ion intermediates.[5a,23] With such radicals as norbornadienyl and triphenylmethyl, the ligand transfer process with cupric carboxylate does not provide sufficient extra driving force over the formation of the resonance-stabilized carbonium ion. Such cases may be properly formulated as being derived primarily from an electron transfer step (see, however, footnote 29).

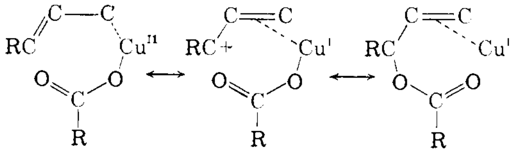
The behavior of cupric carboxylate salts with free radicals generally present in the perester–copper salt reactions is not explained adequately by either the ligand transfer or electron transfer process *alone*. For example, the distribution of products from butenyl radical and cupric carboxylate into mainly the α-methallyl ester (3-acyloxybutene-1) is not indicative of a carbonium ion intermediate. Furthermore, the relatively high yields of butenyl esters obtained in the presence of massive amounts of alcohol and water indicate that the butenyl moiety is not being effectively partitioned by the solvent. The similar distribution of the products into α-methallyl and crotyl derivatives, more or less independent of the substituting group ($C_6H_5CO_2$, CH_3CO_2, CH_3O, HO), is consistent with the postulate that related transition states are involved in each of these reactions (10 and 19). The formation of ethylene from ethyl radicals and cupric carboxylate, moreover, is inconsistent with the occurrence of a ligand transfer process.

We postulate that the oxidation–reduction reactions between butenyl radical and cupric carboxylate, methylate and hydroxide represent intermediate cases in which both ligand transfer and electron transfer contributions must be considered in the transition state IV. The electron transfer

$$[C_4H_7\cdot\cdot S\cdot\cdot Cu^{II} \longleftrightarrow C_4H_7{}^{+}\ S{-}Cu^{I}]$$

IV

contribution to the transition state is approximately the same with all these oxygen-containing ligands. From the consideration of the similar distributions of isomeric products (approx. 85% α-methallyl and 15% crotyl) among several substituents, it is postulated that the bond-making process (ligand transfer) has not progressed as far as the carbonium ion[24] formation (electron transfer) in these oxidation–reduction reactions. We prefer to represent the transition state in the following crude manner



Similarly, the transition state for ethylene formation from ethyl radical and cupric carboxylate contains a sizable component of electron transfer.[11b]

The participation of nucleophiles in the oxidation–reduction reactions is dependent on the process considered. In the electron transfer process the selectivity by the incipient carbonium ion among nucleophiles is less pronounced than it is in the ligand transfer process. The interposition of solvent or other nucleophile directly into the ion-pair leads to substituted products, RS.

In those reactions involving ligand transfer the equilibrium concentration of the complexed cupric ion as well as the rate of the oxidation–reduction reaction is important. The former is dependent on the metathetical reaction 18a. In addition to the mass effect, the stabilities of the $Cu^{II}S$ species must be ascertained

$$Cu^{II}X + HS \rightleftarrows Cu^{II}S + HX \qquad (18a)$$

HS = protic solvent

For $Cu^{II}S$ it is estimated that. $CuCl > Cu^{II}OAc > Cu^{II}OCH_3 > Cu^{II}OH$. Thus, cupric benzoate formed from cuprous salt and *t*-butyl perbenzoate is converted in acetic acid largely to cupric acetate. The rate of ligand transfer from cupric salt, $Cu^{II}S$, to radical in reaction 19 is expected to be in the order[25]: $Br > Cl >> RCO_2 > OH > OCH_3$.

$$R\cdot + Cu^{II}S \longrightarrow RS + Cu^{I} \qquad (19)$$

The reactions between *t*-butyl peresters and butenes yield besides the major constituents, butenyl ester and *t*-butyl alcohol, certain by-products which are indicative of the presence of reactive intermediates. Thus, small amounts of acetone (~3–8%) are formed from the unimolecular fragmentation of *t*-butoxy radicals,[12,26] a step which is competitive with the chain transfer reaction 9. The products formed from methyl radicals were not characterized.

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot$$

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[23] If β-hydrogens are available in the alkyl radical oxidative elimination (*i.e.*, loss of a β-hydrogen to form olefin) also occurs. However, butenyl and α-cumyl radicals which yield reasonably stable carbonium ions show little or no evidence of oxidative elimination with cupric salts.

[24] Neopentyl radicals which do not undergo 1,2-rearrangement react with cupric acetate to produce approximately equal amounts of *t*-amyl acetate and neopentyl acetate.[11b]

[25] *Cf.* H. Taube, "Recent Advances in Inorganic and Radiochemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1960, p. 1.

[26] The absence (<1%) of benzene as product in the reaction carried out with *t*-butyl alcohol or acetic acid as solvent and biphenyl[27]) from the reaction in benzene lends further discredit to benzoxy radical formation in the cuprous reduction of *t*-butyl perbenzoate given in eq. 13. *Cf.* C. Swain, L. Schaad and A. Kresge, *J. Am. Chem. Soc.*, **80**, 5313 (1958), and ref. 12.

[27] Biphenyl, however, has been reported as a by-product in the cuprous chloride-catalyzed reaction of *t*-butyl perbenzoate and methylene-*t*-butylcyclohexane in benzene (B. Cross and G. Whitman, *J. Chem. Soc.*, **1650** (1961)).

