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Allylic Oxidations by Peroxy Esters Catalyzed by Copper Salts. The Potential for Stereoselective Syntheses

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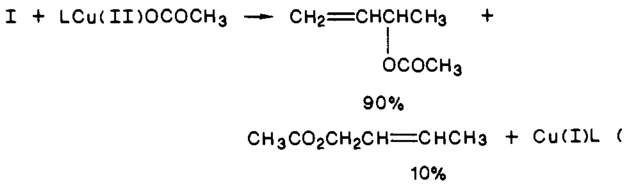
Abstract: The mechanism of the title reaction has been investigated. 1-Butene, *cis*-2-butene, and *trans*-2-butene with *tert*-butyl peroxyacetate and cuprous or cupric salts give 3-acetoxybut-1-ene (90% of ester) and *trans*-acetoxybut-2-ene (10%); *cis*- and *trans*-2-pentene give *trans*-4-acetoxypent-2-ene as the major product. It is concluded that the following steps are involved: formation of an allylic radical, reaction of the radical with Cu(II) carboxylate to form a Cu(III) intermediate in the direction producing the most substituted (stable) alkene, and formation of products from a pericyclic transition state, leading to the trans allylic ester.

Allylic hydrogens are replaced by carboxylate groups in high yields by reaction with peroxy esters in the presence of catalytic amounts of copper salts.[1-5] A noteworthy feature of the reaction is that the thermodynamically less stable alkene predominates in the isomeric allylic esters produced. From terminal alkenes, the isomer with the terminal, unrearranged double bond constitutes 90% of the ester product.[2,5] Thus the results of copper-catalyzed allylic acyloxylation of terminal alkenes by peroxy esters are similar to oxidations by selenium dioxide. The latter has been described as the most reliable and predictable reagent for substitution of an allylic hydrogen by a hydroxy group.[6]

The peroxy ester reaction is a redox chain in copper, as outlined in eq 1–3 for 1-butene and *tert*-butyl peroxyacetate, where L denotes a ligand to copper.[1-5]

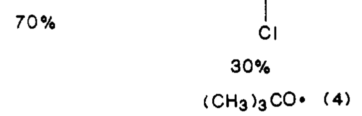
$$(CH_3)_3COOCOCH_3 + Cu(I)L \rightarrow (CH_3)_3CO\cdot + LCu(II)OCOCH_3 \quad (1)$$

$$(CH_3)_3CO\cdot + CH_2{=}CHCH_2CH_3 \rightarrow (CH_3)_3COH + \underset{\mathrm{I}}{CH_2\cdots\dot{C}H\cdots CHCH_3} \quad (2)$$



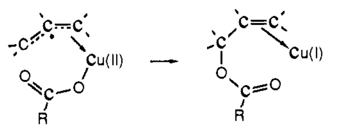
$$\mathrm{I} + LCu(II)OCOCH_3 \rightarrow \underset{90\%}{CH_2{=}CH\underset{OCOCH_3}{\underset{|}{C}}HCH_3} + \underset{10\%}{CH_3CO_2CH_2CH{=}CHCH_3} + Cu(I)L \quad (3)$$

cis-2-Butene and *trans*-2-butene also give the same distribution shown by eq 3. The *cis* or *trans* nature of the minor product has not been determined previously, to our knowledge. The *tert*-butoxy radical has been demonstrated to be the species abstracting allylic hydrogen in eq 2.[5] The distribution of the allylic esters is unusual because reactions of allyl radical I generally give products in which the thermodynamically more stable nonterminal double bond predominates, as might be expected. Reaction of I with *tert*-butyl hypochlorite, eq 4, is an example of such "normal" behavior.[7]



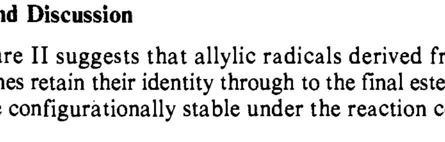
$$\mathrm{I} + (CH_3)_3COCl \rightarrow \underset{70\%}{ClCH_2CH{=}CHCH_3} + \underset{30\%}{CH_2{=}CH\underset{Cl}{\underset{|}{C}}HCH_3} + (CH_3)_3CO\cdot \quad (4)$$

Early suggestions that oxidation of the carbon radical produced a cationoid intermediate[5] gave way later to proposals of more specific interactions between copper and the organic radical. Because of the preponderance of the less substituted alkene in the products of allylic oxidation by copper carboxylates, eq 3, various suggestions have been advanced involving coordination between the incipient double bond of the product and the incipient Cu(I) species.[2b,3,8] Such proposals generally have been depicted by structures such as II. The driving force for the preponderance of the terminal alkene is postulated to be provided by the incipient Cu(I)–alkene interaction which is more favored by a terminal rather than internal double bond.[9]



II

An alternative proposal suggested an organo-copper intermediate, involving a Cu(III) species in a pericyclic reaction, III.[10] A bond between Cu(II) and a radical would be consistent with the paramagnetic nature of Cu(II).



