the benzylic protons in **19** (singlet, τ 6.39, wt 0.41, corresponds to **19** as *ca.* 37% of the mixture). The ketones **6** and **19** were isolated by preparative gas chromatography as described above. The infrared spectrum (neat) of **6** was identical with that of an authentic sample. The ketone **19**, which was obtained as a colorless oil (3 mg), absorbed strongly in the infrared spectrum (neat) at 1705 cm^{-1} (unconjugated C=O) and the mass spectrum showed a molecular ion peak, which was the most intense peak in the spectrum, at *m/e* 214 (calcd for $C_{15}H_{18}O$, 214.29). The product (3 mg) gave a crystalline 2,4-dinitrophenylhydrazone (*ca.* 4 mg, mp 182–189°). Three recrystallizations of the crude derivative from 95% ethanol gave yellow needles, mp 200–202°; however, this material was not pure. The small quantity of material obtained prevented further purification.

Carbonium Ions from Alkyl Radicals by Electron Transfer

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Abstract: Alkyl radicals are oxidized by Cu^{II} complexes in acetonitrile–acetic acid solutions to a mixture of alkenes and alkyl esters (and acetamides). These electron transfer processes have been termed oxidative elimination (alkenes) and oxidative substitution (esters, etc.). The oxidation of four principal classes of alkyl radicals: neopentyl, homoallylic (cyclobutyl, cyclopropylmethyl, and allylcarbinyl), β-arylethyl, and cyclopropyl, has been scrutinized. Oxidative substitution of these radicals by Cu^{II} oxidants affords the same products as those commonly derived from the solvolysis of the corresponding tosylate or nitrosative deamination of the alkylamine. Extensive cationic rearrangement occurs during oxidation of neopentyl and cyclopropyl radicals. Oxidative substitution and elimination are competing processes during oxidation of homoallylic radicals and β-arylethyl radicals by Cu^{II} complexes. Carbonium ions are postulated as intermediates in oxidative substitution, and are formed by electron transfer from the alkyl radical to the Cu^{II} oxidant. On the other hand, alkenes result from oxidative elimination by direct loss of a β-hydrogen synchronously with electron transfer; carbonium ions are not important. The dichotomy between oxidative substitution and elimination is highly accentuated by polar substituents in the β-arylethyl series. Thus, β-anisylethyl radicals are oxidized almost completely to β-anisylethyl acetate, whereas the *meta* isomer or the parent phenethyl radical affords mostly products of oxidative elimination (styrenes). The α- and β-carbon atoms are completely scrambled in the β-anisylethyl acetate derived from oxidation of β-anisylethyl radical (not rearranged). An ethylene-*p*-anisonium ion is presented as an intermediate in the formation of β-anisylethyl acetate.

A variety of alkyl radicals are oxidized by metal complexes, and two principal processes have been delineated: ligand transfer and electron transfer.[1] They form the basis of many oxidation–reduction reactions and play critical roles in the mechanism of metal catalysis of organic reactions.

Ligand transfer oxidations of alkyl radicals (eq 1)

$$R\cdot + M^{n+}X_n \longrightarrow RX + M^{(n-1)+}X_{n-1} \qquad (1)$$

have been examined with Cu^{II}, Fe^{III}, and Pb^{IV} complexes, particularly of halides, such as chloride and bromide,[2] as well as the pseudohalides, cyanide, thiocyanato, and azide.[3] The microscopic reverse process pertains to the reduction of organic halides by Cr^{II} complexes.[4]

Electron transfer oxidations of radicals, on the other hand, have been generally effected by Cu^{II}, Pb^{IV}, Co^{III}, Mn^{III}, Ce^{IV}, and Tl^{III} species which are coordinated to ligands *via* oxygen, especially as aquo and carboxylato complexes (eq 2).[5,6] The principal products in these reactions are alkenes and alkyl derivatives (from

$$R\cdot + M^{n+}Y_n \longrightarrow [R(-H) + RS] + H^+ + M^{(n-1)+}Y_n \qquad (2)$$

nucleophiles present as HS and S$^-$). Both types of products have been well established as characteristic of carbonium ion intermediates from solvolyses, nitrosative deaminations, electrooxidations, etc.[7]

Thus, relatively minor changes in the structure of the metal oxidant are sufficient to alter the course of the reaction from ligand transfer to electron transfer, and *vice versa*. Furthermore, such a change in mechanism imparts major alterations in the electronic demand on the alkyl moiety in the transition state. By a study of the kinetics, solvent and polar substituent effects, as well as rearrangement and products of the reaction, we concluded that stabilization of a cationic charge on the alkyl group is a dominant factor in electron transfer oxidations.[1,8,9] In contrast, charge requirements in the transition state of ligand transfer oxidation of radicals are minimal, and these reactions are akin to atom-

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(1) J. Kochi, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 27, 207 (1966).

(2) (a) J. Kochi and R. Subramanian, *J. Am. Chem. Soc.*, **87**, 1508 (1965); (b) J. Kochi, *ibid.*, **87**, 2500 (1965); *J. Org. Chem.*, 30, 3265 (1965); (c) C. Bamford, A. Jenkins, and R. Johnston, *Proc. Roy. Soc.* (London), **A239**, 214 (1957).

(3) L. Jenkins, unpublished studies.

(4) (a) J. Kochi and D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964); (b) D. Singleton, and J. Kochi, *ibid.*, **89**, 6547 (1967).

(5) H. DeLaMare, F. Rust, and J. Kochi, *ibid.*, **83**, 2013 (1961); **85**, 1437 (1963).

(6) (a) J. Kochi, *ibid.*, **87**, 3069 (1965); (b) J. Kochi, J. Bacha, and T. Bethea, *ibid.*, **89**, 6538 (1967); (c) J. Bacha and J. Kochi, *J. Org. Chem.*, **33**, 83 (1968); (d) S. Lande, R. Sheldon, and J. Anderson, unpublished studies.

(7) (a) C. Bunton, "Nucleophilic Substitution at a Saturated Carbon," Elsevier Publishing Co., New York, N. Y., 1963; (b) D. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963; (c) S. Wawzonek, *Science*, **155**, 39 (1967).

(8) (a) J. Kochi, *J. Am. Chem. Soc.*, **84**, 3271 (1962); (b) J. Kochi and H. Mains, *J. Org. Chem.*, 30, 1862 (1965).

(9) (a) J. Kochi, *Science*, **155**, 415 (1967); (b) C. Walling and A. Zavitsas, *J. Am. Chem. Soc.*, **85**, 2084 (1963); (c) P. Story, *Tetrahedron Letters*, 414 (1962).

transfer processes in other more conventional homolytic processes.

Certain alkyl radicals on electron transfer oxidation by Cu^{II} salts produce rearranged products.[8–10] The same radicals in a ligand transfer process generally do not undergo rearrangement. The possibility of cationic intermediates in electron transfer oxidations has been discussed earlier.[1,8,9]

At this juncture, we are concerned whether carbonium ions are actually intermediates in electron transfer oxidations of radicals. We have chosen four principal classes of alkyl radicals: neopentyl, homoallyl (cyclobutyl; allylcarbinyl, and cyclopropylmethyl), ring-substituted β-phenethyl, and cyclopropyl, for further examination of this question. In this paper, we present evidence for carbonium ions as intermediates in electron transfer processes by an investigation of the products of oxidation. In the following study[11] these observations and conclusions are supported by kinetic and isotopic studies, and a general mechanism for oxidation of alkyl radicals by Cu^{II} complexes is presented.

Results and Discussion

Generation and Oxidation of Alkyl Radicals by Cu^{II} Complexes. The catalytic decomposition of peroxides afforded a convenient method for the generation of free alkyl radicals and a study of their oxidation by Cu^{II} complexes.[10] In contrast to other homolytic decompositions of peroxides, the stoichiometries of the catalyzed reactions given by eq 3[12] are remarkably unequivocal.

$$(RCO_2)_2 + HOAc \xrightarrow[CH_3CN]{Cu^I\text{–}Cu^{II}} CO_2 + RCO_2H + R_{ox} \qquad (3)$$

$$R_{ox} = \text{alkene, alkyl acetate}$$

These radical chain reactions were initiated by cuprous species, which could be employed directly in acetonitrile–acetic acid solutions at various temperatures.[13] The mechanism of the catalytic reactions for the decomposition of diacyl peroxides is given by eq 4–6.

$$(RCO_2)_2 + Cu^I \longrightarrow RCO_2Cu^{II} + RCO_2\cdot \qquad (4)$$

$$RCO_2\cdot \longrightarrow R\cdot + CO_2 \qquad (5)$$

$$R\cdot + Cu^{II}O_2CR \longrightarrow R_{ox} + RCO_2H + Cu^I, \text{etc.} \qquad (6)$$

Diacyl peroxides, particularly those in which the alkyl group R can readily attain cationic character, are prone to undergo carboxy inversion[14] and other thermal reactions. The rearrangement is especially facile in such acidic media as those containing acetic acid.[10a] We found it necessary to carry out most of our studies at 0° to obviate these complications. Since the stoichiometry of the carboxy inversion is similar to the catalyzed reaction, we tested the stability of every peroxide toward rearrangement under reaction conditions. Under these circumstances, the catalyzed decomposition was first order in peroxide and pseudo zero order in Cu^I at suitably high Cu^{II} concentrations.[13] The chain length for decomposition was greater than 20 with most diacyl peroxides (but *vide infra*).

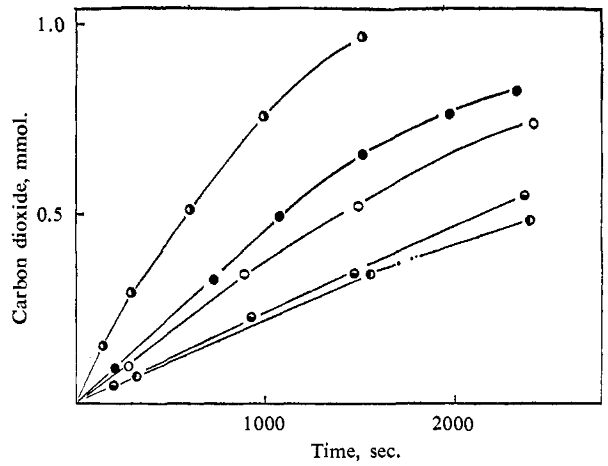

Figure 1. Copper-catalyzed decomposition of *t*-butylacetyl peroxide in 40 vol % acetonitrile–acetic acid at 0° (see Table I for run): ◑, C25D; ●, C25A; ○, C25C; ⊖, C25B; ◐, C25E.

We found that a mixture of acetonitrile and acetic acid was a solvent well suited for our studies, since it simplified the analysis of products. In the presence of acetonitrile, cuprous species form acetonitrile complexes[15] and are not susceptible to disproportionation. Both Cu^{II} and Cu^I salts are in rapid metathesis in acetic acid and exist largely as acetates (eq 7).[16] As a result, the solvolytic products of oxidation of alkyl radicals could be analyzed as the stable acetate esters. A

$$Cu^{I,II}O_2CR + HOAc \rightleftharpoons Cu^{I,II}OAc + RCO_2H \qquad (7)$$

solvent which consisted of 40 vol % acetonitrile–acetic acid was found to be optimum for reactions carried out at 0°, from the standpoint of solubilities of components and freezing point.

Oxidation of Neopentyl Radicals by Cu^{II}. A solution of *t*-butylacetyl peroxide and 0.2 *M* Cu^{II} acetate in 40 vol % acetonitrile–acetic acid was stable indefinitely at 0°. In the presence of catalytic amounts of cuprous acetate, smooth decomposition occurred (Figure 1) and liberated 1 mol of carbon dioxide and *t*-butylacetic acid, in addition to products of oxidation of the neopentyl radical (eq 8, Table I). In each case, the

$$[(CH_3)_3CCH_2CO_2]_2 \xrightarrow[HOAc\text{–}CH_3CN]{Cu^I\text{–}Cu^{II}} CO_2 + (CH_3)_3CCH_2CO_2H + (C_5H_{11})_{ox} \qquad (8)$$

oxidation products $(C_5H_{11})_{ox}$ could be considered as arising *via* a *t*-amyl cation (eq 9–11). In particular, 2-methylbutenes and *t*-amyl acetate are common products of solvolysis or deamination of *t*-amyl and neo-

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(10) (a) J. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963); (b) S. Goldsmith, H. Späth, and L. Beer, *Ann.*, **649**, 1 (1962); (c) J. Kochi and R. Gilliom, *J. Am. Chem. Soc.*, **86**, 5251 (1964); (d) J. Kochi and R. Subramanian, *ibid.*, **87**, 4855 (1965).

(11) J. Kochi, A. Bemis, and C. Jenkins, *ibid.*, in press.

(12) In the following presentation the coordination around Cu will be included only insofar as it is pertinent to the discussion.

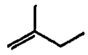
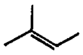
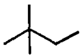
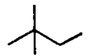
(13) J. Kochi and A. Bemis, *Tetrahedron*, in press.