Finally mixtures of *t*-butyl butyl ethers and *t*-butyl butenyl ethers were formed in minor amounts (approx. 2–5% and 5–10%, respectively). The saturated *t*-butyl *n*-butyl and *t*-butyl *s*-butyl ethers undoubtedly arise *via* an adduct radical resulting from the addition of *t*-butoxy radical to butenes. Although *t*-butoxy radicals, which are generated in reaction 8, react mainly by hydrogen abstraction (9), a small proportion of them add to butenes to form *t*-butoxybutyl radicals V. These produce

$$t\text{-BuO}\cdot + C_4H_8 \longrightarrow \underset{\text{V}}{t\text{-BuOC}_4H_8\cdot} \qquad (18b)$$

t-butyl butyl ethers by chain transfer with hydrogen donor (probably butene). The adduct radicals V are also subject to cupric ion oxidation to form *t*-butyl butenyl ethers (VI) by an oxidation–reduction process described earlier.[5] Thus, the pre-

$$\underset{\text{V}}{t\text{-BuOC}_4H_8\cdot} + Cu^{II} \longrightarrow \underset{\text{VI}}{t\text{-BuOC}_4H_7} + Cu^{I} + H^+ \quad (20)$$

dominant butenyl ether isomer obtained is *t*-butyl crotyl ether from butene-1 and *t*-butyl α-methallyl ether from butene-2. These ethers would result from structures V expected from *t*-butoxy radical addition to butene-1 and to butene-2, *viz.*, 1-*t*-butoxy-2-butyl and 2-butoxy-3-butyl, respectively, by cupric salt oxidation given in eq. 20. Further evidence for the *t*-butyl butenyl ethers arising *via* this mechanism (20) is disclosed by the amounts of *t*-butyl α-methallyl ether formed from *cis*- and *trans*-butene-2. In every case examined, *cis*-butene-2 gave consistently higher yields (4–7 times) of *t*-butyl α-methallyl ether than *trans*-butene-2 under the same conditions, although the yields of *t*-butyl crotyl ether and yields and isomer distributions of the isomeric butenyl esters were relatively unvarying. Similarly under bromine atom catalysis (*vide supra*) in these reactions, *cis*-butene-2 was isomerized to *trans*-butene-2 approximately 5–8 times faster than the reverse isomerization. The similar effects of *cis* and *trans* isomers on the yields of *t*-butyl α-methallyl ether and the degree of isomerization of butene-2 are consistent with a similar process occurring in both cases, *viz.*, a radical addition mechanism (18) and (18b).

The formation of small amounts (~1%) of *t*-butyl crotyl ether from butene-2 (approx. equal amounts from *cis* and *trans* isomers) and *t*-butyl α-methallyl ether from butene-1 indicates that the adduct radical V is not the sole precursor for the *t*-butyl butenyl ethers. An additional route for the formation of *t*-butyl butenyl ethers lies in the cupric oxidation of butenyl radicals given by eq. 21 which is analogous to the formation of butenyl methyl ethers from butenyl radicals in methanol

$$C_4H_7\cdot + Cu^{II}(t\text{-BuO}) \longrightarrow t\text{-BuOC}_4H_7 + Cu^{I} \quad (21)$$

(reaction 19, S = OCH$_3$). The slight enhancement in the yields of *tert*-butyl butenyl ethers in *tert*-butyl alcohol is in accord with this postulate.

The dual route for the formation of *tert*-butyl butenyl ethers will be described in greater detail in a study of benzoxy radicals and butenes, a case in which competitive addition and abstraction processes can be clearly delineated.[11b]

For the copper salt-catalyzed reaction of peresters and butenes it is possible to postulate an alternative scheme for the formation of butenyl esters which does not involve butenyl radical intermediates. Thus, the reduction of peresters by cuprous ion could take the alternative course (13) to produce cupric *tert*-butylate and acyloxy radicals, followed by addition to butene to yield an acyloxybutyl radical adduct VII. Subsequent

$$RCO_2\cdot + C_4H_8 \longrightarrow \underset{\text{VII}}{RCO_2C_4H_8\cdot}$$

oxidation of the adduct radical by cupric ion to butenyl ester is similar to reaction (20).

$$RCO_2C_4H_8\cdot + Cu^{II} \longrightarrow RCO_2C_4H_7 + Cu^{I} + H^+$$

This series of reactions, however, is not applicable to the reactions of peresters and olefins.[28] It has been found[11b] that benzoxy radicals derived from benzoyl peroxide and cuprous salt (reaction 14) do react with olefins predominantly by this route; but results indicate that the isomer distribution between crotyl and α-methallyl benzoates as products from benzoyl peroxide is quite different from that observed with *tert*-butyl perbenzoate. In addition, diacyl peroxides and butenes yield as by-products the saturated butyl esters which are not present in perester reactions.

The reaction scheme represented by eqs. 8, 9 and 10 are also applicable to hydrogen donors other than olefins. With *t*-butyl peresters the reaction is dependent on the rate of the chain transfer step (21):

$$t\text{-BuO}\cdot + RH \longrightarrow t\text{-BuOH} + R\cdot \qquad (21)$$

which must compete with the unimolecular fragmentation of *t*-butoxy radical. In all cases of active substrates it is necessary that the energetics of the chain transfer reaction (21) be favorable. The subsequent oxidation–reduction reaction of cupric species with the various radicals produced in reaction 21 will be explored further.

Acknowledgment.—I wish to thank Mr. Fred Rodgers for very helpful technical assistance.