III

We now report results supporting the validity of the proposal for the intermediacy of III in the formation of allylic esters by the copper-catalyzed reaction of peroxy esters with alkenes.

Results and Discussion

Structure II suggests that allylic radicals derived from cis or trans alkenes retain their identity through to the final ester product, if they are configurationally stable under the reaction conditions.

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

(2) (a) Kochi, J. K. *J. Am. Chem. Soc.* **1961**, *83*, 3162. (b) Kochi, I. K. *Ibid.* **1962**, *84*, 774–784.

(3) Beckwith, A. L. J.; Evans, G. W. *Proc. Chem. Soc.* **1962**, 63–64.

(4) Denney, D. Z.; Appelbaum, A.; Denney, D. B. *J. Am. Chem. Soc.* **1962**, *84*, 4969–4971.

(5) Walling, C.; Zavitsas, A. A. *J. Am. Chem. Soc.* **1963**, *85*, 2084–2090.

(6) Umbreit, M. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 5526–5527.

(7) Walling, C.; Thaler, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877.

(8) Kochi, J. K.; Mains, H. E. *J. Org. Chem.* **1965**, *30*, 1862–1872.

(9) (a) Douglas, B. E. In *The Chemistry of Coordination Compounds*; Bailar, J., Ed., Reinholdt: New York, 1956; p 487. (b) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1958; p 352.

(10) (a) Beckwith, A. L. J.; Gream, G. E.; Struble, D. L. *Aust. J. Chem.* **1972**, *25*, 1081–1105. (b) Beckwith, A. L. J.; Phillipou, G. *Ibid.* **1976**, *29*, 1277–1294.

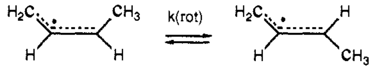
Table I. Percent Distribution of Isomeric Allylic Products from the Methallyl Radical and Carbonium Ion

allylic compd	reagent	X	3-X-1-ene	*trans*-1-X-2-ene	*cis*-1-X-2-ene
1-butene	*t*-BuOCl[a]	Cl	31	41	28
trans-2-butene	*t*-BuOCl[a]	Cl	26	74	
cis-2-butene	*t*-BuOCl[a]	Cl	37		63
but-1-en-3-ol	conc HCl[b]	Cl	38	58	4
but-2-en-1-ol[c]	conc HCl[b]	Cl	31	56	13
3-chloro-but-1-ene[d]	H_2O[e]	HO	67	33	
trans-1-chloro-but-2-ene[d]	H_2O[e]	HO	56	44	
cis-1-chloro-but-2-ene[d]	H_2O[e]	HO	45	1	54

[a] At 70 °C, photolysis, in benzene solvent, radical reaction. [b] At 0 °C, ionic reaction. [c] Mixture of 70% trans and 30% cis isomers. [d] Brubacher, L. J.; Triendl, L.; Robertson, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 4611–4616; hydrolysis postulated to proceed mostly through S_N1. [e] At 40 °C.

Avilable evidence indicates that configurational integrity should be retained in this system. We address this point first.

ESR measurements in the liquid phase between −100 and 0 °C have shown no interconversion of the cis and trans butenyl radicals, IV and V, when the only other available process was termination.[11] Gas-phase measurements at 126 °C gave the sizable value of $\Delta G^{\ddagger} = 21 \pm 3$ kcal/mol for the interconversion.[12] The estimated rate constant is $\log k_{\mathrm{rot}} = 13.5 - (16700/2.3RT)$.[13] The configurational stability of IV and V has been demonstrated in the reactions of the 2-butenes with *tert*-butyl hypochlorite up to 40 °C. The 1-chlorobut-2-ene product from *trans*-2-butene was exclusively trans, while that from *cis*-2-butene was exclusively cis,[7] demonstrating that rotation cannot compete with fast reactions such as eq 4. Available kinetic measurements are consistent with this conclusion. For the equivalent of reaction 4, but with benzyl radicals, the rate constant is 7×10^4 M^{-1} s^{-1} at 40 °C.[14] Assuming a comparable value of k_4 for allyl and comparing with $k_{\mathrm{rot}} = 70$ s^{-1} at 40 °C, the rate of rotation becomes equal to the rate of chlorine abstraction, eq 4, only when the hypochlorite concentration drops to 1×10^{-3} M, well past 99% reaction in the usual systems.