(14) (a) J. Leffler, *J. Am. Chem. Soc.*, 72, 67 (1950); (b) P. Bartlett and J. Leffler, *ibid.*, **72**, 3030 (1950); (c) F. Greene, H. Stein, C. Chu, and F. Vane, *ibid.*, **86**, 2081 (1964).

(15) (a) H. Morgan, *J. Chem. Soc.*, 2901 (1923); (b) B. Hathaway, D. Holah, and I. Postlethwaite, *ibid.*, 3215 (1961); 2444 (1962); (c) I. Nelson, R. Larson, and R. Iwamoto, *J. Inorg. Nucl. Chem.*, **22**, 279 (1961); *Inorg. Chem.*, 1, 151 (1962); *J. Am. Chem. Soc.*, **82**, 3526 (1960); (d) I. Kolthoff and J. Coetzee, *ibid.*, **79**, 1852 (1957); (e) *cf.* J. Espenson, K. Shaw, and D. Parker, *ibid.*, **89**, 5739 (1967).

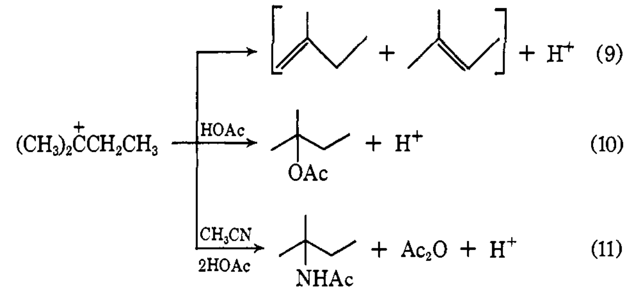
(16) Copper complexes of this type are substitution labile. For example, aquo complexes exchange water at rates greater than 10^{-8} sec. (*Cf.* J. Hunt, "Metal Ions in Aqueous Solution," W. A. Benjamin, Inc., New York, N. Y., 1963, p 73 ff.)

Table I. Copper-Catalyzed Decomposition of *t*-Butylacetyl Peroxide in Acetic Acid–Acetonitrile[a]

Run	$[Cu^{II}]$, *M*	$[Cu^{I}]$, *M*	Ligand[b] (*M*)	Products, mol %: CO_2	RCO_2H[c]	$(CH_3)_4C$			 OAc	 NHAc
C25A	0.20	0.021	None	103	103	3	4	11	43	38
C25B	0.040	0.011	None	103	103	8	3	8	42	35
C25C	0.040	0.017	Py (0.050)	104	103	3	4	10	45	42
C25D	0.040	0.020	Py (0.49)	104	99	2	4	11	41	45
C25E	0.040	0.014	Bipy (0.041)	104	102	13	3	8	39	30

[a] In solutions of 40 vol % acetonitrile–acetic acid containing 0.040 *M* *t*-butylacetyl peroxide at 0.5°. [b] Py = pyridine, Bipy = α,α′-bipyridine. [c] *t*-Butylacetic acid.

pentyl systems in acetic acid.[17] Furthermore, the significant yields of N-*t*-amylacetamide are reminiscent of *t*-amyl cations. These have been derived from the



alcohol or alkene under much more acidic conditions required to generate carbonium ions in the Ritter reaction.[18] A similar behavior has recently been reported from the electrooxidation of *t*-amyl iodide in acetonitrile solutions.[19] It is interesting to note in Table I that the relative amounts of alkene, alkyl ester, and amide are strikingly unaffected by changes in the nature of the Cu^{II} oxidant. This behavior is contrary to that observed in the oxidation of a number of other radicals (*vide infra*).

The *t*-amyl cations involved in the product-forming steps (9–11) are probably formed subsequent to the oxidation of neopentyl radicals (eq 12a). Neopentyl cations are the postulated precursors to *t*-amyl cations (eq 12b).[20]

$$(CH_3)_3CCH_2\cdot + Cu^{II} \longrightarrow Cu^{I} + (CH_3)_3CCH_2^+ \quad (12a)$$

$$(CH_3)_3CCH_2^+ \longrightarrow (CH_3)_2\overset{+}{C}CH_2CH_3 \quad (12b)$$

Aside from the minor amounts of neopentane, we could find no significant amounts of products (*e.g.*, neopentyl acetate or acetamide) derived from the radical in which the neopentyl structure was preserved.[21] The amount of neopentane found was approximately five to ten times greater than butane from either *n*-butyl or *sec*-butyl radicals under equivalent conditions. That neopentane is formed *via* neopentyl radicals (eq 13) is

$$(CH_3)_3CCH_2\cdot + SH \longrightarrow (CH_3)_4C + S\cdot \quad (13)$$

$$SH = CH_3CN,\ CH_3CO_2H$$

shown by the dependence of the yield on the Cu^{II} oxidants (Table I). Qualitatively, these quantities of neopentane indicated the neopentyl radicals were less readily oxidized than either *n*-butyl, isobutyl, *sec*-butyl, or *t*-butyl radicals by Cu^{II}. The significance of these differences in rates of oxidation has been discussed.[10a,11]

Oxidation of Cyclobutyl, Allylcarbinyl, and Cyclopropylmethyl Radicals. Cyclobutyl radicals were generated from cyclobutanecarbonyl peroxide. Although the latter slowly underwent carboxy inversion at room temperature in acetonitrile–acetic acid solutions, at 0° the rearrangement was much too slow compared to the catalyzed reaction to be significant. In the presence of Cu^{I} and Cu^{II}, decarboxylation occurred readily to form 1 mol of carbon dioxide and cyclobutanecarboxylic acid (eq 14). The cyclobutyl radical was accounted for

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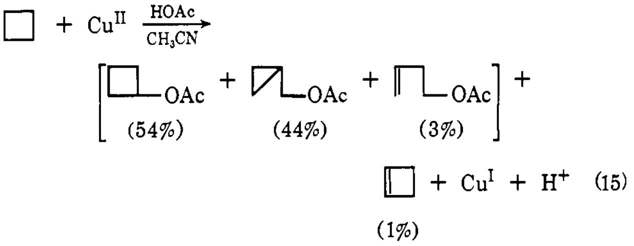
largely (70–90%) as a mixture of homoallylic acetates[22] (eq 15) together with 1–3% cyclobutene, as shown in Table II. Cyclobutyl and cyclopropylmethyl



acetates were stable under reaction conditions. Cyclobutane, 1,3-butadiene, and butene were formed in small

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[17] (a) H. Brown and M. Nakagawa, *J. Am. Chem. Soc.*, **77**, 3610, 3614 (1955); 72, 1223 (1950); (b) M. Silver, *J. Org. Chem.*, **28**, 1686 (1963); *J. Am. Chem. Soc.*, **83**, 3482 (1961); (c) G. Fraser and H. Hoffman, *Chem. Commun.*, 561 (1967); (d) W. Kirmse and K. Hopn, *Tetrahedron Letters*, 1827 (1967); (e) see, however, J. Wilt, R. Stein, and W. Wagner, *J. Org. Chem.*, 32, 2097 (1967).

[18] (a) J. Ritter and P. Minieri, *J. Am. Chem. Soc.*, 70, 4045, 4048 (1948); (b) also *cf.* other carbonium ions from solvolysis, etc.: Y. Pocker and D. Kevill, *ibid.*, 87, 4711 (1965); (c) J. Cast and T. Stevens, *J. Chem. Soc.*, 4180 (1953).

[19] L. Miller and A. Hoffman, *ibid.*, **89**, 593 (1967).

[20] (a) At this point we do not wish to dwell on the nature or state of solvation of these cations. The direction of elimination (alkenes) and solvation of the *t*-amyl and related cations have been extensively discussed[17] and we have nothing additional to contribute. (b) *Cf.* R. Guthrie, *J. Am. Chem. Soc.*, **89**, 6718 (1967). (c) J. Nordlander, S. Jindal, P. Schleyer, R. Fort, J. Harper, and R. Nicholas, *ibid.*, **88**, 4475 (1966). (d) Bridged alkyl cations from alkyldiazonium ions have been proposed: J. Bayless, A. Jurewicz, and L. Friedman, *ibid.*, in press.

[21] Earlier, the oxidation of neopentyl radicals by Cu^{II} in glacial acetic acid was reported to produce small but discrete amounts of neopentyl acetate, in addition to the usual oxidation products. The presence or absence of neopentyl products is not particularly pertinent at this juncture, since such unrearranged derivatives have been found in solvolysis or neopentyl tosylate[17c] and acid-catalyzed decomposition of diazoneopentane.[17d] Oxidation of neopentyl radicals by Cu^{II} *without* rearrangement will be reported later.

[22] (a) For convenience we designate cyclobutyl, cyclopropylmethyl, and allylcarbinyl as *homoallylic derivatives;* (b) J. Kochi and J. Bacha, submitted for publication; (c) *cf.* G. Büchi and J. Marvel, cited by E. Corey and J. Casanova, *J. Am. Chem. Soc.*, **85**, 167 (1963).

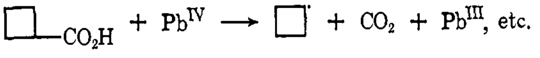
Table II. Copper-Catalyzed Decomposition of Cyclobutanecarbonyl Peroxide in Acetic Acid–Acetonitrile[a]

$[Cu^{II}]$, *M*	$[Cu^{I}]$, *M*	Ligand[b] (*M*)	Products, mol %									
			CO_2	RCO_2H[c]			[d]	C_4H_7OAc	–OAc	–OAc	–OAc	ΣC_4H_7
0.20	0.011		101	105	0.5	0.5	0.2	88[e]	(3)	(53)	(44)	94
0.040	0.0088		105	106	2	0.5	0.1	79	(3)	(53)	(44)	86
0.040	0.0097	Py (0.079)	106	105	0.1	2	1.4	78	(3)	(52)	(45)	84
0.20	0.011	Py (0.49)	102	108	0.2	1	0.6	68	(4)	(50)	(46)	75
0.040	0.010	Bipy (0.033)	100	107	0.1	2	0.8	73	(5)	(46)	(49)	80
0.040	0.027	. . .[f]	104	108	0	0.2	. . .	3		~48	~52	. .

[a] In 40 vol % acetonitrile–acetic acid solutions containing 0.052 *M* cyclobutanecarbonyl peroxide at 0.5°. [b] Py = pyridine, Bipy = α,α′-bipyridine. [c] Cyclobutanecarboxylic acid. [d] Approximately 0.1 % butene-1 also present. [e] Does not include a 5 % mixture of N-cyclobutyl- and N-cyclopropylacetamides (~50:50). [f] Saturated with 1,3-butadiene.

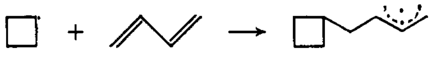
(<2 %) but discrete amounts, especially in runs carried out at low copper concentrations.

Cyclobutyl radicals could also be readily generated from the decarboxylation of cyclobutanecarboxylic acid by Pb^{IV}, and this reaction can be catalyzed by

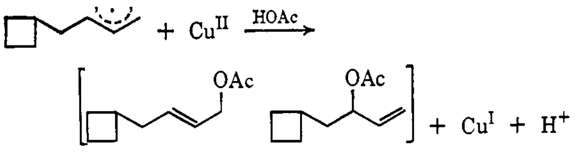


Cu^{II}.[22] The mixture of homoallylic esters obtained by the oxidation of Pb^{IV} or Cu^{II} under these conditions was comparable to that obtained from the catalyzed decomposition of the peroxide described above.

The cyclobutyl radicals formed from the peroxide by reduction with Cu^{I} (eq 15) could be efficiently trapped with excess 1,3-butadiene (eq 16). The allylic adduct


(16)

radical was subsequently oxidized by Cu^{II} to a mixture of cyclobutylbutenyl acetates (eq 17). In the presence of sufficient butadiene eq 14, 16, and 17 constituted a



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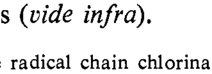
radical chain addition reaction which took precedence over the normal catalytic process (eq 15 and 14). Significantly, we could find no evidence of adducts in which the cyclobutyl moiety had rearranged to an allylcarbinyl structure (*e.g.*, 3-octadien-1,7-yl acetate). The efficient trapping of cyclobutyl radicals constituted direct evidence that the mixture of homoallylic acetates observed in the absence of butadiene was a direct consequence of the oxidation of cyclobutyl radicals by Cu^{II} (eq 15). The rearrangement of cyclobutyl radicals to allylcarbinyl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radicals (eq 18) was too slow[23] under our conditions to compete significantly with oxidation by Cu^{II}, but it was probably responsible for the small amounts of butene-1 (<0.1 %) and 1,3-butadiene (~1 %) observed at low Cu^{II} concentrations (*vide infra*).