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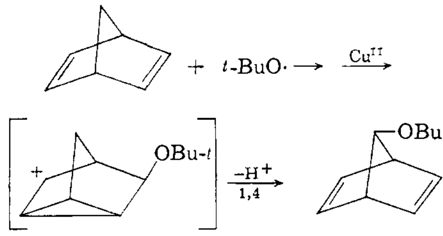
[28] However, olefins[29] such as butadiene, isoprene and styrene, which readily react with free radicals by addition, do yield *tert*-butyl ether products from *tert*-butyl peresters by such processes.[11]

[29] Norbornadiene also undergoes facile addition by free radicals.[30] The formation of 7-*tert*-butoxynorbornadiene from *t*-butyl perbenzoate and norbornadiene[14] may not involve the 7-norbornadienyl radical at all (*vide supra*). This compound may arise *via* an *addition* of the *tert*-butoxy radical intermediate to norbornadiene (by a process similar to the formation of butenyl *tert*-butyl ethers from butenes and peresters) followed by oxidation by cupric ion and rearrangement,



By this series of reactions the 2-carbon atom of norbornadiene would be converted to the 7-carbon atom in the *tert*-butoxy derivative. If the reaction proceeded *via* hydrogen *abstraction* from the 7-position of norbornadiene by *tert*-butoxy radical to produce the 7-norbornadienyl radical, the no skeletal rearrangement is likely. In the latter case, the interchange hypothesized earlier (*vide supra*) is not valid. These possibilities merit further attention.

[30] *Cf.* S. Cristol, G. Brindell, and J. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958), and reference 14.

Experimental

General Method Reaction of Butenes with Peresters.—A 300-ml. heavy-walled Pyrex polymerization bottle equipped with a thermocouple well and sealed with a Teflon-lined screw cap was used in all reactions. It was loaded with approximately 0.2 mole of perester and 100 ml. of solvent and cooled to 0°. The vessel was then flushed with the reactant butene gas while the condensed butene (0.6–0.8 mole) was added. Cuprous bromide (0.2 g.) was added. The system was flushed again and quickly sealed. The vessel was heated in a rocking autoclave. It is important that the temperature be brought up slowly since at approximately 75° an uncontrollable exothermic reaction occurs raising the temperature to 130–140° in 10 minutes. If, however, the reaction is heated at 70° for several hours and the temperature raised incrementally (5°) over a period of 8 hours until a temperature of 85–90° is attained, a sharp temperature break can be avoided. The reaction was heated for a total of 30 hours to ensure complete peroxide decomposition. The resulting mixture varied from blue to light yellow depending on the state of oxidation of the copper ion. Approximately 50–100 mg. of cuprous bromide remained precipitated in reactions involving benzene.

After opening, the bomb was attached to a distillation apparatus and the unreacted butenes were vacuum distilled into a liquid nitrogen trap. The butenes were analyzed by G.L.C. on a 50-foot "dimethylsulfolane–firebrick column at 15 p.s.i. The emergence times are: butene-1, 19.8 min.; *trans*-butene-2, 25.7 min.; *cis*-butene-2, 29.7 min.; pentene-1, 48.2 min.; *trans*-pentene-2, 57.4 min.; *cis*-pentene-2, 62.2 min.

The contents of the bomb were transferred with the aid of 50 ml. of solvent and weighed. A weighed aliquot was washed with sodium bicarbonate to remove acids and water-soluble compounds (*t*-butyl alcohol and acetone). It was weighed, dried and analyzed for saponifiable ester by treatment with alkali followed by back titration of the alkali potentiometrically. An aliquot of the original reaction mixture was also analyzed by G.L.C. to determine the relative yields of the isomeric pairs of the esters, alcohols and ethers. Since the crotyl derivatives were all formed in minor amounts the absolute yields of these compounds were determined by adding a known weight of the crotyl derivative as marker to a weighed amount of the original reaction mixture. After correcting for the crotyl derivative in the original solution the yield of the 3-butenyl derivative was determined by comparing the G.L.C. area to the crotyl marker. In this manner the yields of the esters could be determined within ±2%. In all cases the yields determined by the G.L.C. method were the same to within ±3% as the titrimetric values (Table I). The ester products, therefore, were in most cases (however, see Table II) accounted for as butenyl derivatives. Finally the reaction mixtures were distilled to isolate the components pure. The distilled material was recovered in 90–95% yield (from titrated and G.L.C. indicated values) and compared with authentic samples.

t-Butyl perbenzoate	Lucidol Co. (Wallace and Tiernan) 95% grade, used as such
t-Butyl peracetate	Lucidol Co., Lupersol 7 washed with $NaHCO_3$ and redistilled to remove benzene; b.p. 23–24° (0.5 mm.), $n^{25}D$ 1.4028–1.4031
Butene-1	Matheson Co. C.P. grade; G.L.C. showed no butene-2
cis-Butene-2	Phillips Petroleum Co., research grade; G.L.C. showed no butene-1 or *trans* isomer
trans-Butene-2	Phillips Petroleum Co., pure grade; G.L.C. showed no butene-1 or *cis* isomer
Butene-2	Phillips Petroleum Co., pure grade; G.L.C. showed 55% *cis* and 45% *trans*
Pentene-1	Phillips Petroleum Co., pure grade
Pentene-2	Phillips Petroleum Co., pure grade, mixture *cis* and *trans*
Benzene	Baker and Adamson analytical reagent grade
Acetonitrile	Matheson, Coleman and Bell, spectroscopic reagent
t-Butyl alcohol	Shell Chemical Co., redistilled from CaH_2
Gl. acetic acid	Baker and Adamson, Fischer titration 0.38% water
Methanol	Baker Analyzed reagent
Cuprous bromide	Amend Drug and Chemical Co., C.P.

