Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.43; H, 9.57. Found: C, 71.50; H, 9.55.

Reaction of I and *dl*-Styrene Oxide.—A mixture of 12.0 g. (0.0345 mole) of I and 24.0 g. (0.20 mole) of styrene oxide was heated at 170° (bath) for 24 hours. The cooled reaction mixture was triturated with hexane. The solid residue was washed with hexane and dried *in vacuo* to give 8.5 g. (89%) of triphenylphosphine oxide, m.p. 155–157° (lit.[12] 153°). The hexane solution was concentrated and then fractionated to give 20.3 g. of recovered styrene oxide, b.p. 74° (12 mm.), and 2.0 g. (30%) of ethyl *trans*-2-phenylcyclopropanecarboxylate, b.p. 102° (0.15 mm.), (lit.[13] 105–110°, 2 mm.).

In another experiment, 12.0 g. (0.03 mole) of I and 12.0 g. (0.10 mole) of styrene oxide were heated at 190–200° (bath) for 6 hours. Following the procedure above, 90% of triphenylphosphine oxide, m.p. 156–158°, was obtained. The infrared spectrum was identical to that of an authentic sample.

Distillation afforded, after removal of hexane and styrene oxide, 1.2 g. (21%) of ethyl *trans*-2-phenylcyclopropanecarboxylate, b.p. 103–105° (0.5 mm.).

The ester from another run was converted to the acid by heating 1.90 g. (0.01 mole) with 15 ml. of 6 *N* potassium hydroxide and 6 ml. of methanol for 6 hours. Acidification gave the acid which was recrystallized twice from aqueous ethanol containing a little hydrochloric acid; m.p. 90–91° (lit.[13] 92–93°).

The amide was prepared by boiling 1.0 g. of the acid in 5 ml. of thionyl chloride for 20 minutes. The mixture was poured into 15 ml. of ice-cold concentrated ammonium hydroxide. The amide was recrystallized from aqueous methanol; m.p. 190.5–192° (lit.[13] 190–191°).

Reaction of I and *l*-Styrene Oxide.—A mixture of 10.0 g. (0.029 mole) of I and 10.0 g. (0.084 mole) of *l*-styrene oxide,[14] $[\alpha]^{20}D$ −12.45°, *c* 20 in chloroform, was heated at 200° (bath) for 7 hours. The cooled mixture was dissolved in 30 ml. of methanol and 15 ml. of 6 *N* potassium hydroxide was added. The mixture was boiled for 12 hours. Extraction with chloroform followed by acidification gave 10 g. of an amber semi-solid which was taken up in ether and esterified by adding a solution of diazomethane in ether. The resulting ester was molecularly distilled, b.p. 90° (block) (25 mm.), to give 1.5 g. (28%) of methyl *trans*-2-phenylcyclopropanecarboxylate, $[\alpha]^{20}D$ −31.3°, *c* 13 in chloroform.

The ester was saponified and the acid was converted to the amide, m.p. 192–193° (lit.[13] 190–191° for the *dl*-amide), $[\alpha]^{23}D$ +8.15°, *c* 2 in 95% ethanol.

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[12] G. M. Kosolapoff, "Organophosphorus Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1950, p. 114.

[13] A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).

[14] Prepared according to the procedure of E. L. Eliel and D. W. Delmonte, *J. Org. Chem.*, **21**, 596 (1956).

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

Oxidation of Free Radicals from Unsaturated Compounds by Cupric Salts

BY JAY K. KOCHI[1] AND FREDERICK F. RUST

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Cupric salts react with alkyl radicals by two oxidation–reduction processes which have been described as electron transfer and ligand transfer. We have studied the oxidation of substituted alkyl radicals by examining the competitive rates of oxidation of 5-(methoxycarbonyl)-pentyl and the radicals resulting from its addition to a variety of monomers. By regulating the concentration of monomer and cupric salt, it is possible to oxidize selectively allylic radicals in the presence of the primary hexanoate ester radicals. 5-(Methoxycarbonyl)-pentyl reacts with butadiene in methanol under these conditions to produce methyl methoxydecenoates. Isoprene, chloroprene, styrene and acrylonitrile are also effective radical acceptors. The mechanism of the oxidation of substituted alkyl radicals by cupric salts is discussed.