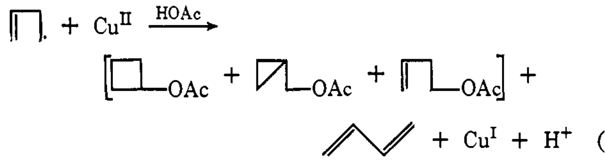
The distribution of homoallylic acetates was essentially independent of the oxidant,[24] and acetonitrile, pyridine, and α,α′-bipyridine complexes of Cu^{II} (see Table II) all afforded 70–90 % yields of mixtures which consisted of cyclobutyl acetate (50–55 %), cyclopropylmethyl acetate (45–50 %), and allylcarbinyl acetate (3–5 %). A minor amount (~5 %) of isomeric N-C_4H_7-acetamides was also formed, but the yields were too small to measure accurately. Qualitatively, the mixture of acetamides consisted of approximately 50 % each of cyclobutyl and cyclopropylmethyl derivatives and much smaller amounts of the allylcarbinyl isomer.

The isomeric **allylcarbinyl radicals** were produced from the relatively stable allylacetyl peroxide, which did not undergo significant carboxy inversion in acetonitrile–acetic acid solutions even at 25°. The cuprous-initiated decomposition of allylacetyl peroxide was examined at 0° in the presence of cupric acetate. In accord with other studies, 1 mol each of carbon dioxide and allylacetic acid was produced (Table III). A variety of products including butene-1 (2–9 %), 1,3-butadiene (20–50 %), a mixture of octadienyl acetates (5–20 %), and homoallylic acetates (10–30 %) accounted for more than 95 % of the material balance based on the allylcarbinyl moiety.

These products could be traced directly to the allylcarbinyl radicals derived by reduction of the peroxide by Cu^{I} (eq 19). Subsequent oxidation of the allyl-

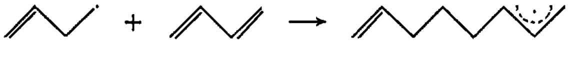
(19)

carbinyl radicals by Cu^{II} yielded 1,3-butadiene and a mixture of homoallylic acetates (eq 20; see Table III). The remainder of the allylcarbinyl radicals could then



(20)

be accounted for as butene-1 and a mixture of octadienyl acetates. The former no doubt arose by hydrogen transfer from solvent, since yields of butene were inversely related to the Cu^{II} concentration (*cf.* eq 13). The octadienyl acetates were derived by addition (eq


(21)

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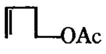
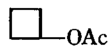
(23) (a) Similarly, the radical chain chlorination of cyclobutane by chlorine[23b] or *t*-butyl hypochlorite[23c] gave excellent yields of cyclobutyl chloride. Allylcarbinyl chloride was not detected and could not have been formed in significant quantities; (b) J. Roberts and R. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); (c) C. Walling and J. Fredericks, *ibid.*, **84**, 3327 (1962).

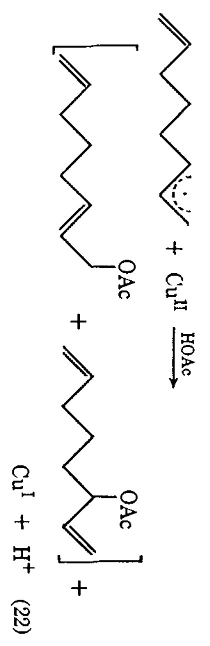
(24) In this regard, the oxidation of cyclobutyl and neopentyl radicals by Cu^{II} are alike.

Table III. Copper-Catalyzed Decomposition of Allylacetyl and Cyclopropylacetyl Peroxides in Acetic Acid–Acetonitrile[a]

[Cu^{II}], *M*	[Cu^{I}], *M*	Ligand[b] (*M*)	Products, mol %											
			CO_2	RCO_2H[c]			C_4H_7OAc[d]				$C_8H_{13}OAc$[e]	3-OAc	1-OAc	ΣC_4H_7[f]
			Allylacetyl Peroxide											
0.20	0.17	None	102	98	2	43	24	(41)	(29)	(30)	12	(54)	(46)	93
0.20	0.18	None	102	99	3	41	24	(39)	(27)	(34)	13	(53)	(47)	94
0	0.14	None	109	102	7	17	21	(35)	(32)	(33)	20	(54)	(46)	85
0	0.10	None	102	104	9	16	21	(36)	(32)	(32)	20	(55)	(45)	86
0.20	0.16	Py (2.5)	102	102	0	82	7	(77)	(11)	(12)		..	..	89
0.072	0.0097	None	100	101	2	37	33	(21)	(35)	(44)	7	(78)	(22)	86
0.0065	0.013	None	100	104	9	17	28	(19)	(37)	(44)	14	(80)	(20)	82
0.0093	0.0065	Py (0.042)	98	107	2	53	28	(34)	(32)	(34)	6	(81)	(19)	95
0.026	0.0097	Py (0.082)	105	100	1	69	31	(41)	(26)	(33)	3	(80)	(20)	107
0.0072	0.0085	Bipy (0.030)	99	95	3	50	30	(77)	(10)	(13)	..	(62)	(38)	95
0.20	0.010	Py (0.51)	109	108	..	..	14	(68)	(14)	(18)	ND[g]			..
0	0.13	None	108	105	..	..	~1	..	..	..	ND[g]			..
			Cyclopropylacetyl Peroxide											
0.038[h],[k]	0.045[j]	None	92	104[l]	9	10	29	16)	(37)	(47)	18	(60)	(40)	84
0·[k]	0.066	None	95	98[l]	14	18	20	(23)	(39)	(39)	17	(53)	(47)	86

[a] In solutions of 40 vol % acetonitrile–acetic acid containing 0.040 *M* allylacetyl peroxide at 0.5° unless stated otherwise. [b] Py = pyridine, Bipy = α,α'-pyridine. [c] Allylacetic acid, unless noted otherwise. [d] Total yield of homoallylic acetates. [e] Total yield of octadienyl acetates, 1-acetoxyoctadiene-2,7, and 3-acetoxyoctadiene-1,7. [f] Total C_4H_7 fragments accounted for, includes a factor of 2 for octadienyl acetate yield. [g] Not determined but yields high qualitatively. [h] A solution of 0.23 *M* cyclopropylacetyl peroxide decomposed at 2° in 63 vol % acetonitrile–acetic acid. [i] A solution of 0.10 *M* cyclopropylacetyl peroxide decomposed at −8° in 48 vol % acetonitrile–acetic acid. [j] Cuprous chloride. [k] Experiments by H. Mains. [l] Cyclopropylacetic acid.

21) of allylcarbinyl radical to butadiene (from eq 20), followed by oxidation by Cu^{II} (eq 22).[8b] The lower yields of adducts at higher Cu^{II} concentrations could be

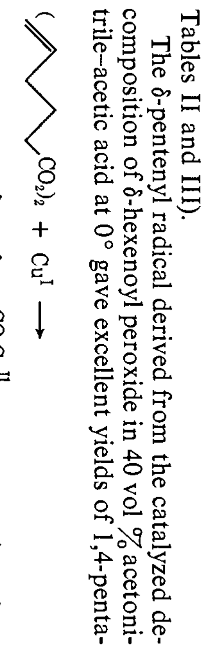


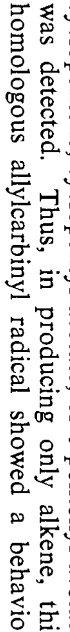
(22)

attributed to competition from the oxidation step (eq 20); conversely, deliberate addition of excess butadiene suppressed the yields of homoallylic acetates and excellent yields of octadienyl acetates could be obtained. In the latter case, no isomeric adducts such as cyclobutylbutenyl acetates (*vide supra*) or cyclopropylpentenyl acetates were found. Thus, questions related to the rearrangement of allylcarbinyl radical to cyclobutyl or cyclopropylcarbinyl radicals were not pertinent.[16,25]

There are two features concerning the allylcarbinyl system which merit further discussion. The composition of the isomeric mixture of octadienyl acetates varied according to the Cu^{II} oxidant. This observation has been examined relative to the oxidation of allylic radicals generally (eq 17 and 22), and we wish to refer this point to our earlier discussion.[8b] Secondly, in contrast to our observations with cyclobutyl radicals (*vide supra*), *the mixture of homoallylic acetates obtained from the oxidation of allylcarbinyl radical was highly dependent on the nature of the Cu^{II} oxidant* (see Table III). The ratio of cyclobutyl and cyclopropylmethyl acetates remained approximately invariant with various Cu^{II} oxidants, but allylcarbinyl acetate increased in importance in the presence of pyridine- or α,α'-bipyridine-copper(II) complexes. Furthermore, in every case the proportion of allylcarbinyl acetate in the homoallylic mixture from the oxidation of allylcarbinyl radicals was significantly higher than that derived from the oxidation of cyclobutyl radicals by various Cu^{II} species[26] (*cf.* Tables II and III).

The δ-pentenyl radical derived from the catalyzed decomposition of δ-hexenoyl peroxide in 40 vol % acetonitrile–acetic acid at 0° gave excellent yields of 1,4-pentadiene and small amounts of pentene-1. No (<0.2%) cyclopentene, cyclopentyl acetate, or δ-pentenyl acetate was detected. Thus, in producing only alkene, this homologous allylcarbinyl radical showed a behavior





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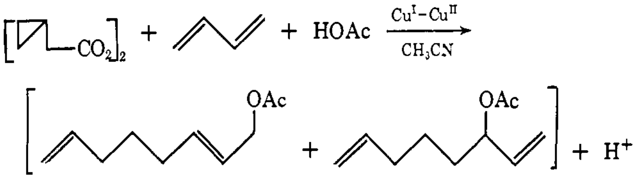
(25) C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 440 ff.

(26) (a) The amount of allylcarbinyl derivative and the ratio of allylic isomers were also dependent to a degree on the initial Cu^{I} concentration, and increased with the latter. It may relate to reactions of a complexed allylcarbinyl radical. Further studies are in progress. (b) There is no doubt that these esters are formed under kinetic rather than thermodynamic control, since no rearrangement occurs under reaction conditions. It is possible, however, that the postulated alkylcopper intermediate[11] (*vide infra*) isomerizes, but we consider this unlikely.

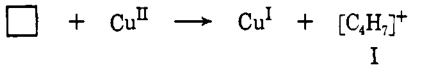
toward Cu^{II} which was typical of other primary alkyl radicals.[10]

Cyclopropylacetyl peroxide underwent carboxy inversion very readily in solutions containing acetic acid.[27] The rearrangement was minimal at −8 to 0° in 50 vol % acetonitrile–acetic acid solutions, but could not be suppressed entirely. It was clear, however, that the cuprous-initiated decomposition constituted the major pathway at 0°. Good yields of carbon dioxide and cyclopropylacetic acid were obtained. The cyclopropylmethyl radical was accounted for entirely by the same products derived from allylcarbinyl radical, *i.e.*, butene-1, 1,3-butadiene, and a mixture of octadienyl acetates and homoallylic acetates. Moreover, the characteristic distribution of the allylic and homoallylic isomers in the mixture of octadienyl acetates and C_4H_7 acetates, respectively, varied in the same way with changes in the Cu^{II} oxidants for both isomeric radicals (see Table III). In the presence of excess butadiene, the catalytic decomposition of cyclopropylacetyl peroxide afforded excellent yields of octadienyl acetates. We could find no methylcyclopropane or methylenecyclopropane, the former even when the reaction was carried out in chloroform. In the latter case, butene-1 was the principal product, and the kinetic chain length for decomposition was short (cuprous consumed). From this evidence we deduce that the unimolecular rearrangement of cyclopropylmethyl radicals to allylcarbinyl radicals (eq 23)[28] occurs much faster than any bimolecular reaction with butadiene or Cu^{II}, and all products we observed were derived from allylcarbinyl radicals subsequent to rearrangement.[29]




(23)

Carbonium Ions from Oxidation of Homoallylic Radicals. We conclude from the behavior shown by cyclobutyl and allylcarbinyl (cyclopropylmethyl) radicals toward Cu^{II} oxidants that carbonium ions can be noteworthy intermediates. One of the important criteria we apply, among others, is the invariance of the product composition with the nature of the oxidant. On this basis, we attribute the formation of homoallylic acetates from the oxidation of cyclobutyl radicals to the solvation (eq 25) of a homoallylic C_4H_7 cation(s), I, formed as an intermediate by electron transfer (eq 24).[30]



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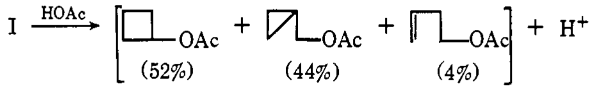
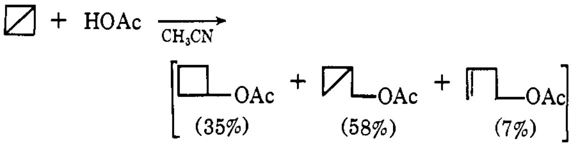


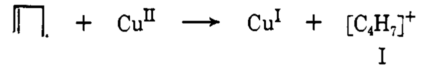
(25)

The distribution among cyclobutyl (47 %), allylcarbinyl (5 %), and cyclopropylmethyl acetates (48 %) derived by solvolysis and deamination of various homoallylic derivatives[31] is approximately that observed in the oxidation of cyclobutyl radicals. Furthermore, the acetolysis of bicyclobutane under conditions used in the catalytic decomposition of peroxide also gives a similar mixture of homoallylic acetates (eq 26).[32]



(26)

We postulate that cyclobutyl and cyclopropylmethyl acetates arise from the oxidation of allylcarbinyl radicals *via* the same C_4H_7 cation I (eq 27) as that derived from the cyclobutyl radical (eq 24). Allylcarbinyl acetate from the solvation of I is produced in essentially the same proportion (eq 25) as it is from the oxidation of cyclobutyl radicals or solvolysis mentioned above. *The extra allylcarbinyl acetate observed only in the oxidation of allylcarbinyl radicals (vide supra) must arise via an independent competing process.*[26b] The latter appears to be facilitated by pyridine- and bipyridine-copper(II) complexes as well as by high Cu^{I} and Cu^{II} concentrations. Direct substitution of this type is unique with allylcarbinyl radicals,[33] since it is not observed with δ-pentenyl or *n*-butyl radicals. We tentatively postulate that such a substitution is a direct consequence of γ,δ-unsaturation and occurs by complexation between allylcarbinyl radical with the Cu^{II} oxidant, reminiscent of a similar proposal for the oxidation of the homologous allyl radical.[8,34]



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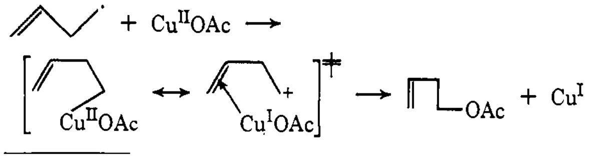

(28)

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[27] *Cf.* H. Hart and R. Cipriani, *J. Am. Chem. Soc.*, **84**, 3697 (1962).