Reaction of *t*-Butyl Perbenzoate with Butenes.—In a typical charge, 41 g. of *t*-butyl perbenzoate, 100 ml. of benzene, 43 g. of butene-1 and 0.204 g. of cuprous bromide were allowed to react at 80–90° for 30 hours. The clear blue solution in which a small amount (~50 mg.) of insoluble, colorless cuprous bromide was present, was vacuum distilled into a liquid nitrogen trap. The recovered butene (18 g.) contaminated with a small amount of acetone and benzene were examined on G.L.C. The only component found was butene-1. No *cis*- or *trans*-butene-2 was found. The reaction mixture was transferred to an erlenmeyer flask with the aid of 50 ml. of benzene. After extracting a small amount for G.L.C. analysis the remainder (199 g.) was washed three times with sodium bicarbonate. The bicarbonate washes on acidification yielded 4.7 g. of benzoic acid. An aliquot was removed and hydrolyzed with an aliquot of standard NaOH. Back titration with acid potentiometrically yielded 0.083 equiv./100 g. (74% based on peroxide charged). The remainder of the washed solution was distilled at atmospheric pressure to remove the benzene. There was obtained 23.6 g. (63.5%) of mixed butenyl esters boiling at 58–72° (0.5 mm.) It was resolved into 17.4 g. boiling at 58–62° (0.5 mm.) ($n^{25}D$ 1.5032–1.5055) which is 3-benzoxybutene-1 and 2.3 g. boiling at 64–70° (0.5 mm.) ($n^{25}D$ 1.5082–1.5105) which was crotyl benzoate. An intermediate fraction (3.9 g.) was a mixture of the two isomers. The infrared spectra and G.L.C. behaviors were the same as authentic samples (*vide infra*). The butenyl esters were hydrogenated with platinum in ethyl acetate to the corresponding butyl esters. The ratio of the isomeric pairs of butenyl esters was found by comparing the areas of the chromatogram of the crude material. Calibration showed a one- to- one correspondence between the areas and weights. For example, in several determinations the following values were found for percentage 3-benzoxybutene-1 in the mixture: 89.5%, 90.4%, 91.0%. Finally, the infrared spectrum of the residual material (1.9 g.) from the distillation indicated it to be an ester mixture containing some undistilled crotyl benzoate in addition to unidentified material. Acetone and benzene were determined by an inspection of the G.L.C. (10 ft. Ucon polar on Chromosorb W at 65°): emergence times, acetone, 3.5', and benzene, 9.5'. The butenyl ethers were determined by direct distillation of the crude reaction mixture. G.L.C. analysis on the Ucon polar column was based on *t*-butyl alcohol 6.5', *t*-butyl α-methallyl ether, 7.1', and *t*-butyl crotyl ether, 18.4'. *t*-Butoxy crotyl ether could be separated from benzene by distillation, but the isomeric α-methallyl ether could not. The crotyl ether was compared with an authentic sample prepared from lithium aluminum reduction of *t*-butoxybutenyl chloride[11b]) and it was hydrogenated over platinum to *t*-butyl *n*-butyl ether.[31] *t*-Butoxy α-methallyl ether was only determined indirectly by isolating it in a *t*-butyl alcohol solution and hydrogenating it to *t*-butyl *sec*-butyl ether.[31]

The yields of *t*-butyl butenyl ethers were obtained from the G.L.C. curves. The yields of each isomer were found to be highly dependent on the reactant olefin. Thus, butene-1 yielded 5–10% *t*-butyl crotyl ether and less than 0.5% *t*-butyl α-methallyl ether. *trans*-Butene-2 yielded 2–5% *t*-butyl α-methallyl ether and approximately 0.5% crotyl isomer. *cis*-Butene-2 yielded 6–10% *t*-butyl α-methallyl ether and approximately 0.5% crotyl ether.

Crotyl Benzoate.—Crotyl alcohol (Eastman Kodak Co. practical) was redistilled to yield material boiling at 120.9–121.5° (760 mm.) ($n^{25}D$ 1.4237–1.4242). It was esterified with benzoyl chloride at 25° by the Schotten–Baumann method to yield in 85% crotyl benzoate boiling at 78–81° (1 mm.) ($n^{25}D$ 1.5159–1.5160); G.L.C. analysis on a 10-foot diethylene glycol succinate–Chromosorb W at 174° (emergence time 29.8 min.) showed it to be uncontaminated with 3-benzoxybutene-1. On an 8-foot Craig succinate–Chromosorb acid-washed column at 185° similar results (emergence time 20.4 min.) were obtained.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.0 ; H, 6.88; ester value, 0.568; bromine no., 91. Found: C, 74.9; H, 6.9; ester value, 0.568; bromine no., 91.

3-Benzoxybutene-1.—1-Butenol-3 (Aldrich Chemical Co.) was redistilled (b.p. 97.0–97.5° (760 mm.), $n^{25}D$ 1.4114). It was esterified by the Schotten–Baumann method to yield in 89% yield 3-benzoxybutene-1 (b.p. 49–51° (3 mm.), $n^{25}D$ 1.5061–1.5065); G.L.C. on diethylene glycol succinate–

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(31) J. Norris and G. Rigby, *J. Am. Chem. Soc.*, **54**, 2005 (1932).