Introduction

The oxidation of relatively simple free alkyl radicals by cupric salts was previously described[2] as involving either a ligand transfer process or an electron transfer process depending on the particular cupric salt employed. Part of the problem encountered in describing these reactions in a more quantitative manner is the difficulty in obtaining meaningful rate data. Competitive experiments based on product isolation at present forms the basis of obtaining some semi-quantitative kinetic information. In this paper we wish to present studies on the competitive oxidation of substituted carbon free radicals by examining the products from the oxidation by cupric salts of 5-(methoxycarbonyl)-pentyl (I) in the presence of unsaturated compounds. The competitive reactions are (a) the oxidation of the 5-(methoxycarbonyl)-pentyl, (b) the addition to an unsaturated compound and (c) the oxidation of the resulting adduct radical. 5-(Methoxycarbonyl)-pentyl was chosen because of the relative ease of isolation of its oxidation products.

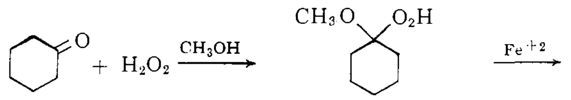
$$\underset{\text{I}}{CH_3O_2C(CH_2)_5\cdot} + Cu^{II}X_n \xrightarrow{a} \text{oxidation products} + Cu^{I}X_m$$

$$CH_3O_2C(CH_2)_5\cdot + CH_2{=}CHX \xrightarrow{b} CH_3O_2C(CH_2)_6\dot{C}HX$$

$$CH_3O_2C(CH_2)_6\dot{C}HX + Cu^{II}X_n \xrightarrow{c} \text{oxidation products} + Cu^{I}X_m$$

Results

Cyclohexanone and hydrogen peroxide react to form a complex mixture of adducts.[3] In methanol this mixture reacts with ferrous sulfate to produce the radical 5-(methoxycarbonyl)-pentyl.



$$CH_3O_2C(CH_2)_5\cdot + Fe(OH)^{+2}$$

This radical will react with a variety of unsaturates.[4] In the case of butadiene, for example, 5-(methoxycarbonyl)-pentyl adds to produce an

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[1] Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio.

[2] H. E. De La Mare, J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **83**, 2013 (1961); to be published; J. K. Kochi, *ibid.*, **84**, 774, 1572, 1192, 2121, 2785 (1962); *Tetrahedron*, **18**, 483 (1962).

[3] M. S. Kharasch and G. Sosnovsky, *J. Org. Chem.*, **23**, 1322 (1958).

[4] M. S. Kharasch and W. Nudenberg, *ibid.*, **19**, 1921 (1954). D. D. Coffman and H. N. Cripps, U. S. Patent 2,811,551 (to du Pont), Oct. 29, 1957.

allylic radical, II, which dimerizes to form a mixture of eicosadienedioic acid esters, III, in 65–75% yield.[4] Our earlier studies[2] showed that, in the

$$\underset{\text{I}}{CH_3O_2C(CH_2)_5\cdot} + C_4H_6 \longrightarrow \underset{\text{II}}{CH_3O_2C(CH\ )_6CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2}$$

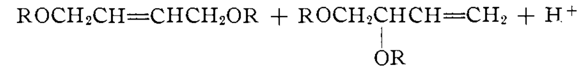
$$2CH_3O_2C(CH_2)_6CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH \longrightarrow \underset{\text{III}}{\text{3 isomeric dimethyl eicosadienedioates}}$$

presence of Cu^{+2}, saturated primary radicals are

$$RCH_2CH_2\cdot + Cu^{+2} \longrightarrow RCH{=}CH_2 + Cu^{+} + H^{+} \quad (1)$$

oxidized to terminal olefins. Likewise in the presence of Cu^{+2}, allylic radicals derived from *t*-butoxy and butadiene ($t\text{-}C_4H_9OCH_2CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2$) were oxidized to allylic carbonium ion intermediates (see ref. 13), which in the presence of a protic solvent led to the alkoxylated product.[2,13]

$$ROCH_2CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2 + Cu^{+2} \longrightarrow [ROCH_2CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]^{+} + Cu^{+} \quad (2)$$