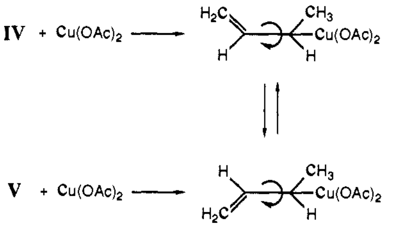
IV V

We extended the hypochlorite measurements to 70 °C and found that the butenyl radicals IV and V remain configurationally stable. *cis*-2-Butene reacted with *tert*-butyl hypochlorite under photolysis at 70 °C to give a 93% yield of allylic chlorides, the major component being *cis*-1-chlorobut-2-ene; no trans isomer was detected. *trans*-2-Butene, under the same conditions, gave a 86% yield of allylic chlorides, the major component being *trans*-1-chlorobut-2-ene; no cis isomer was detected. 1-Butene gave a 94% yield of chlorides, with the nonterminal alkene again being the major product; the distribution of 1-chlorobut-2-ene was 59.4% trans and 40.6% cis. This distribution is thought to reflect primarily the conformation of 1-butene at the moment of hydrogen abstraction when it becomes frozen.[7] The results are outlined in Table I.

The reaction of carbon radicals with $Cu(OAc)_2$ has been described as nearly diffusion controlled, with rate constants between 4×10^7 and 5×10^8 M^{-1} s^{-1} at 57 °C.[15] While $Cu(OAc)_2$ in acetic acid tends to dimerize, the measured equilibrium constant[15] indicates that, at our concentrations of approximately 6.7×10^{-3} M total $Cu(OAc)_2$, 2.1×10^{-3} M is in the active monomeric form. Assuming conservatively that the rate constant for reaction of the allylic radical with cupric is 4×10^7 M^{-1} s^{-1} at 70 °C, the available data indicate $k_3[Cu(OAc)_2] \approx 8.4 \times 10^4$ s^{-1}, while $k_{\mathrm{rot}} \approx 7.2 \times 10^2$ s^{-1}. The reaction is thus at least 100 times faster than rotation of the butenyl radicals at 70 °C, and IV and V would be expected to be configurationally stable in the peroxy ester/copper system, should they react through intermediates such as II.

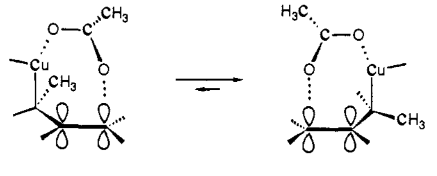
Cationoid intermediates equivalent to IV and V also have been reported to retain preferentially the original cis or trans arrangement. This is borne out by the products we obtained from the reaction of but-2-en-1-ol and but-1-en-2-ol with concentrated hydrochloric acid, as summarized in Table I, along with previously reported results from the S_N1 hydrolysis of butenyl chlorides.

Unlike structure II, the intermediacy of structure III requires that the cis or trans nature of the butenyl radicals be lost upon formation of the Cu(III) intermediate which produces 1-acetoxybut-2-enes, eq 5. If, as is shown, free rotation occurs in the intermediate, all three butenes should afford the same mixture of *cis*- and *trans*-1-acetoxybut-2-ene.



(5)

The pericyclic arrangement of structure III also provides a basis for predicting that the nonterminal alkene component of the ester product should be predominantly the trans isomer. Examination of models of the conformations of III leading to cis or trans ester shows that no bond strain is involved in either case in order to bring the carbonyl oxygen into position for favorable interaction with the p orbital of the terminal carbon atom. However, for reaction to occur with minimum energy requirements, the forming O–C1 bond must be parallel to the p orbital at C2 and to the breaking bond between copper and C3, as shown in VI and VII



VI (cis product) **VII** (trans product)

for the conformations leading to cis and trans product, respectively. This restriction of parallelism forces the C4 methyl in VI toward the inside of the seven-membered ring (pseudo-axial). Under the same restriction, the conformation leading to trans ester, VII, is favored, having the C4 methyl pointed outward (pseudo-equatorial). As a result, the intermediacy of III requires not only that all butenes lead to the same composition of trans to cis in the 1-acetoxybut-2-ene, but that the trans isomer predominates strongly.

The reaction of *cis*-2-butene, *trans*-2-butene, or 1-butene with *tert*-butyl peroxyacetate in the presence of copper salts at 70 °C in acetic acid solvent gave 3-acetoxybut-1-ene as the major product, favored by approximately 9:1 over the allylic isomer 1-acetoxybut-2-ene. The products were analyzed by gas chromatography with 25-m capillary columns and comparison with authentic materials and by fully decoupled ^{13}C NMR. The 1-acetoxybut-2-ene was exclusively trans from *trans*-2-butene and 1-butene, while *cis*-2-butene also produced a trace of *cis*-1-acetoxybut-2-ene, usually in quantities of $^1/_{10}$ or smaller than the trans isomer (less than 0.7% yield). The amount of butene used was always at least 4 times greater than that of the peroxy ester to avoid multiple attack. A change of solvent from acetic acid to benzene or to a large excess of butene had no significant effect

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[11] Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* **1968**, *90*, 7157–7159.