TABLE I

THE REACTION OF *t*-BUTYL PERBENZOATE AND BUTENES

Run	Olefin, g.	*t*-Butyl perbenzoate, g.	CuBr, g.	Solvent, ml.	Over-all yield butenyl esters, %[a]	Benzoic acid,[b] g.	Crotyl ester,[c] %
10	Butene-1, 43	43.3	0.200	Benzene, 100	74.0	..	10.0
13	Butene-2, 46	42.0	.215	Benzene, 100	76.5	4.7	10.6
14	Butene-1, 45	41.0	.216	Benzene, 100	73.5	6.3	13.5
16	Butene-2, 66	42.0	.211	Benzene, 100	74.0 (77)	5.0	13.4
30	*c*-Butene-2, 47	42.0	.203	Benzene, 100	72.0	4.1	6.2
32	*t*-Butene-2, 46	41.8	.199	Benzene, 100	71.0 (72)	1.0	13.8
44	*t*-Butene-2, 44	39.8	.204	Benzene, 100	74.0 (79)	3.8 (21)	15.7
45	*c*-Butene-2, 44	39.9	.203	Benzene, 100	70.5 (75)	2.5 (23)	9.8
22	Pentene-1, 45[d]	43.7	.202	Benzene, 100	68.0[e]	7.4	12.0[f]
18	Butene-1, 44	42.7	.225	Acetonitrile, 100	74.0 (72)	4.0	9.0
27	*t*-Butene-2, 46	41.3	.205	*t*-Butyl alcohol, 100	76.5 (80)	3.6	8.7
43	*t*-Butene-2, 40	39.8	.204	*t*-Butyl alcohol (100),[g] water (25)	57[h] (55)	8.2	12.7
49	Pentene-1, 30[i]	30.9	.204	*t*-Butyl alcohol (100),[j] water (20)	39[h]	7.9	9.6[l]
26	*t*-Butene-2, 42	40.9	.199	Acetic acid, 100	61[m] (62)	15.4	9.7[n]
50	Pentene-1, 32[p]	30.8	.203	Acetic acid, 100	71[q]	13.3	8.7[r]

[a] Butenyl ester yield determined by saponification; includes all esters. Quantity in parentheses is value determined by G.L.C. marker technique; includes only crotyl and α-methallyl esters. [b] Amount precipitated from saturated solution; not quantitative. Quantity in parentheses is titrated yield. [c] Remainder 3-acyloxybutene-1, benzoates unless stated otherwise. [d] Contains 18.1 g. of crotyl benzoate, reisolated unchanged. [e] Pentenyl benzoates, does not include added crotyl benzoate. [f] 1-Benzoxypentene-2, remainder 3-benzoxypentene-1. [g] Heterogeneous, approximately 5 ml. separated aqueous phase. [h] In addition to 8% butenols, consisting of 7% crotyl alcohol and 93% 1-butenol-3. [i] Contains 14.2 g. of added crotyl benzoate, recovered unchanged. [j] Homogeneous. [k] In addition to pentenols not identified, presumably 1-pentenol-3 and 2-pentenol-1; does not include added crotyl benzoate. [l] 1-Benzoxypentene-2, remainder 3-benzoxypentene-1. [m] Mixture of butenyl acetates (77%) and butenyl benzoates (23%). [n] Composition of butenyl benzoate fraction, remainder 3-benzoxybutene-1. Composition of butenyl acetate fraction is 11.3% crotyl acetate, remainder is 3-acetoxybutene-1. [p] Contains 13.3 g. of crotyl benzoate, reisolated unchanged except for approximately 1% crotyl acetate. [q] Mixture consists of 7% pentenyl benzoate, remainder (93%) is pentenyl acetate. Does not include added crotyl benzoate. [r] Percentage 1-acetoxypentene-2 in pentenyl acetate fraction, remainder is 3-acetoxybutene-1. Pentenyl benzoate fraction not completely analyzed, approximately 90% 3-benzoxypentene-1.

TABLE II

THE REACTION OF *t*-BUTYL PERACETATE AND BUTENES

Run	Olefin, g.	*t*-Butyl[a] peracetate, g.	Copper salt, g.	Solvent, ml.	Acetic acid, %[b]	Total esters, %[c]	Butenyl esters, %[d]	Crotyl ester, %[e]
42	*cis*-Butene-2, 44	36.9[f]	CuBr, 0.212	Benzene, 100	17	83	84	9.8
53	*trans*-Butene-2, 33	20.0	CuBr, .152	*t*-Butyl alcohol (100)–water (20)	..	48	45[g]	14.5
63	Butene-1, 79	32.7[f]	CuBr, .209	Methanol, 75	27	70	43[h]	5.5
64	*cis*-Butene-2, 60	33.1[f]	CuBr, .261	Methanol, 70	27	72	45[j]	3.1
81	*cis*-Butene-2, 58	15.3	CuBr, .0878	Methanol, 10	27	76	47[k]	7.0
82	*trans*-Butene-2, 44	14.6	CuBr, .0869	Methanol, 7	26	74	56[l]	10.5
106	Butene-1, 50	23.3	CuBr, .201	*t*-Butyl alcohol (100)–water (20)	39	61	52[m]	9.0
107	Butene-1, 52	23.1	CuBr, .200	*t*-Butyl alcohol, 100	22	78	78	8.0
177	Butene-2, 45.7[n,p]	20.2	CuCl, .201	Benzene, 100	15	79	74	11.0
178	Butene-2, 43.3[n,q]	20.4	CuCl, .201	Acetic acid, 100	..	44	41	8.2
184	Butene-2, 48.9[n,r]	20.2	CuCl, .203	Benzene, 100	16	76	73	11.0
185	*cis*-Butene-2[s]	20.3	CuCl, .205	Benzene, 100	20	79	72	9.2