[28] L. Montgomery and J. Matt, *ibid.*, **89**, 3050, 6556 (1967); (b) T. Halgren, M. Howden, M. Medof, and J. Roberts, *ibid.*, **89**, 3051 (1967); D. Neckers, A. Schaaf and J. Hardy, *ibid.*, **88**, 1269 (1966).

[29] (a) It is possible, however, that allylcarbinyl radicals are formed *directly* from cyclopropyl acetyl peroxide on reduction with Cu^{I}. (b) No evidence for such a concerted cleavage–rearrangement was found in the thermolysis of the peroxide [H. Hart and R. Cipriani, *J. Am. Chem. Soc.*, **84**, 3698 (1962)], although enhancement in rate relative to cyclohexanecarboxyl peroxide was observed. However, lability to carboxy inversion partially vitiates these results. (c) Homolytic decomposition of cyclopropylmethylazo compounds do show enhanced rates of decomposition [C. Overberger and A. Lebovitz, *ibid.*, **76**, 2725 (1954)]. (d) *Cf.* J. Martin, J. Schultz, and J. Timberlake, *Tetrahedron Letters*, 4629 (1967).

[30] (a) Our studies do not distinguish between a nonclassical bicyclobutonium or rapidly equilibrating homoallylic cation. (b) *Cf.* discussion by G. Sargent, *Quart. Rev.* (London), 20, 301 (1966). (c) P. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965. (d) M. Hanack and H.-J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967). (e) P. von R. Schleyer and G. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).

[31] R. Breslow, ref 25, p 254 ff. For a recent study see R. Moss and F. Shulman, *Tetrahedron*, **24**, 2881 (1968); *J. Am. Chem. Soc.*, **90**, 2731 (1968).

[32] (a) J. Bayless, L. Friedman, J. Smith, F. Cook, and H. Shechter, *ibid.*, **87**, 663 (1965). (b) We wish to thank Dr. J. Bayless for a sample of bicyclobutane.

[33] The *benzo* analog, β-phenethyl radical, behaves in a similar manner (*vide infra*).

[34] The transition state in eq 28 is similar to that for oxidative elimination (eq 29).

Table IV. Copper-Catalyzed Decomposition of Hydrocinnamoyl Peroxide in Acetonitrile–Acetic Acid[a]

$[Cu^{II}]$, *M*	$[Cu^I]$, *M*	Ligand[b] (*M*)	Products, mol %: CO_2	RCO_2H[c]	$PhCH_2CH_3$	$PhCH{=}CH_2$	$PhCH_2CH_2OAc$	Dimeric prodt[d]	R(−H)[e]	ROAc[f]
0.040	0.0086	None	102	89	2	53	8	30	(17)	(83)
0.040	0.0078	Py (0.077)	104	109	<0.2	81	5	ND	..	..
0.20	0.014	Py (0.49)	103	101	<0.2	85	3	ND	..	..
0.040	0.0067	Bipy (0.034)	99	108	<0.2	87	4	ND	..	..
0.19	0.035	None	100	ND	ND	68	5	16	(35)	(65)
0.19	0.030	None	100	ND	ND	75	6	13	(23)	(77)
0.056	0.024	None	100	ND	ND	61	7	40	(34)	(66)

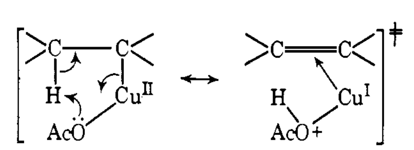
[a] In solutions of 40 vol % acetonitrile–acetic acid containing 0.040 *M* hydrocinnamoyl peroxide at 0.5°. [b] Py = pyridine, Bipy = α,α′-bipyridine. [c] Hydrocinnamic acid. [d] Total yield, includes factor of 2. [e] 1,4-Diphenylbutene-1. [f] 1,4-Diphenylbutyl acetate.

Table V. Catalyzed Decomposition of *p*-Methylhydrocinnamoyl Peroxide in Acetonitrile–Acetic Acid[a]

$[Cu^{II}]$, *M*	$[Cu^I]$, *M*	Ligand[b] (*M*)	Products, mol %[c]: CO_2	RCO_2H	RH	R(−H)	ROAc	Dimeric adducts[d]	Alkene[e]	Acetate[f]
0.20	0.15	None	100	93	0.5	52	28	5	(15)	(85)
0.18	0.090	Py (0.97)	97	100	0	75	9	ND	..	..
0.044	0.029	None	100	ND	1.5	37	49	8	(27)	(73)
0.044	0.046	Py (0.10)	100	108	0	64	38	ND	..	..
0.036	0.043	Bipy (0.053)	103	100	0	87	14	ND	..	..
0.040	0.057	Bipy (0.048)	103	ND	0	91	13	ND	..	..
0.20	0.11	None	99	107	0.5	69	34	5	(12)	(88)
0.21	0.033	None	98	107	0.5	41	47	4	(30)	(70)
0.20	0.044	Py (0.97)	99	100	9	74	11	0.5	(23)	(73)
0.036	0.043	None	100	110	1.5	40	33	10	(40)	(60)
0.044	0.053	Py (0.12)	96	108	0	62	29	2	(26)	(74)

[a] In solutions of 40 vol % acetonitrile–acetic acid containing 0.023 *M* *p*-methylhydrocinnamoyl peroxide at 0°. [b] Py = pyridine, Bipy = α,α′-bipyridine. [c] RCO_2H = *p*-methylhydrocinnamic acid, RH = *p*-ethyltoluene, R(−H) = *p*-methylstyrene, ROAc = β-*p*-tolylethyl acetate. [d] Total yields, includes a factor of 2. [e] 1-Phenyl-1-*p*-tolylbutene-1. [f] 1-Phenyl-4-*p*-tolylbutyl acetate.

The yields of products of *oxidative elimination*, such as cyclobutene, 1,4-pentadiene, and 1,3-butadiene (especially) from cyclobutyl, δ-pentenyl, and allylcarbinyl radicals, respectively, vary with the nature of the Cu^{II} oxidant. Ligands such as pyridine and α,α′-bipyridine facilitate oxidative elimination compared to oxidative substitution when such competition exists. This dichotomy is also influenced by solvent.[22b] We postulate an independent route for alkene formation that does not involve the same cationic intermediate presented for oxidative substitution.[11] A transition state for oxidative elimination involving loss of a β-proton synchronous with electron transfer is presented below.[11,22b]



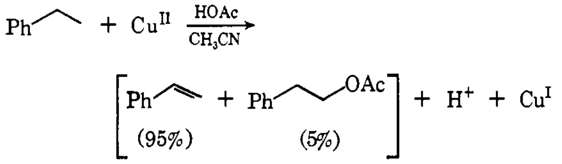
(29)

Finally, we wish to comment on the relatively minor amounts of cyclobutene and major yields of butadiene produced in the oxidation of cyclobutyl and allylcarbinyl radicals, respectively. If alkene and ester are formed in competing reactions, as we suggest, we would expect more ester from that radical which has the lower oxidation potential. On this basis, cyclobutyl, being a secondary radical, would be more readily ionized than the primary allylcarbinyl radical.[35] The higher yields of homoallylic esters from the oxidation of cyclobutyl radical are consistent with this postulate. However, these conclusions are not unequivocal, since oxidative elimination (eq 29) should be less favored with cyclobutyl radicals compared to allylcarbinyl radicals due to strain in cyclobutene and conjugation in butadiene. Nonetheless, we hope to demonstrate (in the next section) by the examination of the β-arylethyl system that stabilization of a cationic charge is a dominant factor influencing the relative yields of ester and alkene from electron transfer oxidation.

Oxidation of β-Arylethyl Radicals. Hydrocinnamoyl peroxide and its derivatives (*p*-methyl and *m*- and *p*-methoxy), like other primary acyl peroxides, did not undergo significant ionic rearrangement in acetic acid solutions. Each of these peroxides was smoothly decomposed in 40 vol % acetonitrile–acetic acid solutions at 0° in the presence of cupric acetate and cuprous initiation, to afford 1 mole of carbon dioxide and the parent hydrocinnamic acid (Tables IV, V, and VI).

$$(ArCH_2CH_2CO_2)_2 \xrightarrow[HOAc-CH_3CN]{Cu^I-Cu^{II}} CO_2 + ArCH_2CH_2CO_2H + (ArCH_2CH_2)_{ox}$$

The **β-phenethyl radicals** produced in this manner from hydrocinnamoyl peroxide were oxidized by Cu^{II} complexes largely to styrene (70%) and β-phenethyl acetate (5%, eq 30). The remainder of the β-phenethyl



(30)[36]

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(35) (a) D. Turner, *Advan. Phys. Org. Chem.*, 4, 31 (1966). (b) Provided that ionization does not lead to the same cation, since energies of the radicals are not expected to be widely different.

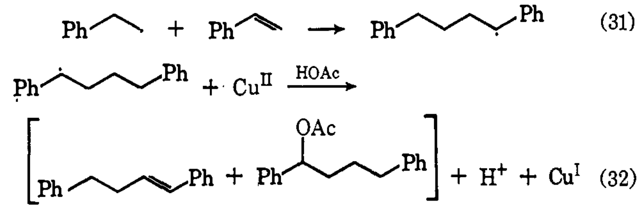
(36) The relative yields of styrene and phenethyl acetate given in the parentheses are *normalized* values, which exclude dimeric adducts and acetamide derivatives. More accurate values are given later.[11]

Table VI. Copper-Catalyzed Decomposition of *m*- and *p*-Methoxyhydrocinnamoyl Peroxides in Acetonitrile–Acetic Acid[a]

[Cu^{II}], *M*	[Cu^{I}], *M*	Ligand (*M*)	Products, mol % CO$_2$	 RH	 R (−H)	 RO-Ac	 RN-HAc
p-Methoxyhydrocinnamoyl Peroxide[b]							
0.20	0.026	None	97	1	1	92	6
0.040	0.025	None	93	3	1	96	6
0.040	0.024	Py (0.10)	98	0.2	3	93	4
0.20	0.026	Py (0.51)	93	ND	5	79	5
0.040	0.017	Bipy (0.056)	90	0.1	14	75	3
m-Methoxyhydrocinnamoyl Peroxide[c]							
0.050	0.032	None	98	1	55	3	ND
0.045	0.037	None	100	2	54	3	ND
0.045	0.049	Bipy (0.056)	99	ND	86	2	ND
0.057	0.052	Bipy (0.073)	97	ND	86	3	ND

[a] In solutions of 40 vol % acetonitrile–acetic acid at 0.5°. [b] *p*-Methoxyhydrocinnamoyl peroxide (0.036 *M*). Products: RH = *p*-ethylanisole, R(−H) = *p*-methoxystyrene, ROAc = β-anisylethyl acetate, RNHAc = N-β-anisylethylacetamide. *p*-Methoxyhydrocinnamic acid not analyzed quantitatively. Large yields qualitatively found. [c] *m*-Methoxyhydrocinnamoyl peroxide (0.023 *M*). Products: RH = *m*-ethylanisole, R(−H) = *m*-methoxystyrene, ROAc = β-*m*-methoxyphenethyl acetate. *m*-Methoxyhydrocinnamic acid and dimeric adducts not determined quantitatively.

radicals added to styrene (eq 31), and the adduct was subsequently oxidized (eq 32) to a mixture of 1,4-diphenylbutene-1 (6%) and 1,4-diphenylbutyl acetate (10%) (see Table IV). These dimeric adducts, together with ethylbenzene, were less important at higher Cu^{II} concentrations due to competition from oxidation (eq 30). No (<0.1%) α-phenethyl acetate was found, although it was stable under reaction conditions. All of these products accounted for more than 90% of the β-phenethyl radicals available from the peroxide, and other processes such as telomerization could not have been important.