[12] Crawford, R. J.; Hamelin, J.; Strehlke, B. *J. Am. Chem. Soc.* **1971**, *93*, 3810.

[13] (a) Golden, D. M. *Int. J. Chem. Kinet.* **1969**, *1*, 127. (b) For a full discussion of the configurational stability of allyl radicals, see: Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic Press: New York, 1980; pp 162–283.

[14] Zavitsas, A. A.; Blank, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 4603–4608; by using a more recent value for coupling of benzyl radicals, $2k_t = 5 \times 10^9$ M^{-1} s^{-1}.

[15] Kochi, J. K.; Subramanian, R. V. *J. Am. Chem. Soc.* **1965**, *87*, 4855–4866.

Table II. Reaction Conditions, Yields, and Product Distributions for the Reaction of Butenes with *tert*-Butyl Peroxy Esters

run no.	butene	solvent	total[a] ester, %	fractn[b] 3-acetoxybut-1-ene	fractn[b] *trans*-1-acetoxybut-2-ene	Cu salt	h at 70 °C
1	*trans*-2	*trans*-2	68	0.89[c]	0.11	CuCl	115
2	*trans*-2	PhH	75	0.93[d]	0.07	$Cu(OAc)_2$	120
3	*trans*-2	AcOH	56	0.97	0.03	$Cu(OAc)_2$	120
4	*cis*-2	*cis*-2	54[e]	0.92	0.08	CuCl	66
5	*cis*-2	PhH	69	0.94	0.054[f]	$Cu(OAc)_2$	120
6	*cis*-2	AcOH	59	0.97	0.027[f]	$Cu(OAc)_2$	120
7	*cis*-2	AcOH	58	0.97	0.03	CuCl	167
8	1	AcOH	41[e]	0.94[g]	0.04	CuCl	336[h]
9	1	PhH	67	0.93	0.07	CuCl	112
10	1	PhH	67	0.95	0.05	$Cu(OAc)_2$	135
11	1	AcOH	54	0.94	0.06	CuI	140
12	1	PhH	70	0.92	0.08	CuCl	163
13	1	PhH	72	0.92	0.08	CuCl	233
14	*cis*-2	PhH	82[i]	0.94	0.053[j]	CuCl	118
15	1	PhH	81[i]	0.91[k]	0.09	CuCl	116

[a] Percent yield based on peroxy ester; by GC. [b] Fraction of the total ester by GC. [c] 0.87 by ^{13}C NMR. [d] 0.89 by ^{13}C NMR. [e] incomplete decomposition of peroxy ester. [f] The 1-acetoxybut-2-ene fraction is 91% trans and 9% cis by ^{13}C NMR. [g] 0.96 by ^{13}C NMR. [h] At 51 °C. [i] The peroxy ester was *tert*-butyl peroxybenzoate; the ester was the benzoate. [j] The 1-(benzoyloxy)but-2-ene is 88% trans and 12% cis by ^{13}C NMR, which also indicates that the fraction terminal alkene is 0.92. [k] 0.86 by ^{13}C NMR.

on the product distribution; the ester yields were somewhat lower in acetic acid. The nature of the copper salt did not appear to have a significant effect, cuprous chloride or iodide or cupric acetate giving essentially the same products. This is consistent with the redox chain nature of the reaction, eq 1–3, since some thermal, uncatalyzed decomposition of the peroxy ester will lead to carbon radicals capable of reducing cupric, when the starting catalyst is exclusively in that oxidation state. Cupric acetate was used at 1 mol % relative to peroxy ester, and usually all dissolved; cuprous salts were used at 2 mol %, and generally some insoluble material remained.

tert-Butyl peroxybenzoate gave results equivalent to those obtained with peroxyacetate; approximately 80% yields of butenyl benzoates were obtained, over 90% of which was 3-(benzoyloxy)but-1-ene. The minor ester product was again *trans*-1-(benzoyloxy)but-2-ene, while a trace of the cis isomer was also detectable from *cis*-2-butene. The results of the product analyses and the reaction conditions are summarized in Table II. The products are stable under the reaction conditions,[2,5] and their distribution is not a function of extent of reaction (see runs 4 and 8, Table II).

tert-Butyl alcohol was obtained in yields equal to or somewhat greater than the combined ester products. Acetic acid was also formed from the peroxyacetate in variable amounts, ranging between 5% and 10% yield when the solvent was benzene or excess alkene. The peroxybenzoate gave similar yields of benzoic acid.