[a] Distilled peracetate. [b] Determined by potentiometric titration. [c] Total saponification value, includes all esters. [d] Crotyl and α-methallyl acetates determined by G.L.C. marker technique. [e] Remainder α-methallyl acetate. [f] 85% *t*-butyl peracetate in benzene unless otherwise stated. [g] In addition to 10% butenols; composition of butenols is 81% α-methallyl alcohol and 19% crotyl alcohol. [h] In addition to 11% butenyl methyl ethers; composition of ether mixture is 85% crotyl and 15% α-methallyl methyl ethers. [j] In addition to 9% butenyl methyl ethers (85% α-methallyl and 15% crotyl) and 3% butenols. [k] In addition to 4% butenyl methyl ethers (predominantly α-methallyl isomer). [l] In addition to 3% butenyl methyl ethers. [m] In addition to 6.4% butenols (predominantly α-methallyl). [n] 37.5% *trans*-butene-2 and 62.5% *cis*-butene-2. [p] 38.5 g. of butene-2 recovered (38.9% *trans*, 61.2% *cis*). [q] 36.2 g. of butene-2 recovered (39.2% *trans*, 61.8% *cis*). [r] 41.3 g. of butene-2 recovered (39.0% *trans*, 61.0% *cis*). [s] 37.5 g. of butene-2 recovered (1.2% *trans*, 97.8% *cis*).

Chromosorb W at 174° (emergence time 17.2 min.) indicated the absence of the crotyl isomer.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.88; ester value, 0.568. Found: C, 74.8; H, 6.8; ester value, 0.584.

Reactions of *t*-Butyl Peracetate with Butenes.—The reactions were carried out in the same manner as those described for the perbenzoate analog. The products, crotyl acetate and 3-acetoxybutene-1, were compared with authentic samples.

Crotyl Acetate.—Crotyl alcohol (16 g.) obtained earlier was treated with 25 ml. of acetic anhydride and 30 ml. of pyridine at room temperature overnight. Ether was added and the solution washed twice with dilute HCl and twice with $NaHCO_3$. After drying with Na_2SO_4 the solution was distilled to yield crotyl acetate (b.p. 130–131° (760 mm.), n^{25}D 1.4141–1.4148, 22 g.).

Anal. Calcd. for $C_6H_{10}O_2$ (114.14): C, 63.13; H, 8.83; ester value, 0.877. Found: C, 63.08; 63.06; H, 8,90, 8.94; ester value, 0.871.

3-Acetoxybutene-1.—1-Butenol-3 (13 g.) was treated with 25 ml. of acetic anhydride and 30 ml. of pyridine. It yielded 15 g. of 3-acetoxybutene-1 boiling at 109–110° (760 mm.) (n^{25}D 1.4013).

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.13, H, 8.83; ester value, 0.88; bromine no., 140. Found: C, 63.17, 63.18; H, 8.80, 8.83; ester value, 0.89; bromine no., 138.

Crotyl acetate, 3-acetoxybutene-1, crotyl alcohol and 1-butenol-3 are cleanly separated by G.L.C. on a 10-foot diethylene glycol–20–30 firebrick column at 95°. The emergence times are: 3-acetoxybutene-1, 7.0 min.; 1-butenol-3, 8.5 min.; crotyl acetate, 14.6 min.; crotyl alcohol, 18.9 min. The 1-butenol-3 is not cleanly separated from its acetate on a Ucon polar column.

Crotyl Meth0l Ether.—Crotyl chloride (25 g.) was added dropwise to a solution prepared from the reaction of 8. g. of NaH and 200 ml. of methanol (carefully). The reaction was stirred at 60° for 10 hours. To the reaction was added 50 ml. of isopentane and excess water. The aqueous phase was re-extracted with isopentane. The combined isopentane fractions were dried with sodium sulfate and distilled. It yielded 15 g. of material boiling at 77–78° (760 mm.) (n^{25}D 1.3968). G.L.C. of the crude pentane solution indicated the absence of 3-methoxybutene-1.

Anal. Calcd. for $C_5H_{10}O$ (86): C, 69.7; H, 11.7; bromine no., 186. Found: C, 69.3, 69.5; H, 11.7, 11.7; bromine no., 183, 186.

3-Methoxybutene-1.—3-Chlorobutene-1 (40 g.) was treated with a solution of 46 g. of sodium methoxide in 400 ml. of methanol. The reaction was stirred at 64° for 12 hours. Isopentane and water were added and the reaction worked up in the usual manner. It yielded 10 g. of material boiling at 50–55° (760 mm.) (n^{25}D 1.3830) and 1 g. of material boiling at 55–60°. The latter is a mixture of 3-methoxybutene-1 and crotyl methyl ether; G.L.C. of the crude pentane extract indicated the ratio of 3-methoxybutene-1 and crotyl methyl ether to be approximately 10 to 1.

Anal. Calcd. for $C_5H_{10}O$: C, 69.7; H, 11.7; bromine No. 186; Zeisel alkoxyl (equiv./100 g.), 1.163. Found: C, 69.3, 69.4; H, 11.6, 11.6; bromine no., 178, 177.5; Zeisel alkoxy (equiv./100 g.), 1.215.

The isomeric butenyl methyl ethers are separated on a 10-foot G.L.C. column consisting of diethylene glycol succinate at 37°. The emergence times are: isopentane, 1.8 min.; 3-methoxybutene-1, 7.3 min.; crotyl methyl ether, 18.5 min.; benzene, 37.0 min.

The reaction of *t*-butyl peracetate with butene in methanol solution represents an interesting case of competitive reactions. Thus in addition to the expected butenyl acetates and ethers there was obtained formaldehyde[32]) (determined as the methone derivative, m.p. 187–188° after recrystallization once from ethanol and the 2,4-DNP, m.p. 164–165°) from the oxidation of methanol, methyl acetate (from ester interchange with the butenyl acetate)[33] and acetic acid (determined titrimetrically).