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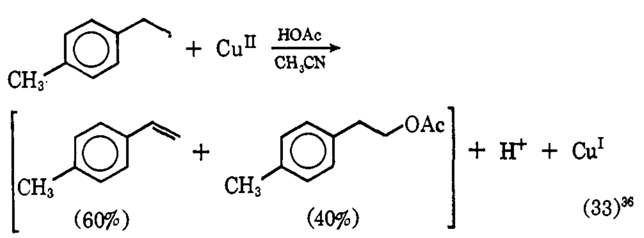
(32)

The **β-*p*-tolylethyl radicals** generated from *p*-methylhydrocinnamoyl peroxide under similar conditions also led to products of the type obtained from β-phenethyl radicals. Thus, *p*-methylstyrene (50%) and β-*p*-tolylethyl acetate (30%) and the dimeric adducts, 1-*p*-tolyl-4-phenylbutene-1 (0.6%) and 1-*p*-tolyl-4-phenylbutyl acetate (5%), accounted for greater than 85% of the β-tolylethyl radicals generated in the catalytic decomposition of the peroxide (Table V). The relative extent of oxidative elimination and substitution of β-*p*-tolylethyl radicals was highly sensitive to the Cu^{II} oxidant. Thus, pyridine- and α,α′-bipyridinecopper(II) complexes generated significantly more *p*-methylstyrene than the acetonitrile complex.[37]



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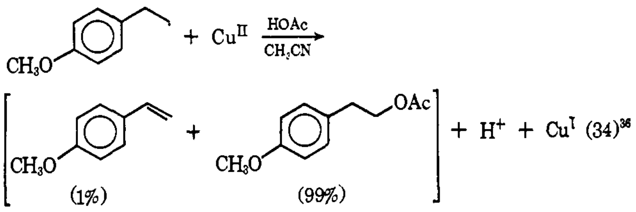
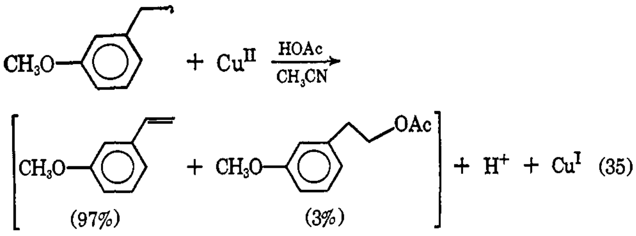
The oxidation of **β-anisylethyl radicals** from *p*-methoxyhydrocinnamoyl peroxide by Cu^{II} afforded excellent yields of β-anisylethyl acetate (92%). Only small amounts of *p*-methoxystyrene (1%) and N-β-anisylethylacetamide (6%) were found (Table VI). *p*-Methoxyethylbenzene, formed in small amounts by reaction with solvent, could be eliminated in runs at high Cu^{II} concentrations. No significant amounts of dimeric adducts were found. They could not have been present in yields greater than 2%, since the aforementioned products accounted for 98% of the β-anisylethyl radicals potentially available from the peroxide. No (<0.2%) α-anisylethyl acetate was found.



(34)[36]

The oxidation of the isomeric **β-*m*-methoxyphenethyl radicals** by Cu^{II} afforded a mixture of products which was much more akin to that obtained from the oxidation of β-phenethyl radicals rather than that from β-anisylethyl radicals. Thus, *m*-methoxystyrene (70%) was the major product (Table VI), together with the associated dimeric adducts which were not analyzed quantitatively. The ester, β-*m*-methoxyethyl acetate (3%), and *m*-methoxyethylbenzene (1%) were minor products.



(35)

The effect of adding pyridine or α,α′-bipyridine to complex the Cu^{II} oxidant was to increase the relative amount of the methylstyrene at the expense of the β-arylethyl acetate.[37,38] Furthermore, the yields of dimeric adducts (diarylbutenes and butyl acetates) were also diminished. The latter could be accounted for by the increased reactivity of pyridine and bipyridine-copper(II) complexes toward alkyl radicals relative to acetonitrilecopper(II) complexes extant in acetonitrile solutions.[37a] Enhanced rate of oxidation (eq 35) would

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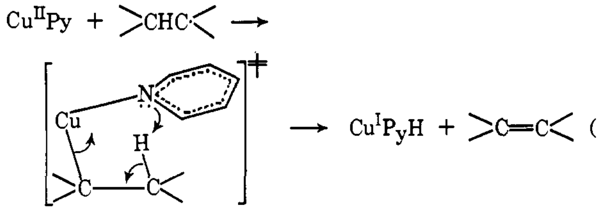
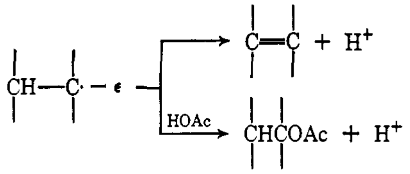
(37) (a) The addition of pyridine and α,α′-bipyridine to a copper catalyst generally leads to an enhanced rate of decomposition of the peroxide (eq 4) as well as increased efficiency in scavenging the alkyl radicals (eq 6). (b) These ligands also promote oxidative elimination (relative to substitution) with a number of alkyl radicals.[22] (c) These effects are associated with the formation of pyridine– and bipyridine–Cu^{II} complexes, and not with a general base effect. Bipyridine forms much more stable complexes with Cu^{II} than pyridine, but is also effective at much lower concentrations [L. Sillen and A. Martell, Special Publication No. 17, The Chemical Society, London, 1964, pp 440, 664].

(38) (a) The amount of *p*-methylstyrene relative to the acetate also appeared to *increase* with Cu^{I} concentration, but was rather insensitive to Cu^{II} (see Table V). This effect is similar to that observed with allylcarbinyl radical,[26a] and merits further attention. The trend is also present in β-phenethyl radicals, but it is not as pronounced due to the large amounts of styrene formed.

lead to lower steady-state concentrations of β-arylethyl radicals and curtail addition to the styrene. Enhancement of oxidative elimination by nitrogen ligands may be due to an intramolecular proton transfer (*cf.* eq 29).


(36)

Carbonium Ions from the Oxidation of β-Arylethyl Radicals. Conversion of an alkyl radical to an alkene or an acetate ester (in the presence of acetic acid) both require a 1-equiv oxidation, which can be represented by the standard (half-cell) reactions 37 and 38, respectively.


(37)

(38)

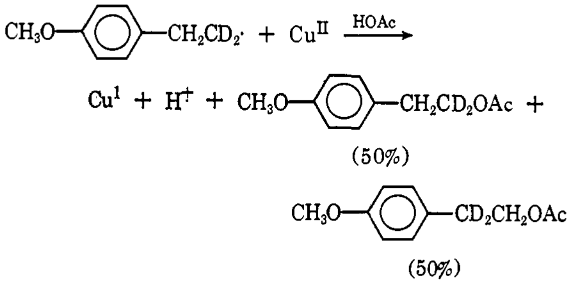
An examination of the products derived from the oxidation of a series of ring-substituted phenethyl radicals clearly shows that the dichotomy between formation of alkenes (styrenes) and esters (phenethyl acetates) is highly dependent on the substituent. Furthermore, the trend observed with cyclobutyl and allylcarbinyl (cyclopropylmethyl) radicals persists with β-arylethyl radicals. Esters prevail over alkenes as the ring hydrogens are replaced by substituents which stabilize a cationic species (*p*-methoxy > *p*-methyl > H > *m*-methoxy). Thus, predominance of styrene as a product of oxidation of phenethyl radicals is completely reversed in the oxidation of *p*-anisylethyl radicals. *p*-Methoxystyrene is the minor product and β-anisylethyl acetate, the major product. Methyl substitution (*para*) has an intermediate influence between *p*-methoxy and hydrogen, followed by *m*-methoxy as shown in Table VII. In this table, the relative rates of oxidation of alkyl radicals by Cu^{II} to alkene (elimination) and ester (substitution) were obtained from the product distribution, after correction for the dimeric adducts. The relative rates of formolysis of the alkyl *p*-toluenesulfonates and the Hammett substituent constants (σ) are also included for comparison.

Table VII. Effect of Polar Substituents on the Relative Rates of Oxidative Elimination and Substitution of Alkyl Radicals

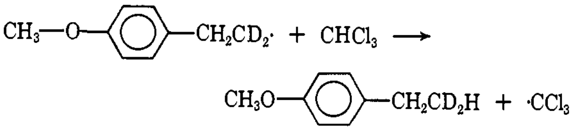
Alkyl radical	Oxidation products, mol %		k_s/k_e[a]	σ	k_{solv}[b]	Ref
	Elimn	Substn				
$XC_6H_9CH_2CH_2\cdot$						
X = *m*-Methoxy	97	3	0.03	+0.115	0.4	*c*
Hydrogen	95	5	0.06	0	1	*d*
p-Methyl	60	40	0.7	−0.170	9	*d*
p-Methoxy	1	99	99	−0.268	76	*d*
Cyclobutyl	1	99	99		~10^4	*e*
Allylcarbinyl	64	36	0.6		4	*f*
n-Butyl	100	0	<0.01		1	*f*

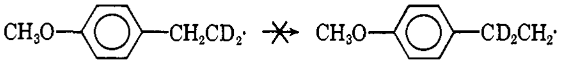
[a] k_s and k_e are second-order rate constants for oxidative substitution and elimination, respectively. [b] Relative first-order rate constants for formolysis of the alkyl tosylate at 50°. *n*-Butyl tosylate ≃ β-phenethyl tosylate, *cf.* footnotes *d* and *f*. [c] Extrapolated from data in footnote *d*. [d] H. Brown, R. Bernheimer, C. Kim, and S. Scheppele, *J. Am. Chem. Soc.*, **89**, 370 (1967). [e] Extrapolated from data of J. Roberts and V. Chambers, *ibid.*, 73, 5034 (1951). *k*(cyclobutyl)/*k*(allylcarbinyl) = 5 × 10^2 in glacial acetic acid. Further, assume a factor of 5 in going from glacial acetic acid to formic acid [S. Winstein, *et al.*, *ibid.*, **74**, 1120 (1952); **75**, 147 (1953)]. [f] K. Servis and J. Roberts, *ibid.*, **86**, 3773 (1964).

The high yield of acetate from the oxidation of β-anisylethyl radicals is associated with the delocalization of a cationic charge on the ring. Moreover, the effect of methoxy substitution is specific, and is not attributable to a generally enhanced electron density in the ring, since the *meta* isomer produces even *more* alkene than phenethyl radical itself. Oxidation of α,α-dideuterio-β-anisylethyl radicals by Cu^{II} proceeds with complete scrambling of the α- and β-carbon atoms, and an equimolar mixture of α,α- and β,β-dideuterio-β-anisylethyl acetate was formed.

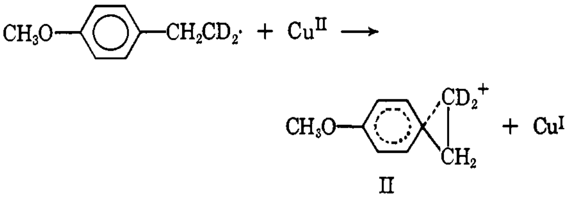

(39)

The copper-catalyzed decomposition of α,α-dideuterio-*p*-methoxyhydrocinnamoyl peroxide in the presence of chloroform afforded sufficient dideuterio-*p*-methoxyethylbenzene to examine. Only β,β-deuterio-*p*-methoxyethylbenzene was formed (eq 40). Thus, β-anisylethyl radicals, like β-phenethyl radicals examined by other workers,[39] do not rearrange under these conditions.


(40)

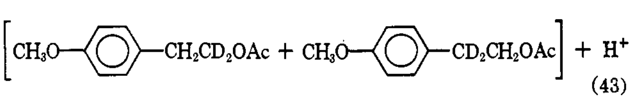

(41)

Rearrangement of the β-anisylethyl moiety is, therefore, associated with the oxidation process, and we conclude that it is the ethylene-*p*-anisonium ion II which is directly involved.[40] β-Anisylethyl radicals on oxidation by Cu^{II} are preferentially diverted to this cation II (eq 42), which undergoes subsequent solvation (eq 43)


(42)

II

II + HOAc ⟶


(43)

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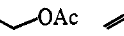
(39) (a) L. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959); (b) W. Smith and J. Anderson, *ibid.*, **82**, 656 (1960); (c) D. Curtin and J. Kauer, *J. Org. Chem.*, **25**, 880 (1960); (d) C. Walling, ref 25, p 409 ff.