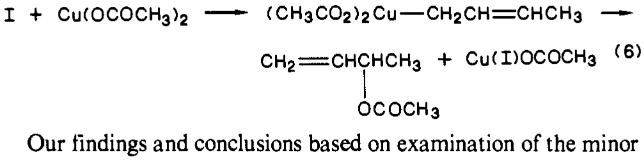
A reaction of *tert*-butoxy radicals that always competes with abstraction of allylic hydrogen is addition to the double bond;[16] the adduct, a secondary alkyl radical, can be oxidized by cupric to give, primarily, an alkenyl ether. Such ethers have been reported previously, along with other very minor products including those derived from β-scission of the *tert*-butoxy radical to methyl radical and acetone.[2] We find at least eight minor peaks in the chromatographic analyses of the reaction products. The competition between abstraction and addition by *tert*-butoxy radicals was found to be significant only when the alkene has only primary allylic hydrogens available. Thus *cis*- and *trans*-2-butene give yields of *tert*-butyl butenyl ether varying between 3% and 16%. In 1-butene, the greater reactivity of the secondary allylic hydrogens reduces the yield of this ether to approximately 2% or less. The yields of each of the other detected minor byproducts is generally a few tenths of one percent, occasionally rising to as high as 2%.

A minor byproduct from the reaction of *cis*- and *trans*-2-butene occasionally elutes from the GC at a retention time very similar to that of *cis*-1-acetoxybut-2-ene and may be mistaken for that compound. Careful analyses by fully decoupled ^{13}C NMR (over 12 000 scans) showed that it was not the cis ester from *trans*-2-butene and that only one-half to one-quarter of it was the cis ester from *cis*-2-butene. Thus the trace amounts of *cis*-1-acetoxybut-2-ene were determined by NMR by comparing the relative intensities of the signals of the C3 carbons of the cis and trans esters. Calibration with mixtures of authentic materials showed the relative intensities due to these two similar carbons to be proportional to the relative concentrations, within 3%.

The distribution of the isomeric alkenes in the ester products reported in Table II, 93.5 ± 1.1% terminal and 6.5 ± 1.1% nonterminal, is marginally different from previously reported values of 90.0 ± 2.1% terminal and 10.0 ± 2.1% nonterminal;[2] the difference is evidently the result of the higher temperatures used in the previous work (up to 90 °C).[2] This temperature difference could also account for our finding only small yields of ethers from 1-butene, compared to reported 5–10% yields.[2]

The fact that the intermediate allylic moiety loses its cis or trans identity in forming ester products strongly argues in favor of a Cu(III) intermediate, capable of rotation around the C2–C3 bond, eq 5. The fact that the 1-acetoxybut-2-ene product is the trans isomer argues strongly for the pericyclic transition state VII.

The intermediacy of organo–copper compounds is also consistent with the observed distribution of the isomeric allylic acetates in favor of the terminal double bond, in terms of attack by copper on the least hindered carbon of the allylic system (which also produces the strongest Cu–C bond). More importantly, it should be noted that in the Cu(III) intermediate leading to the major product from the butenes or terminal alkenes, copper adds to the allylic system so as to give predominantly the more substituted internal double bond, eq 6. Thus, the thermodynamically more stable alkene is formed preferentially, not in the product-forming but in the preceding and product-determining step.



$$\mathrm{I} + Cu(OCOCH_3)_2 \longrightarrow (CH_3CO_2)_2Cu{-}CH_2CH{=}CHCH_3 \longrightarrow CH_2{=}CH\underset{\substack{|\\ OCOCH_3}}{C}HCH_3 + Cu(I)OCOCH_3 \quad (6)$$

Our findings and conclusions based on examination of the minor ester product from the butenes were confirmed by examination of the major ester product from the reaction of 2-pentene with *tert*-butyl peroxyacetate and copper salts, 4-acetoxypent-2-ene. This product, formed by preferential abstraction of the secondary allylic hydrogens, has been reported to account for 68% of the ester yield;[5] its cis or trans nature was not examined at the time. Advantage can be taken of the stereoselective nature of the reaction to prepare specifically *trans*-4-acetoxypent-2-ene from the 2-pentenes.

The nature of the allylic radical formed by abstraction of a secondary allylic hydrogen from 2-pentene depends on the alkene conformation which is frozen at the moment of abstraction.[7] *trans*-2-Pentene gives both trans–trans and trans–cis radicals, in

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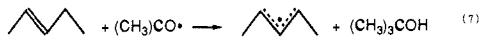
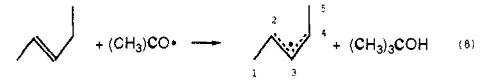
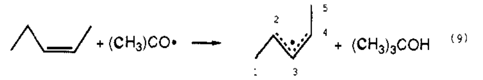
(16) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5106–5108.

the ratio of 2.0:1.0 in favor of the former at 40 °C, eq 7–8.