A reaction of 79 g. of butene-1, 32.7 g. of *t*-butyl peracetate (85% in benzene) in 75 ml. of methanol with 0.209 g. of cuprous bromide yielded 0.066 mole of formaldehyde (gravimetric by methone formation, recrystallized once from ethanol, m.p. 187–188°), 0.0576 equiv. of acetic acid and 0.148 equiv. of total ester (saponification). The ester fraction consisted of 0.0741 equiv. α-methallyl acetate, 0.003 equiv. of crotyl acetate, and 0.0645 equiv. of methyl acetate. In addition there was formed 0.0177 equiv. of methyl butenyl ethers (86.5% α-methallyl isomer) and 0.0045 equiv. of α-methallyl alcohol.

A similar reaction was constituted of 15.3 g. of redistilled *t*-butyl peracetate, 10 ml. of methanol, 58 g. of butene-1 and 0.0878 g. of cuprous bromide. The homogeneous clear blue reaction mixture was diluted with 80 ml. of *n*-pentane and analyzed. There was formed 0.032 equiv. of acetic acid, 0.168 equiv. of *t*-butyl alcohol, 0.0194 equiv. of formaldehyde (gravimetric methone) and 0.088 equiv. of total ester. The ester fraction consisted of 0.0547 equiv. of α-methallyl acetate, 0.005 equiv. of crotyl acetate and 0.010 equiv. methyl acetate. In addition there was formed 0.0046 equiv of α-methallyl methyl ether and approximately 0.003 equiv. of butenols.

Under slightly different conditions 60 g. of *cis*-butene-2, 33.1 g. of *t*-butyl peracetate (85% in benzene) in 70 ml. of methanol with 0.261 of cuprous bromide yielded 0.053 mole of formaldehyde (by titration),[34] 0.059 equiv. of acetic acid and 0.152 equiv. of total ester. The ester fraction was analyzed by G.L.C. to contain 0.095 equiv. of α-methallyl acetate and 0.057 equiv. of methyl acetate. In addition, 0.0153 equiv. of butenyl methyl ethers (containing 85% α-methallyl isomer) and 0.015 equiv. of butenols were formed.

A reaction consisting of 14.6 g. of redistilled *t*-butyl peracetate, 7 ml. of methanol, 44 g. of *trans*-butene-2 and 0.0869 g. of cuprous bromide yielded 0.029 equiv. of acetic acid, 0.020 equiv. of formaldehyde (methone), 0.097 equiv. of *t*-butyl alcohol and 0.082 equiv. of total esters. The ester fraction consisted of 0.0561 equiv. of α-methallyl acetate, 0.006 equiv. of crotyl acetate and 0.012 equiv. of methyl acetate. Approximately 0.0028 equiv. of butenols (mainly α-methallyl alcohol) and 0.0051 equiv. of α-methallyl methyl ether were formed.

In all the methanol runs, the material balance between acetic acid, methyl acetate and butenyl esters and the perester charged is good.

Solvolysis of Butenyl Chlorides in Acetic Acid with Silver Acetate.—To a suspension of 19 g. silver acetate in 100 ml. glacial acetic acid was added at room temperature a solution of 7.7 g. 3-chlorobutene-1 in 10 ml. acetic acid. The reaction was vigorously stirred at 30° for one hour and gradually heated to 100° in one hour with stirring. Benzene (50 ml.) and excess water were added and the products separated. The benzene solution was washed with water, $NaHCO_3$ and water, dried over Na_2CO_3 and distilled. It yielded 5 g. of mixed butenyl acetates boiling at 105–135° (760 mm.); G.L.C. of the crude benzene solution indicated that the butenyl acetate fraction consisted of 48.2% 3-acetoxybutene-1 and 51.8% crotyl acetate.

In an analogous manner, 19 g. of silver acetate and 8.1 g. of crotyl chloride in 110 ml. of acetic acid were allowed to react. It yielded 4.5 g. of mixed butenyl acetates. The composition of the benzene extracted was analyzed by G.L.C. and found to contain 45.7% 3-acetoxybutene-1 and 54.3% crotyl acetate.

The Cuprous-Salt-catalyzed Acetolysis of Butenyl Benzoates.—A 50% v. solution of glacial acetic acid–acetonitrile and crotyl benzoate was heated in an evacuated sealed ampoule for 18 hours at 127°. The mixture was quenched with water and extracted with *n*-pentane. The pentane extract was analyzed by G.L.C. for butenyl acetates and benzoates. Less than 5% of the benzoates was converted to acetates. There was no isomerization of the benzoate. Similar results were obtained with α-methallyl benzoate in glacial acetic acid.

Cuprous bromide is soluble (0.1 *M*) in 50% v. acetic acid–acetonitrile solutions. Upon heating a solution of α-methallyl benzoate in this medium for 8 hours at 127°, approximately 40% solvolyzed to a mixture of acetates containing 64% α-methallyl isomer. After 15 hours approximately 70% reacted to form a mixture containing 69% α-methallyl acetate. After prolonged heating (31 hr.) the α-methallyl acetate formed was slowly destroyed. Under these conditions crotyl benzoate reacted approximately 20% after 18 hours to form a mixture of acetates containing equimolar amounts of each isomer. At 100° and 11 hours the reaction yielded approximately 15% acetates which contained 60% α-methallyl isomer.