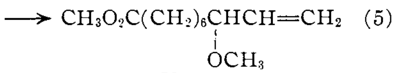


$$[ROCH_2CHCHCH_2]^{+} + ROH \longrightarrow ROCH_2CH{=}CHCH_2OR + ROCH_2\underset{\displaystyle OR}{\underset{|}{C}}HCH{=}CH_2 + H^{+}$$

Butadiene.—We have now intercepted with cupric ion the allylic radical II produced from the addition of 5-(methoxycarbonyl)-pentyl to butadiene—and other unsaturates—and related the findings to a number of reaction variables in order to understand better the mechanisms involved.

$$[CH_3O_2C(CH_2)_6CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]\cdot + Cu^{-2} \longrightarrow [CH_3O_2C(CH_2)_6CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]^{+} + Cu^{+} \quad (3)$$

$$[CH_3O_2C(CH_2)_6CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]^{+} + CH_3OH \longrightarrow \underset{\text{IV}}{CH_3O_2C(CH_2)_6CH{=}CHCH_2OCH_3} \quad (4)$$



$$\longrightarrow \underset{\text{V}}{CH_3O_2C(CH_2)_6\underset{\displaystyle OCH_3}{\underset{|}{C}}HCH{=}CH_2} \quad (5)$$

In addition, there are obtained products from the reaction of Cu^{+2} with the 5-(methoxycarbonyl)-pentyl.

$$CH_3O_2C(CH_2)_5\cdot + Cu^{+2} \longrightarrow \underset{\text{VI}}{CH_3O_2C(CH_2)_3CH{=}CH_2} \quad (6)$$

$$\longrightarrow CH_3O_2C(CH_2)_4CH_2^{+} \xrightarrow{CH_3OH} \underset{\text{VII}}{CH_3O_2C(CH_2)_5OCH_3} \quad (7)$$

The distribution of products III, IV, V, VI and VII is highly dependent on the cupric ion concentration and to a lesser degree on the butadiene concentration. If the hexanoic ester radical I is generated in the absence of butadiene, termination occurs at this stage. Thus, it reacts with cupric sulfate in methanol solution to produce methyl 5-hexenoate and methyl ω-methoxyhexanoate in 47% and 27% yields, respectively. With cupric chloride under the same conditions methyl ω-chlorohexanoate is formed in 69% yield and neither methyl 5-hexenoate nor methyl ω-methoxyhexanoate is formed. In those reactions containing butadiene, extreme conditions of cupric ion and butadiene concentrations can be considered. In the absence of cupric ion, the predominant products are the C_{20}-dibasic acid esters III. At low cupric ion and high butadiene concentrations the product is still predominantly the C_{20}-diester. At high cupric ion and low butadiene concentrations the important products are the C_6-esters VI and VII. The yields of C_{10}-esters IV and V can be optimized at critical cupric ion concentrations. The results are summarized in Table I. In these reactions a mixture of cyclohexanone and 30% hydrogen peroxide is stirred for ten minutes and then allowed to react with a chilled methanolic solution of sulfuric acid. The cupric salt (sulfate) and butadiene are added quickly with subsequent dropwise addition of ferrous sulfate.

TABLE I

YIELD OF C_{10}-ESTERS AND C_{20}-DIESTERS AS A FUNCTION OF Cu^{+2} AND BUTADIENE CONCENTRATION[a]

$CuSO_4$, g.	Butadiene, moles	C_{10}-Ester,[b] %	C_{20}-Diester,[c] %
None	1.0	10	65
0.5	2.0	23	43
1.5	0.4	51	11
1.5	1.0	61	6
1.5	2.0	41	20
1.5	3.0	18	29
3.0	1.0	47	15
6.0	0.4	32	5
6.0	1.0	37	16
12.5	1.0	31	14

[a] In reactions containing 0.20 mole of cyclohexanone, 11.5 g. (0.10 mole) of (30%) hydrogen peroxide, 20 ml. of concd. sulfuric acid and 41.7 g. of ferrous sulfate in 750 ml. of methanol. [b] Mixture of allylic isomers IV,V. [c] Mixture of C_{20}-diesters III.