Because of steric repulsions, the rotamers of *cis*-2-pentene that would lead to a cis–cis radical are of too high energy to contribute significantly to the population, and *cis*-2-pentene gives only trans–cis radicals, eq 9. Atom or ligand transfer to the trans–trans radical must give only trans products, but the cis–trans species would be expected, on statistical grounds, to give equal amounts of cis and trans products. Hence, if no equilibration occurs, chlorination of *cis*-2-pentene with *tert*-butyl hypochlorite should give the cis and trans isomers of 4-chloropent-2-ene in equal yield, while *trans*-2-pentene should give 83% of the trans and 17% of the cis product. Previous results accord with this view.[17]

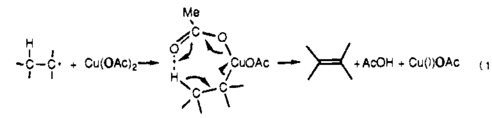


Our own results are also consistent with this analysis. Upon photolysis with *tert*-butyl hypochlorite at 40 °C, a mixture of 75.5% *trans*- and 24.5% *cis*-2-pentene produced a mixture of allylic chlorides in high yield. The major component was 4-chloropent-2-ene, whose distribution was 24% cis and 76% trans. The theoretical distribution is 25% cis and 75% trans.

The same mixture of 2-pentenes, when treated with *tert*-butyl peroxyacetate and cuprous chloride in excess alkene as solvent at 70 °C, gave as the major product (70% of the ester) 4-acetoxypent-2-ene, whose distribution was 96.4 ± 2.7% trans and only 3.6 ± 2.7% cis as determined by both GC and ^{13}C NMR. This preponderance of trans ester again is consistent with a pericyclic transition state similar to VII. Attack by copper at C4 (eq 8–9) can lead to a cis double bond between C4 and C3 only if the methyl group denoted C5 attains the unfavorable quasi-axial position similar to VI; hence, very little cis product is observed. The minor ester products from 2-pentene were 3-acetoxypent-1-ene (27.9% of the ester) and *trans*-1-acetoxypent-2-ene (2.2%) with a barely detectable trace of the corresponding cis isomer; there was also obtained a 5% yield of *tert*-butyl pentenyl ether.

The proposed intermediacy of III is also consistent with much other information available in the literature. The existence of inorganic Cu(III) species in well-established,[18] and Cu(III) intermediates of organic radicals with aqueous Cu(II) have been detected spectroscopically.[19] Structure III also provides an explanation for the observation that Cu(II) is exceedingly reactive toward allylic radicals, while it is rather indifferent to benzyl.[20] The ionization potentials are ca. 8.3 eV for allyl and 7.8 eV for benzyl, in reverse order to the ease of reaction, as has been noted.[20] Structures such as III are not possible for $PhCH_2^•$ without loss of aromaticity, and the reaction must proceed by some other pathway of higher energy such as direct ligand transfer or, more likely, oxidation to a cationoid intermediate. In contrast, no cationoid intermediate need develop in the pericyclic alternative available to allylic radicals.

The pericyclic Cu(III) species III also provides a unifying view of the reactions of cupric carboxylates to produce oxidative substitution in allylic radicals as opposed to mostly oxidative elimination in alkyl radicals possessing a β hydrogen, eq 10. Structures similar to VIII for oxidative elimination with alkyl radicals have been proposed as possible transition states;[21–24] a vinyl radical–Cu(III) intermediate has also been proposed recently.[25] We note that VIII provides an explanation for the ease of oxidative formation of alkenes from primary alkyl radicals,[20] despite their high oxidation potentials. No cationoid intermediate need be formed, and the primary alkyl radical provides a strong ligand to copper.

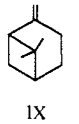


VIII

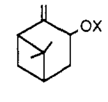
It should be noted that formation of species with high carbocation character has been demonstrated repeatedly for some reactions of carbon radicals with Cu(II).[5,21,25] e.g., neopentyl radicals give rearranged products (2-methylbut-2-ene and 2-methylbut-1-ene) typical of carbocation behavior,[5] and β-arylethyl radicals yield β-arylethyl acetates with complete scrambling of the α and β carbons.[21] In these cases, however, special circumstances mitigate against structures such as VIII or provide lower energy alternative pathways. Neopentyl radicals have no β hydrogens, and pericyclic elimination cannot occur. The phenethyl radical results were obtained in 40 vol % acetonitrile–acetic acid solvent, where Cu(II) is an extremely powerful oxidizing agent because of the very effective solvation of Cu(I) by the nitrile.[18] It has also been demonstrated that even in allylic oxidations the distribution of esters obtained shifts more toward that expected of cationic allylic intermediates in the presence of good complexing species for Cu(I) such as pyridine.[5] The involvement of cationoid intermediates in our allylic systems can be discounted since such species tend to retain their cis or trans nature (Table I).