***t*-Butyl Hypochlorite and Butene-2.**—A deaerated solution of 21.8 g. of *t*-butyl hypochlorite, 100 ml. of benzene and 40.1 g. of butene-2 (46.7% *trans*, 53.3% *cis*) was irradiated for 13 minutes with two 200-watt Mazda lamps at 20–25° (water-bath). The unreacted butenes were recovered by distillation with liquid nitrogen traps in two fractions, which were analyzed (fraction 1, 16.9 g., 50.7% *trans*, 49.3% *cis*; fraction 2, 11.8 g., 48.3% *trans* and 51.7% *cis*). The material balance between butene consumed (0.20 mole) and *t*-butyl hypochlorite charged (0.20 mole) is good. The butenes

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[32] Although methylal could be determined by G.L.C. (DEGS, 35°), there was no evidence by G.L.C. for its presence in the original reaction mixture.

[33] The resulting butenol was also determined by G.L.C. However, less than 20% of the methyl acetate was accountable as the butenol. Therefore, either the methyl acetate was also formed by an alternative path not involving ester interchange (*e.g.*, interchange with the *t*-butyl peracetate) or some of the butenol was destroyed.

[34] Hydroxylamine; methone formation (m.p. 187–188°, one recrystallization from ethanol) yielded 0.047 equiv. of formaldehyde; 2,4-DNP formation yielded 0.0342 equiv. of formaldehyde.

consumed correspond to 0.078 mole of *trans* and 0.121 mole of *cis*. The relative reactivities are *trans*, 1, and *cis*, 1.34. The yields of *t*-butyl alcohol were determined titrimetrically (nitrite ester method) and found to be 102%. The butenyl chlorides were formed in 85% yield (determined by KOH hydrolysis followed by Volhard chloride). The composition of the butenyl chloride mixture corresponding to 60–70% crotyl chloride and 40–30% 3-chlorobutene-1 was found by G.L.C. (10-foot "DEG" on Chromosorb W at 35°; 3-chlorobutene-1 2.0 min. and crotyl chloride 3.8 min.).

[CONTRIBUTION NO. 2706 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

Small-Ring Compounds. XXXVI. 3-Methylenecyclobutyl Bromide and 1-Methylcyclobut-2-enyl Bromide[1]

BY EDGAR F. KIEFER[2] AND JOHN D. ROBERTS

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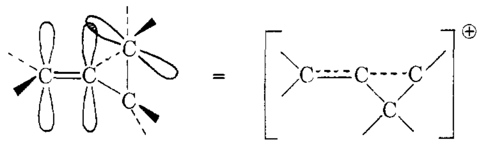
3-Methylenecyclobutyl bromide and 1-methylcyclobut-2-enyl bromide have been synthesized from the cycloaddition products of allene with acrylonitrile and vinyl benzoate. The rate constants for solvolysis of the two bromides in aqueous ethanol have been determined and correlated with the solvolysis rates of a series of analogous bromides. 1-Methylcyclobut-2-enyl bromide appears to exhibit some rate enhancement due to cross-ring π-type interaction of the electrons formally centered on the 3-position with the electron-deficient 1-position in the transition state.

Introduction

The possibility of "homoallylic" resonance[3] in carbonium ion intermediates has received considerable attention since the suggestion by Winstein and Adams[4] that delocalization of electrons between orbitals separated by an intervening saturated carbon atom might be responsible for the unexpectedly high solvolysis reactivity of cholesteryl derivatives. Application of the simple LCAO molecular-orbital method to homoallylic systems[3,5,6] has resulted in semi-quantitative predictions and correlations of carbonium ion stabilization energies, which in certain cases have been at least qualitatively verified by experiment.

So far, virtually all cases for which homoallylic resonance is regarded as important involve carbonium ions having the proper geometry for σ-type overlap between the vacant *p*-orbital and one or more of the *p*-orbitals of a double bond, as in I. It was therefore of interest to investigate the possibility of 1,3-electron delocalization in unsaturated cations, which, if planar like cyclobutene,[7a] methylenecyclobutane,[7b] 1,3-dimethylenecyclobutane[7c] and 1-methyl-3-methylenecyclobutane,[7c] could be stabilized 1,3-π overlap (if not by the σ-bond delocalization postulated for the cations formed from the saturated cyclobutyl halides).[8] Particularly interesting in this connection are the cations II and III, for which simple MO calculations predict delocalization energies of 0.8–4.7 kcal./mole and 4.1–10.9 kcal./mole, respectively,[9] when the 1,3-resonance integrals (β_{13}) are assigned values of 0.2–0.5β which are reasonable for the distances involved.[5] While the predicted stabilizations are not large, they might be expected to lead to significant differences in the first-order solvolysis rate constants between the corresponding bromides and appropriate model compounds.



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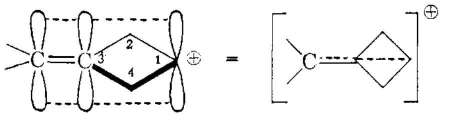

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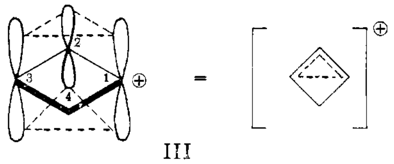

III

Results and Discussion

The synthesis of 3-methylenecyclobutyl bromide (IV) was achieved in two ways, using cycloaddition reactions[10] as shown in Fig. 1. These syntheses feature formation of a cycloadduct from vinyl benzoate and allene (vinyl acetate and allene do not undergo cycloaddition)[11] and the deamination of 3-methylenecyclobutylamine[12] to 3-methylenecyclobutanol in good yield. The uncomplicated character of this deamination is in marked contrast to the behavior of 3-methylcyclobutylamine,

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[2] National Science Foundation Predoctoral Fellow, 1958–1960.

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