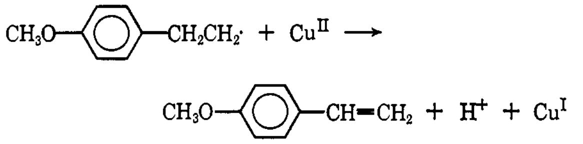
(40) (a) G. Olah, M. Comisarow, E. Namanworth, and B. Ramsey, *J. Am. Chem. Soc.*, **89**, 711 (1967); (b) J. Nordlander and W. Deadman, *ibid.*, 90, 1590 (1968).

Table VIII. Copper-Catalyzed Decomposition of Cyclopropanecarboxyl Peroxide in Acetonitrile–Acetic Acid[a]

			Products, mol %				
$[\mathrm{Cu^{II}}]$, *M*	$[\mathrm{Cu^{I}}]$, *M*	Ligand[b] (*M*)	$\mathrm{CO_2}$	$\mathrm{RCO_2H}$[c]		 OAc	 NHAc
0.20	0.027	None	64	133	43	3	0
0.20	0.024	Py (0.51)	89	117	13	49	6
0.20	0.15	None	76	ND	59	12	ND
0.20	0.16	Bipy (0.066)	72	ND	16	53	ND
0.20	0.16	None	73	131	53	9	ND
0.20	0.16	Bipy (0.077)	68	138	28	36	ND

[a] In solutions of 40 vol % acetonitrile–acetic acid containing 0.040 *M* cyclopropanecarboxyl peroxide at 0.5°. [b] Py = pyridine, Bipy = α,α'-bipyridine. [c] $\mathrm{RCO_2H}$ = cyclopropanecarboxylic acid.

in preference to oxidative elimination (eq 44). Even in the presence of ligands such as pyridine and α,α'-bipyridine, which usually favor the latter process,[37b] the major oxidative pathway for β-anisylethyl radicals is substitution (eq 42 and 43).

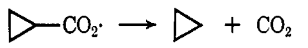


(44)

At this juncture we cannot distinguish between a symmetrically bridged phenonium or a rapidly equilibrating π-bridged cationic intermediate.[41] Whichever it may be, there is no doubt of extensive charge delocalization of the primary carbon center in the ring *via* an anisyl $\mathrm{Ar_1}$-3 participation, since rapid equilibration of the α- and β-carbon atoms occurs.[42] We observed no products resulting from hydride rearrangement (α-anisylethyl acetate or α-phenethyl acetate) in the oxidation of β-arylethyl radicals. The absence of such rearrangement is consistent with a delocalized β-arylethyl cation rather than an open primary cation.[43]

Oxidation of Cyclopropyl Radicals. Cyclopropanecarbonyl peroxide was unique among the diacyl peroxides reported in this study. This peroxide was very stable to carboxy inversion,[44] and underwent the copper-catalyzed decarboxylation much more sluggishly than the others. The chain length for catalyzed decomposition was low, since as much as 40 mol % $\mathrm{Cu^{I}}$ was *consumed* during decomposition. Less than molar amounts of carbon dioxide and more than molar amounts of cyclopropanecarboxylic acid were formed (Table VIII). Furthermore, the hydrogen transfer product, cyclopropane (eq 47), was formed in larger amounts than usually observed.[45] The oxidation product was allyl acetate, which was formed in reasonable yields only when the more effective pyridine- or bipyridinecopper(II) complexes were employed as oxidants. Small amounts of N-allylacetamide were also found in the latter cases. No cyclopropyl acetate or acetamide (<0.2%) was found. The presence of cyclopropene was not examined, nor did we attempt to determine whether it was able to withstand reaction conditions.

(45)



(46)

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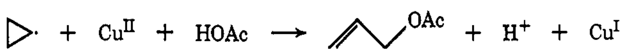
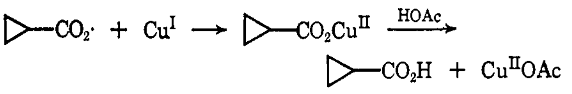


(48)

These results indicate that relative to decarboxylation, cyclopropanecarboxy radicals are more akin to aroyloxy and cinnamoyloxy radicals than they are to aliphatic acyloxy radicals in stability.[46] As a result, reduction by $\mathrm{Cu^{I}}$ (eq 49) becomes a more serious complication in the catalytic decomposition of this peroxide. The high yields of cyclopropanecarboxylic acid, low yields of carbon dioxide, and short chain lengths are all in accord with this formulation.[47] A similar retardation in the radical chain process by $\mathrm{Cu^{I}}$ consumption was



(49)

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(41) (a) S. Winstein, C. Lindegren, H. Marshall, and L. Ingraham, *J. Amer. Chem. Soc.*, **75**, 147 (1953); (b) H. Brown, R. Bernheimer, C. Kim, and S. Scheppele, *ibid.*, **89**, 370 (1967); (c) H. Brown, K. Morgan, and F. Chloupek, *ibid.*, **87**, 2137 (1965); (d) D. Cram, *ibid.*, **86**, 3767 (1964); (e) E. Jenny and S. Winstein, *Helv. Chim. Acta*, 41, 807 (1958).

(42) (a) C. Lee, G. Slater, and J. Spinks, *Can. J. Chem.*, **35**, 1417 (1957); **39**, 1510 (1961); (b) W. Saunders, S. Asperger, and D. Edison, *J. Am. Chem. Soc.*, 80, 2423 (1958); (c) E. Hedaya and S. Winstein, *ibid.*, **89**, 1661 (1967).

(43) (a) Lack of hydride rearrangement is similar to results of solvolyses.[41,42] Under certain conditions, ethylenephenonium ions do undergo such rearrangement which may be indicative of the open-chain form. We thank Dr. J. Nordlander for this interpretation.[40b] (b) *Cf.* also W. Saunders and R. Glaser, *J. Am. Chem. Soc.*, **82**, 3586 (1960). (c) We attribute the formation of N-alkylacetamides to reaction of the carbonium ion with acetonitrile (*e.g.*, eq 11). In this regard, it is interesting to note that *t*-amyl cation yields much more acetamide than the β-anisylethyl cation. If the latter were an open form, being primary, we would have expected it to be less selective than a *t*-amyl cation and lead to relatively more N-β-anisylethylacetamide. A maximum of 6% of the latter was found, in contrast to more than 40% of *t*-amylacetamide.

(44) *Cf.* H. Hart and D. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959).

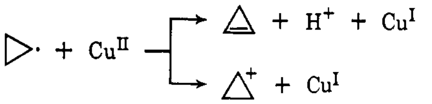
(45) (a) In the reverse reaction, the inertness of cyclopropane has been noted; (b) J. Kerr, *Chem. Rev.* **66**, 477 (1966); (c) J. McNesby and A. Gordon, *J. Am. Chem. Soc.*, **79**, 825 (1957).

(46) (a) G. Hammond and L. Soffer, *ibid.*, 72, 4711 (1950); (b) E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Inc., New York, N. Y., 1961; (c) P. Bartlett and R. Hiatt, *J. Am. Chem. Soc.*, 80, 1398 (1958); (d) L. Singer and N. Kong, *ibid.*, **88**, 5213 5219 (1966); (e) J. Kampmeir and R. Fantazier, *ibid.*, **88**, 1959 (1966); (f) O. Simamura, K. Tokumaru, and H. Yui, *Tetrahedron Letters*, 514 (1964). (g) Unpublished results, C. Jenkins. (h) In general, the ease of fragmentation of carboxy radicals is related to the hybridization of the α-carbon atom, and is slowest with α,β-unsaturated ($\mathrm{sp^2}$ hybridized) acids. Cyclopropanecarboxy radicals in this regard have more s character in the cyclopropylcarbonyl bond than other aliphatic analogs. (i) G. Grieg and J. Thynne, *Trans. Faraday Soc.*, **63**, 1369, 2197 (1967); (j) W. Braun, L. Rajenbach, and F. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

(47) In view of the relatively slow rate of oxidation of cyclopropyl radicals by $\mathrm{Cu^{II}}$, it is possible that some cyclopropane may have arisen by reduction of the radical by $\mathrm{Cu^{I}}$ (*cf.* eq 49).

observed in the catalytic decomposition of *t*-amyl hydroperoxide at 0°.[13,48]

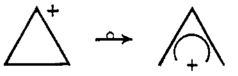
The oxidation of cyclopropyl radicals was not as facile as that of other radicals, including neopentyl radicals (*vide supra*). The low rates of oxidation qualitatively observed were probably due to an unfavorable oxidative elimination (by imposing ring strain in cyclopropene formation).[49] In order to effect electron transfer the



(50)

(51)

more potent pyridine- or bipyridinecopper(II) oxidants were required. We postulate that the cyclopropyl cation (eq 51) is the intermediate which leads to allyl acetate, since cyclopropyl radicals do not readily rearrange to allyl radicals.[44,45e,50] The absence of cyclopropyl acetate is similar to results of other studies such as solvolysis and deamination designed to probe cyclopropyl cations.[51] Rearrangement to allyl cations (eq 52) followed by solvation (eq 53) was the preferred route to products.[52,53]



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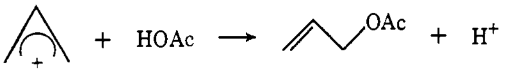

(53)

Summary

Carbonium Ions from Alkyl Radicals by Electron Transfer. The oxidation of alkyl radicals by Cu^{II} complexes in acetonitrile–acetic acid solutions affords alkenes and alkyl acetates. The relative amounts of each depend on the alkyl moiety and the Cu^{II} oxidant. Generally, we observe a correlation between increased substitution (relative to elimination) and rate of solvolysis of the corresponding alkyl *p*-toluenesulfonate and other reactions which evoke carbonium ion behavior (*cf.* Table VII). Furthermore, esters are favored products from oxidations carried out in polar solvents such as acetonitrile and sulfolane compared to nonpolar solvents such as benzene, ethyl acetate or tetrahydrofuran.[22,54] We attribute the substitution product (alkyl acetate and acetamide) directly to solvation of a carbonium ion (eq 55) formed as an intermediate in electron transfer (eq 54).[55] As a result, substitution products from electron-transfer oxidation of neopentyl,

$$R\cdot + Cu^{II} \longrightarrow R^+ + Cu^I \qquad (54)$$

$$R^+ + SH \longrightarrow RS + H^+ \qquad (55)$$

cyclobutyl, allylcarbinyl, β-arylethyl, cyclopropyl, and other alkyl radicals do follow established patterns of carbonium ion rearrangement commonly observed in other reactions.

Alkenes, on the other hand, are formed from alkyl radicals without rearrangement in a parallel oxidation. Thus, such primary radicals as *n*-butyl or isobutyl yield only butene-1 and isobutylene, respectively (no butene-2), on oxidation with Cu^{II}.[10] The exceptions are those radicals which either rearrange spontaneously (cyclopropylmethyl) or possess no β-hydrogens for direct removal (neopentyl). In the former radicals, alkenes arise from oxidation of the rearranged radical, and in the latter by loss of a proton from the cation generated by electron transfer from the radical.

The properties of Cu^{II} complexes as oxidants vary according to ligands such as acetate, acetonitrile, pyridine, or α,α′-bipyridine. It is reasonable to expect that a particular Cu^{II} oxidant would influence the relative amounts of elimination or substitution if it were involved in the product-determining step. Variations in yields of alkene and ester observed with various Cu^{II} oxidants (Tables III and V, particularly) indicate that either (or both) involve Cu^{II} directly in the step prior to its formation. By the same criterion, the mixture of 2-methylbutenes, *t*-amyl acetate, and acetamide, as well as the mixture of homoallylic acetates from the oxidation of neopentyl and cyclobutyl radicals, respectively, are formed from intermediates (*t*-amyl and homoallylic C_4H_7 cations) subsequent to electron transfer. In the following paper we will attempt to support, by kinetic arguments, the postulation that esters are formed *via* carbonium ion intermediates and alkenes by a competing oxidative process.[11]

Oxidative elimination and *oxidative substitution*, strictly speaking, only represent *categories* of reactions between alkyl radicals and metal oxidants by an electron transfer process.[11,22b] We do not intend to imply that alkenes can only arise by the former and esters only by the latter mechanism. Thus, carbonium ions in protic media usually prefer to undergo solvation, but elimination is not unknown. Furthermore, esters need not always arise *via* carbonium ions, since there is evidence for ligand transfer in the oxidation of allyl and allylcarbinyl radicals. The distinction between oxidative elimination and substitution is particularly obscured in such systems as *t*-alkyl, α-phenyl-

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(48) (a) J. Kochi, *Tetrahedron*, **18**, 483 (1962); (b) C. Walling and A. Zavitsas, *J. Am. Chem. Soc.*, **85**, 2084 (1963).

(49) (a) From values of the ionization potential of cyclopropane, the cyclopropyl cation is not particularly better off than other cycloalkyl cations. If the strain energy is included, the formation of cyclopropyl cations may be even more unfavored. (b) D. Turner, *Advan. Phys. Org. Chem.*, 4, 31 (1966). (c) R. Breslow, ref 25, p 256. (d) R. Pottie, A. Harrison, and F. Lossing, *J. Am. Chem. Soc.*, **83**, 3204 (1961).