It is apparent that regioselective allylic acyloxylations of terminal alkenes can be performed with peroxy esters and copper salts in yields equivalent to those of reactions of SeO_2 or SeO_2/hydroperoxide combinations. Some comparisons are given below.

SeO_2/hydroperoxide with 1-decene gives a yield of 61% dec-1-en-3-ol along with 8% of the corresponding ketone,[6] while *tert*-butyl peroxyacetate/Cu with 1-octene gives an 83% yield of 3-acetoxyoct-1-ene, plus 12% of the allylic isomer,[5] which is easily separated.[26] β-Pinene, IX, with SeO_2/hydroperoxide gives a yield of 85% pinocarveol,[6] Xa, while *tert*-butyl peroxybenzoate/Cu yields 90% of the ester Xb, specifically identified as the trans isomer.[27] The stereoselective nature of the reaction is again demonstrated.



IX



X a. X=H; b X=COPh)

In the case of nonterminal alkenes, the SeO_2 oxidation can give mixtures of products depending on which olefinic carbon is attacked, even in the absence of double bond shifts; the peroxyester/Cu oxidations also yield mixtures with nonterminal alkenes, depending on which allylic hydrogens are abstracted preferentially and which allylic isomer is favored in the product. Finally, another common feature is the trans nature of the double bond in the predominant product of allylic oxidation: SeO_2 with *cis*-2-octene gives *trans*-oct-2-en-4-ol,[6] while *tert*-butyl peroxyacetate/Cu and the 2-pentenes give *trans*-4-acetoxypent-2-ene. Evidently the loss

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(17) Reference 7 gives the following distributions of 4-chloropent-2-ene at 40 °C: from *trans*-2-pentene, 85.9% trans and 14.1% cis; from *cis*-2-pentene, 56.8% trans and 43.2% cis.

(18) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980; pp 800–821. (b) Wells, A. F. *Structural Inorganic Chemistry, 5th Ed.* Oxford University Press: London, 1984; p 1101.

(19) Freiburg, M.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1825–1837.

(20) Bacha, J. D.; Kochi, J. K. *J. Org. Chem.* **1968**, *33*, 83–93.

(21) Kochi, J. K.; Bemis, A. *J. Am. Chem. Soc.* **1968**, *90*, 4038–4050.

(22) Struble, D. L.; Beckwith, A. L. J.; Gream, G. E. *Tetrahedron Lett.* **1970**, 4795.

(23) (a) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843–865. (b) Kochi, J. K. In *Frontiers of Free Radical Chemistry*, Pryor, W. A., Ed., Academic Press: New York, 1980; p 297–354.

(24) Beckwith, A. L. J.; Gream, G. E.; Struble, D. L. *Aust. J. Chem.* **1972**, *25*, 1081–1105.

(25) Kitamura, T.; Kobayashi, S. *J. Am. Chem. Soc.* **1986**, *108*, 2641–2645.

(26) The boiling points of the isomeric allylic acetates often are quite different: e.g., 3-acetoxybut-1-ene, bp 108 °C; 1-acetoxybut-2-ene, bp 130 °C.

(27) Villenave, J.-J.; Francois, H.; Lalande, E. *Bull. Soc. Chim. Fr.* **1970**, 599–606.

of the C2–C3 double bond and the pericyclic requirements of the transition states involved in both cases lead to similar conformational preferences.

Experimental Section

Analyses. NMR spectra were obtained on a JEOL model JNM-FX-200, at 199.5 MHz for ^{1}H and at 50.16 MHz for ^{13}C. All ^{13}C spectra were obtained on the fully decoupled mode with 50 vol % $CDCl_3$ solvent; at least 12 000 scans were obtained for detection of trace cis compounds. Calibration with authentic materials showed that the intensities of the vinyl carbon γ to the allylic substituent were proportional (±3%) to the relative amounts of the trans and cis isomers. All reported frequencies are in ppm downfield from Me_4Si. Infrared spectra were obtained with a Perkin-Elmer Model 683 or, for small samples, Model 1800 Fourier transform instruments. Analyses by gas chromatography were performed on a Varian 6000 with 25-m capillary columns of dimethyl silicone (dimethylsiloxane) or methyl phenyl silicone; the response of the flame ionization detector was calibrated with authentic compounds.