(50) (a) E. Renk, P. Shafer, W. Graham, R. Mazur, and J. Roberts, *ibid.*, **83**, 1987 (1961). (b) Furthermore, no propylene has been observed in these reactions. (c) A. Stefani, G. Chuang, and J. Hathaway, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p S8.

(51) J. Roberts and V. Chambers, *J. Am. Chem. Soc.*, **73**, 3176, 5034 (1951); (b) P. Lipp, J. Buchkremer, and H. Seeles, *Ann.*, **499**, 1 (1932); (c) E. Corey and R. Atkinson, *J. Org. Chem.*, **29**, 3703 (1964); (d) C. DePuy, L. Schnack, J. Hausser, and W. Wiedemann, *J. Am. Chem. Soc.*, 87, 4006 (1965); (e) J. Hausser and N. Pinkowski, *ibid.*, **89**, 6981 (1967).

(52) (a) Recently, Schleyer[52b] and DePuy,[52c] *et al.*, have rationalized solvolysis rates of cyclopropyl derivatives in terms of a concerted rearrangement–ionization process. (b) P. von R. Schleyer, F. Van Dine, U. Schollkopf, and J. Paust, *J. Am. Chem. Soc.*, **88**, 2868 (1966). (c) C. DePuy, L. Schack, and J. Hausser, *ibid.*, **88**, 3343 (1966). (d) It does not follow that the same is applicable to nitrosative deamination of cyclopropyl amines or oxidation of cyclopropyl radicals by Cu^{II} oxidants. Driving force for formation of a cyclopropyl cation should be greater in the latter case, although we cannot at this point rule out oxidation accompanied by rearrangement (*i.e.*, eq 51 + 52). (e) *Cf.* W. Kutzelnigg, *Tetrahedron Letters*, 4965 (1967).

(53) (a) Rearrangement is not always observed. (b) W. Kirmse and H. Schutte, *J. Am. Chem. Soc.*, **89**, 1284 (1967). (c) *Cf.* also J. Landgrebe and L. Becker, *ibid.*, **89**, 2506 (1967). (d) H. Hart and R. Martin, *ibid.*, **82**, 6363 (1960).

(54) Unpublished studies.

(55) In these discussions, we have adopted an operational definition of carbonium ions, largely in terms of their behavior and similarity to other systems. We do not wish to delineate their nature further (in terms of solvation, ion-pair formation, complexation, etc.), experimental support notwithstanding.

alkyl, etc.[56] For these reasons, we rely on the examination of specific examples to classify systems.

Experimental Section

Materials. Hydrocarbons. Ethane, ethylene, propane, propylene, cyclopropane, *n*-butane, butene-1, and 1,3-butadiene were from Matheson Co. Isopentane, neopentane, 2-methylbutene-1, 2-methylbutene-2, 1,3-butadiene, pentane-1, and ethylbenzene were Phillips Petroleum Co. pure grade materials. Methylcyclopropane, cyclopentane, cyclopentene, and styrene were from Columbia Organic Chemicals. 1,4-Pentadiene was from Aldrich Chemical Co.

p-Methoxystyrene was from K and K Laboratories and *p*-methylstyrene was from Aldrich Chemical Co. Cyclobutane and cyclobutene were characterized in another study.[22b] 1,4-Diphenylbutene-1 was prepared from 1,4-diphenylbutanol-1 by treatment in glacial acetic acid with 10% sulfuric acid. It was the same as a partially hydrogenated sample of 1,4-diphenyl-1,3-butadiene (Strem Chemical Co.). Both afforded 1,4-diphenylbutane on complete hydrogenation. *p*-Ethylanisole was an Eastman Kodak White Label material.

Esters. Neopentyl and *t*-amyl acetates were prepared from neopentyl and *t*-amyl alcohols, respectively, by treatment with acetyl chloride and pyridine. The preparation of the homoallylic (allylcarbinyl, cyclopropylmethyl, and cyclobutyl) alcohols and their acetates was described previously.[22b] Cyclopentyl and penten-4-yl acetate were prepared from their alcohols with acetic anhydride. Phenethyl (α- and β-) acetates were from K and K Laboratories. β-Anisylethyl, β-*m*-methoxyphenylethyl, and β-*p*-tolylethyl acetates were prepared *via* *p*-methoxy-, *m*-methoxy-, and *p*-methylphenylacetic acids, respectively, by lithium aluminum hydride reduction followed by treatment with acetyl chloride. α-Tolylethyl acetate was prepared from *p*-tolualdehyde and methylmagnesium iodide followed by acetylation. α-Anisylethyl acetate was prepared from the copper-catalyzed acetoxylation of *p*-ethylanisole with *t*-butyl peracetate in 60 vol % acetic acid–acetonitrile solution.[6c]

Cyclopropyl acetate was prepared from cyclopropylmethyl ketone and *m*-chloroperbenzoic acid.[57] Allyl acetate was Eastman Kodak White Label material. 1,4-Diphenyl-1-butyl acetate was prepared by acetylation of 1,4-diphenylbutanol-1. The latter was prepared from 3-phenylpropylmagnesium bromide and benzaldehyde.

Acetamides. N-*t*-Amylacetamide was prepared from *t*-amyl alcohol and acetonitrile by the Ritter procedure.[18a] The N-alkyl acetamides were prepared by acetylation of the following amines: allylamine (Matheson Coleman and Bell), β-anisylethylamine and cyclopropylmethylamine (Aldrich Chemical Co.). Cyclobutylamine was kindly supplied by Dr. John Bayless who prepared it from cyclobutanecarboxylic acid by the Schmidt procedure.

Acids. Cyclopropanecarboxylic acid was from K and K Laboratories. Cyclobutanecarboxylic, 3- and 4-methoxyhydrocinnamic, 3- and 4-methoxyphenylacetic, and *p*-tolylacetic acids were from Columbia Organic Chemical Co. Allylacetic acid was from Peninsular ChemResearch, Inc. Cyclopropylacetic acid was prepared from vinylacetic acid and methylene iodide by the Simmon–Smith procedure.[22b] Hydrocinnamic acid was Eastman Kodak White Label grade.

t-Butylacetic acid was prepared by carboxylation of neopentylmagnesium chloride. 5-Hexenoic acid was prepared from cyclohexanone and hydrogen peroxide with a ferrous–cupric sulfate mixture.[5]

Peroxides. Most of the peroxides were prepared from the corresponding acid chloride and hydrogen peroxide by a typical procedure described below.

To a cooled (−10°) mixture of 158 ml (2 mol) of pyridine and 50 ml of ether, 62.5 ml (0.55 mol) of 30% hydrogen peroxide was added dropwise without allowing the temperature to exceed 10°. One mole of the acid chloride was then added dropwise, keeping the heterogeneous reaction mixture well agitated at −5 to −10°. The stirring was continued at 0° for 2 additional hr. After neutralizing with chilled, dilute (~10%) sulfuric acid, the reaction mixture was extracted twice with ether and pentane was washed with dilute sulfuric acid, aqueous sodium carbonate, and distilled water (below 0°). The extract was then dried over anhydrous sodium sulfate, and the solvent was evaporated by a rotary evaporator at ice-bath temperatures. The colorless peroxide (~90% yield) was determined by titration to be greater than 99% pure. The peroxidic doublet at 5.52 and 5.62 μ was observed in the infrared spectrum, uncontaminated by other carboxylic adulterants (~5.85 μ).

In each case, a small amount of the acid chloride was treated separately with methanol and the methyl ester analyzed carefully by gas chromatography for rearrangement or impurities. The following diacyl peroxides were prepared by this procedure: *t*-butylacetyl,[10a] cyclobutanecarbonyl,[44] allylacetyl,[8b] cyclopropanecarbonyl,[44] hydrocinnamoyl,[58] *p*-methoxy- and *p*-methylhydrocinnamoyl peroxides. Cyclopropylacetyl peroxide[27] was recrystallized several times from isopentane at −30° and melted at approximately 5°. This peroxide should be handled with extreme caution at room temperature, since it exploded on several occasions. None of the other peroxides showed this lability. Each of these peroxides was analyzed iodometrically by Swern and Silbert's procedure,[59] followed by gas chromatographic analysis of the liberated acid. The stoichiometry for a series of diacyl peroxides derived from low molecular weight acids corresponded to the following.

$$(RCO_2)_2 + 2I^- \longrightarrow I_2 + 2RCO_2^-$$

Hydrocinnamoyl peroxide was also prepared directly from the acid with hydrogen peroxide and dicyclohexylcarbodiimide.[60] This method was also employed with *m*-methoxyhydrocinnamic and *p*-methoxyhydrocinnamic-α,α-d_2 acids (*vide infra*), since the procedure could be readily adapted for small-scale preparations.

Cupric acetate monohydrate, $Cu(OAc)_2 \cdot H_2O$, was analytical reagent grade from Mallinckrodt Chemical Co. Pyridine, from Eastman Organic Chemicals, was redistilled from potassium hydroxide pellets. 2,2′-Bipyridine was Eastman Organic White Label. Glacial acetic acid (<0.1% water) was Du Pont reagent grade and used as such. Acetonitrile (Fisher reagent) was refluxed over phosphorus pentoxide and then redistilled through a 3-ft Oldershaw column.

Cuprous oxide was prepared by reduction of cupric tartrate with hydrazine by a slightly modified procedure.[61] Sodium potassium tartrate (75 g) and sodium hydroxide (75 g) were dissolved in 600 ml of warm water, and 50 g of cupric sulfate pentahydrate was added. A solution of 7 g of hydrazinium sulfate was added slowly with stirring and the reaction mixture heated to boiling. The mixture was allowed to cool and the brown precipitate separated and washed several times with water by decantation. It was then washed successively with ethanol and ether, and then air dried. The dried cuprous oxide (approximately 10 g) was free of copper metal or cupric ion and analyzed for Cu_2O by ceric titration.

General Procedure for Catalyzed Decomposition of Peroxides at 0°. Cupric acetate, cuprous oxide, and pyridine or α,α'-bipyridine (as needed) were weighed into a 125-ml erlenmeyer flask. The flask was cooled to 0° and the required amount of glacial acetic acid added by pipet to the flask over the weighed-out materials. The acetic acid froze immediately. A measured amount of acetonitrile was introduced by pipet and the flask closed with a tight-fitting, self-sealing rubber septum. Immediately, the flask was flushed for 10 min with a stream of argon or nitrogen introduced with a stainless steel hypodermic needle below the liquid surface. The mixture was allowed to warm to room temperature while being stirred magnetically until homogeneous. This method allowed for a greater than 99.5% accounting of the cuprous ion by ceric titration.

After recooling to 0° the mixture (40 vol % acetonitrile–acetic acid) remained homogeneous. To commence reaction, a degassed solution of the diacyl peroxide in acetonitrile–acetic acid was added by hypodermic syringe. No significant decomposition occurred at 0° for several hours in the absence of cuprous initiator. Reac-

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[56] (a) A similar duality exists in solvolytic substitution (SN1) and elimination (E1) processes.[7] (b) For example, see also M. Cocivera and S. Winstein, *J. Am. Chem. Soc.*, **85**, 1702 (1963). (c) J. Roberts and V. Chambers, *ibid.*, 73, 5034 (1951). (d) P. Skell and W. Hall, *ibid.*, **85**, 2851 (1963). (e) D. Cram and M. Sahyun, *ibid.*, **85**, 1257 (1963). (f) P. Bartlett, *et al.*, *ibid.*, **87**, 1314, 1308 (1965); (g) L. Blackwell, A. Fischer, and J. Vaughan, *J. Chem. Soc., B*, 1084 (1967).

[57] *Cf.* W. Emmons and G. Lucas, *J. Am. Chem. Soc.*, 77, 2287 (1955).

[58] E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Inc., New York, N. Y., 1961.

[59] L. Silbert and D. Swern, *Anal. Chem.*, 30, 385 (1958).

[60] F. Greeene and J. Kazan, *J. Org. Chem.*, 28, 2168 (1963).

[61] G. Schlessinger, "Inorganic Preparations," Chemical Publishing Co., New York, N. Y., 1962, p 11.

tions were ordinarily stirred for 2–3 hr to ensure completion, but were checked for completion (by analysis of carbon dioxide) before removal from the constant-temperature bath.

Analyses. The reaction flasks were equilibrated at room temperature, and a small sample of the gas was withdrawn with a hypodermic syringe. It was analyzed qualitatively for various volatile components by gas chromatography. On a 15-ft column of 30% Dowtherm on Firebrick at room temperature and 10 psi, the following relative retention times were observed (air = 1.0): ethane, 1.25; propane, 2.1; propene, 2.6; isobutane, 3.1; cyclopropane, 3.9; butane, 4.4; butene-1 and isobutylene (not separated), 5.25; *trans*-butene-2, 6.6; *cis*-butene-2, 7.8; cyclobutene, 9.7; cyclobutane, 11.0; methylenecyclopropane, 12.3. Analysis on silver nitrate–benzyl cyanide (20-ft column) on Chromosorb at room temperature and 10 psi revealed the following relative retention times: isobutane, 1.0; *n*-butane, 1.3; cyclopropane, 1.8; *trans*-butene-2, 2.4; isobutylene, 2.6 (*trans*-butene-2 and isobutylene not separated); butene-1, 3.4; and *cis*-butene-2, 4.2. Use of an 8-ft Porapak Q column at 60° with 15-psi pressure gave the following retention times (air = 1.0): carbon dioxide, 1.7; ethylene, 3.0; ethane, 3.9. A 2-ft, Porapak Q column at room temperature and 10 psi gave similar relative retention times, but more rapid analysis.