Materials. The butenes were commercially available materials used as received. *tert*-Butyl peroxybenzoate was commercial material described as "technically pure liquid"; it assayed at 96.5 ± 1.5% by iodometric titration and was used as received. But-2-en-1-ol was obtained as "crotyl alcohol", mixture of cis and trans isomers; comparison with the known IR spectra,[28] GC analyses, and ^{13}C NMR spectra showed it to be 70% trans and 30% cis. 2-Pentene was obtained as a mixture of isomers; ^{13}C NMR spectra and GC showed it to be 75.5% trans and 24.5% cis.

tert-Butyl hydroperoxide was obtained as 70% solution in water. Extraction with an equal volume of benzene and salting out transferred 90% of the material to the organic solvent; 4 M.

tert-Butyl peroxyacetate was prepared from the hydroperoxide solution by treatment with acetyl chloride, bp 27 °C at 1.5 mmHg. IR showed less than 3% contamination by hydroperoxide. Iodometric titration gave an assay of 99.6% oxidant as peroxy ester: ^{13}C NMR 167.8, 82.8, 71.7, 26.0, and 25.6; IR 2982, 1782, 1368, 1183, 860 cm^{-1}. Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.58; H, 9.13.

tert-Butyl hypochlorite was prepared as benzene solution; 4.12 M, as previously described.[14]

3-Acetoxybut-1-ene (methallyl acetate) was prepared from the alcohol by acetylation with acetic anhydride in pyridine; bp 108.5 °C (uncorrected). GC showed greater than 98.0% purity: ^{13}C NMR 168.6, 137.2, 114.5, 69.8, 20.8, and 19.0. Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.17; H, 8.97.

1-Acetoxybut-2-ene (crotyl acetate) was prepared from the alcohol by acetylation with acetic anhydride in pyridine; bp 130 °C (uncorrected). GC indicated purity greater than 98.5% and two isomers with the predominant one (70.5%) eluting first. IR confirmed a mixture of cis and trans, while ^{13}C NMR showed the major component to be the trans: 131.1, 125.5, 65.1, 17.7; for the cis: 129.3, 124.6, 60.0, 12.2; common: 169.1 (carbonyl), 20.8 (acetate methyl). Composition based on the C3 intensities: 70.4% trans; 29.6% cis. Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 64.21; H, 8.56.

1-(Benzoyloxy)but-2-ene (crotyl benzoate) was prepared from the alcohol by esterification with benzoyl chloride in pyridine–ether; bp 50 °C at 3 mmHg. GC indicated purity greater than 98.5% and two isomers with the predominant one (70.6%) eluting first. IR showed a mixture of trans and cis isomers, 1678 and 1647 cm^{-1} respectively. ^{13}C NMR showed the major isomer (73%) to be the trans. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.98; H, 7.05.

All other reagents were commercial materials redistilled as needed before use. The copper salts were used as received.

Reactions were performed in sealed glass tubes made of 2-mm thick Pyrex glass. In a typical experiment, 0.010 g of CuCl (0.1 mmol) was charged to the tube, followed by 4.5 mL of solvent benzene and 0.7 g of *tert*-butyl peroxybenzoate (5.3 mmol). The tube was then placed in ice and was flushed with *cis*-2-butene until approximately 2.2 mL condensed (approximately 25 mmol). The tube was connected to a vacuum line, frozen with liquid nitrogen, evacuated, and sealed. The tubes were placed in a 70 °C ± 1 °C bath and were heated for the times indicated in Table II. The distribution of the ester products did not change with time over a 1-month period.

Reactions of *tert*-butyl hypochlorite were also performed in deaerated sealed tubes, the entire charging operation being performed with illumination from a 25-W red bulb only. The products of reaction with 2-pentene showed a small change in composition with time; e.g., the distribution of 4-chloropent-2-ene obtained from a mixture (24.5:75.5) of *cis*- and *trans*-2-pentene changed over a 3-day period at room temperature from 76% trans and 24% cis to 81% trans and 19% cis.

Registry No. *t*-BuOCl, 507-40-4; CuCl, 7758-89-6; $Cu(OAc)_2$, 142-71-2; *tert*-butyl hydroperoxide, 75-91-2; *tert*-butyl peroxyacetate, 107-71-1; acetyl chloride, 75-36-5; 3-acetoxybut-1-ene, 6737-11-7; (*Z*)-1-acetoxybut-2-ene, 7204-36-6; (*E*)-1-acetoxybut-2-ene, 7204-29-7; (*Z*)-crotyl benzoate, 104664-93-9; (*E*)-crotyl benzoate, 88927-00-8; 1-butene, 106-98-9; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1; but-1-en-3-ol, 598-32-3; (*E*)-but-2-en-1-ol, 4088-60-2; (*Z*)-but-2-en-1-ol, 504-61-0; 3-chlorobut-1-ene, 563-52-0; (*E*)-1-chlorobut-2-ene, 4894-61-5; (*Z*)-1-chlorobut-2-ene, 4628-21-1; *tert*-butyl peroxybenzoate, 614-45-9.

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(28) Gredy, B. *Bull. Soc. Chim. Fr.* **1935**, *2*, 1029.