The routine procedure was to analyze aliquots of the reaction for carbon dioxide until evolution ceased, whereupon aliquots were also analyzed for hydrocarbon where appropriate. Aliquots of gases used as internal standards ("markers") were then added, the flasks thoroughly mixed, and the contents analyzed gas chromatographically. Known volumes of pure gases were mixed in various ratios of volumes. They were equilibrated over the solvent used and analyzed to obtain a calibration factor which related the gas chromatographic result to the molar ratios of the components. The calibration factor was not affected by the presence of Cu^I in solution, and it did not change over the range of molar ratios of gases studied. After analysis of gas-phase products was complete, the flasks were opened and aliquots were removed for analysis of liquid-phase products.

Analysis for free carboxylic acids was accomplished by extraction of the acid from an acidified, aqueous aliquot with ether. An isomeric acid was added as an internal standard, and the entire procedure calibrated as described previously to obtain distribution and calibration factors. The analysis was performed on a 3-ft column of 20% FFAP (Varian Aerograph) on acid-washed Chromosorb W at 142° and 10 psi. Relative retention times of the acids were: butyric, 1.00; 2-methylbutyric, 1.22; isovaleric, 1.22; *n*-valeric, 1.60; cyclopropanecarboxylic, 2.08; allylacetic, 2.20; cyclobutanecarboxylic, 2.70. Reaction mixtures were also analyzed directly (before work-up) as a check.

Esters and liquid hydrocarbons were also analyzed quantitatively by gas–liquid partition chromatography using the internal marker method. Analyses were performed on at least two different columns coated with substrates of different polarities, *e.g.*, diethylene glycol succinate or FFAP (Varian Aerograph) and SF-96 silicone (General Electric Co.). Where pertinent, the materials were trapped from the chromatograph and their infrared and/or nuclear magnetic resonance spectra compared with authentic samples (*vide supra*).

Analyses for carbon dioxide were accurate to ±6–7%, and were usually high. The lower molecular weight acids were readily analyzed to within 5%, but the higher molecular weight acids (hydrocinnamic, etc.) were more difficult to analyze. The other components (hydrocarbons, esters, etc). were determined quantitatively to within 3–4%.

Acetolysis of Bicyclo[1.1.0]butane. Bicyclobutane, which was generously supplied by Dr. John Bayless, was prepared by decomposition of N-nitroso-N-cyclopropylmethylacetamide in refluxing xylene.[32] It was contaminated with a small amount of methylenecyclopropane. The gas was led into a 40 vol % acetonitrile–acetic acid solution containing 0.083 *M* cuprous oxide and 0.20 *M* cupric acetate held at 0°. The latter was a reasonable representation of the reaction mixture employed for peroxide decomposition. No hydrocarbon gases were produced. The reaction mixture was then worked up in the usual manner.

Iodometric Titration.[59] Approximately 1 mmol of diacyl peroxide (0.2 g of valeryl peroxide) was dissolved in 10 ml of chloroform and 2 ml of a saturated sodium iodide solution was added, followed by addition of 15 ml of a 0.002% ferric chloride in glacial acetic acid solution. After 15 min, 50 ml of water was added and the solution titrated with approximately 0.1 *N* sodium thiosulfate. Flushing with nitrogen or carbon dioxide did not change the results. Substitution of acetic acid or acetic acid–acetonitrile solutions for the chloroform did not interfere with the analysis. Use of much larger concentrations of ferric chloride led to low results with some peroxides.

Ceric Titration. The material to be analyzed (usually contents of a reaction flask) was added to 50 ml of 0.31 *M* $FeCl_3$ and 3.7 *M* HCl. An additional 50 ml of water was used as a rinse when required. The solution was then titrated potentiometrically with 0.1 *N* ferric ammonium sulfate. The potentiometric titration gave identical results with the visual titration employing ferrous phenanthroline as indicator. However, the latter method suffered in the presence of Cu^{II} species due to obscuring of the end point.

***p*-Methoxyhydrocinnamic-α,α-d_2 acid** was prepared from *p*-methoxyhydrocinnamic acid (50 g, 0.28 mol) and 30 g of sodium methoxide in 150 ml of deuterium oxide by refluxing for several days with the exclusion of air. The method is essentially the same as that used by Saunders and Glaser[62] to prepare *p*-methoxyphenylacetic-α,α-d_2 acid. The alkaline solution was poured into 10% sulfuric acid and the acid washed several times with water and dried in a vacuum desiccator. It was re-treated with 30 g of sodium methoxide and 150 ml of D_2O and refluxed for several more days. Reisolation of the dideuterio-*p*-methoxyhydrocinnamic acid afforded colorless crystalline material. The nuclear magnetic resonance spectrum in pyridine solution was obtained on a Varian A-60A spectrometer. *p*-Methoxyhydrocinnamic acid showed typical proton resonances for the following (chemical shifts in δ, ppm): methoxy singlet (3.7) and methylene multiplets (2.9). The spin–spin multiplet pattern of the A_2B_2 system for the pair of methylene hydrogen overlapped one another due to inadequate chemical shift differences. However, the ratio of the methoxy relative to all of the methylene protons had the expected relative intensity, 3.0 to 4.0. The same protons in the prepared sample of *p*-methoxyhydro cinnamic-α,α-d_2 acid were in the ratio 3.0:2.1, respectively. The *p*-methoxyhydrocinnamic-α,α-d_2 acid was also analyzed by combustion followed by the falling drop method for deuterium.[63] *Anal.* Calcd for $C_{10}H_{10}D_2O_3$: C, 66.7; H, 5.61; D, 1.11; O, 26.62. Found: C, 66.5; H, 5.55; D, 1.10; 1.95, 1.98 atoms of D/molecule.

p-Methoxyhydrocinnamic-α,α-d_2 acid was also reduced with lithium aluminum hydride in ether to γ-anisylpropyl-β,β-d_2 alcohol. The proton resonances characteristic of the β-hydrogens at τ 1.8 were absent. The integration of the nmr spectrum otherwise showed that the methoxy (3.8), benzyl (2.8), α (3.7), and aromatic (7.1) protons were in the expected ratio 3:2:2:4, respectively. The chemical shifts of the aliphatic hydrogens corresponded to those of γ-phenylpropyl alcohol prepared by lithium aluminum hydride reduction of hydrocinnamic acid.

β-Anisylethyl acetate in carbon tetrachloride exhibited a well-resolved, first-order spectrum. Integration of the methoxy (3.7), benzyl (2.8), α (4.2), acetoxy (1.9), and aromatic (6.9) protons showed relative intensities in the expected ratios of 3.1:2.0:2.0:3.0:4.1. The aliphatic hydogens had similar chemical shifts with those in authentic β-phenethyl acetate.

The dideuterio-β-anisylethyl acetate obtained from the copper-catalyzed decomposition of *p*-methoxyhydrocinnamoyl-α,α-d_2 peroxide was isolated from the reaction mixture by trapping of the effluent from the gas chromatograph. The chemical shifts of this material were the same as those of an undeuterated sample except that the relative intensities of the various proton resonances were: methoxy:benzyl:α:acetoxy:aromatic in the ratio 3.1:1.0:1.0:3.0:4.0. Furthermore, the pair of methylene triplets was now a pair of unresolved multiplets as expected from deuterium splitting. We feel that the dideuterio-β-anisylethyl acetate is an equimolar mixture of the α,α-d_2 and β,β-d_2 isomers rather than the α,β-d_2 isomer, since we expect a pair of doublets in the latter case. However, deuterium splitting may obscure the doublet.

The nmr spectrum of the aliphatic hydrogens in *p*-ethylanisole is well resolved and first order. Integration of the methoxy (3.7), methylene (2.6), and methyl (1.2) proton resonances shows relative intensities in the ratio 3:2:3, respectively. A sample of dideuterio-*p*-ethylanisole was trapped by gas chromatography from a mixture obtained by the decomposition of *p*-methoxyhydrocinnamoyl-α,α-d_2 peroxide with a Cu^I–Cu^{II} catalyst in chloroform at 25°. Both the methylene and methyl resonances were separately unresolved multiplets, but integration indicated the relative intensities for the methoxy, aromatic, methylene, and methyl protons to be 3.1:3.9:1.9:1.0, respectively.

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(62) (a) W. Saunders and R. Glaser, *J. Am. Chem. Soc.*, **82**, 3586 (1960). (b) We wish to thank Dr. David Lemal for suggesting this procedure. (c) J. Atkinson, J. Csakvary, G. Herbert, and R. Stuart, *ibid.*, **90**, 498 (1968).

(63) Analysis performed by Mr. Josef Németh, University of Illinois.

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Carbonium Ions with Multiple Neighboring Groups. I. Synthesis[1a]

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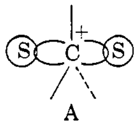
Abstract: Carbonium ions with more than one neighboring group available for interaction with the cation center are an unexplored class of considerable potential interest. Among the phenomena expected are fluctuating coordinated structures, intramolecular solvation, and possibly pentacoordination of carbon. This paper describes the synthesis of 26 substituted triphenylcarbinols, and the related carbonium ions, as well as five benzophenone derivatives. The subsequent paper details studies on the interaction between the neighboring groups and carbonium ion (and ketone) centers.

The chemistry of neighboring group interactions has played a dominant role in the study of carbonium ions.[2] In a sense the coordination of an oxygen or sulfur or halogen atom from a neighboring group with a carbon cation center is a form of internal solvation of such a center. In contrast to typical solvent molecules, however, the atom in the neighboring group is readily identified chemically and spectroscopically because of its additional attachment to the carbonium ion. Furthermore, in cases where internal solvation is sterically possible it generally has great entropy advantages over the analogous interaction with a similar solvent molecule from the external environment. Remarkably, no study has apparently yet been undertaken of carbonium ions with more than one neighboring group available for participation. We felt that such species might have a number of interesting properties.

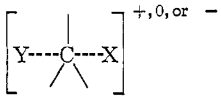
1. Fluctuating Structures. If one after the other of the neighboring nucleophilic groups becomes coordinated with the carbon cation, one should have species which are perpetually undergoing nucleophilic substitution reactions. These would be at the least chemical curiosities, and they might also be useful in adding to our general understanding of such reactions.

2. Doubly Solvated Ions. According to the Doering–Zeiss hypothesis[3] two solvent molecules may interact with a carbonium ion by coordination on the two faces (A). Despite some efforts to detect this phenomenon by kinetic means[4] there is not yet good evidence for the type of pentacoordinate carbon represented in A. Extensive work has been done on two other types of pentacoordinate carbon: the carbons in molecules with delocalized π electrons have three σ bonds and two partial π bonds, while carbons in nonclassical carbonium ions, and in hexamethyldialuminum,[5] have pentacoordinate carbons in which a single lobe of a hybrid orbital is involved in three-center bonding. Pentacoordination of the trigonal-bipyramid type, as in A, is, of course, well known for silicon and other elements below the first row, and is presumably found in CH_5^+, detectable in the mass spectrometer.[6] If a structure such as A represents an important mode of solvation of carbonium ions, this might be detected in at least some molecules with two neighboring groups able to take up positions on the two carbon faces.



A

3. The S$_N$2 Intermediate. Pentacoordinate species related to A represent real reaction intermediates in substitution reactions at elements below the first row, such as silicon.[7] For the S$_N$2 reaction at carbon, considerable interest has centered around the question of whether the trigonal bipyramid (B) is an intermediate (at the bottom of some kind of energy well) or simply an unstable atomic configuration along the reaction path. There is no solid evidence yet available



B

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[1] (a) Partial support by the Hoffman-La Roche Research Foundation is gratefully acknowledged; (b) NSF Postdoctoral Fellow, 1964–1965; (c) NIH Predoctoral Fellow, 1966–1967.

[2] For a partial review, *cf.* A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[3] W. von E. Doering and H. H. Zeiss, *J. Am. Chem. Soc.*, **75**, 4733 (1953).

[4] C. G. Swain and E. E. Pegues, *ibid.*, **80**, 812 (1958), and earlier papers.

[5] For review, *cf.* K. Ziegler in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 5.

[6] Reference to studies on this long-known species can be found in F. H. Field and M. S. Munson, *J. Am. Chem. Soc.*, **87**, 3289 (1965).

[7] C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, pp 103–113; *cf.* J. Y. Carey and R. West, *J. Am. Chem. Soc.*, **85**, 4035 (1963), for an isolated pentacoordinate siliconium ion.