The best yield of C_{10}-esters obtained in our runs was 61% (based on hydrogen peroxide charged). The results in Table I show that at optimum cupric ion concentration it is possible to intercept the C_{10}-ester radical II quite selectively. The formations of the C_{10}-adducts IV and V depend on the relative concentrations of the C_6-radical I, the C_{10}-allylic radical II and cupric ion.

Saturated alkyl radicals such as I, in general, show enhanced reactivity relative to allylic radicals such as II in free radical reactions involving hydrogen transfer, addition, disproportionation, etc. It could, then, be expected that the steady state[5] concentration of radical I could be lower than radical II, especially in systems containing an excess of butadiene. By keeping the cupric ion concentration sufficiently low to minimize reactions such as 6 and 7 with radical I, yet high enough to react with allylic radicals, it is possible to effect oxidation primarily at the allylic radical II stage. The selectivity arises, we believe, not primarily due to the difference in the reactivity of the two types of radicals toward cupric ion but in a less direct manner by the difference in their "steady state" concentrations. If one assumes that the electron transfer reactions represented by 6 and 7 and 3 are equally fast, then it is possible to account for the selectivity that has been observed in the cupric ion oxidations on the basis of the relative rates of the reactions 6, 7 and 3 being dependent mainly on the concentrations of I and II, respectively.

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[5] The term "steady state" is employed loosely here.

Earlier studies[6] on the reactions of free radicals with cupric ion indicated that in the presence of chloride ion an additional oxidation–reduction reaction involving ligand transfer occurred; *e.g.*

$$\mathrm{RCH_2CH_2\cdot + CuCl_2 \longrightarrow RCH_2CH_2Cl + CuCl} \quad (8)$$

In order to prepare the chloro analogs of the C_{10}-esters IV and V such as VIII, 5-(methoxycarbonyl)-pentyl was added to butadiene in the presence of ferrous and cupric chloride salts. The product is not the expected allylic chloride VIII but consists

$$\mathrm{[CH_3O_2C{-}(CH_2)_6CH{\cdots}CH{\cdots}CH_2]\cdot + CuCl_2 \longrightarrow \underset{\text{VIII}}{CH_3O_2C(CH_2)_6CH{=}CH{-}CH_2Cl}} \quad (9)$$

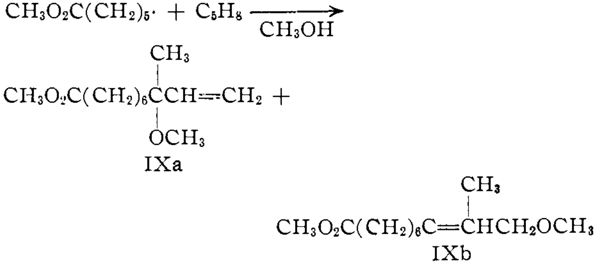
of the same isomeric mixture of allylic ethers IV and V found in the cupric sulfate oxidations; they are also formed in the same yields. When the reaction is repeated using concentrated hydrochloric acid instead of sulfuric acid in order to maximize the chloride ion concentration, the yields of C_{10}-esters IV and V and C_{20}-diesters III are greatly diminished. The products are methyl ω-chlorohexanoate (55%), the isomeric C_{10}-allylic chlorides VIII (~5%), the C_{10}-esters IV and V (5%) and C_{20}-diesters IV (3%). Under the mild reaction conditions employed it is not expected that the allylic chlorides are intermediates which solvolyze to the allylic ethers found.

Thus the formation of allylic chlorides from allyl radicals and cupric chloride occurs only under conditions in which chloride ions are in large excess and then it is the minor product. At such high chloride ion concentrations the C_6-ester radicals are preferentially trapped as methyl ω-chlorohexanoate. It appears that under conditions of high trapping efficiency with cupric chloride the C_{10}-allylic radical II is not formed. Moreover, under conditions when the C_{10}-allylic radical is formed at lower chloride concentrations it reacts with the cupric species to form carbonium ion intermediates (eq. 2) rather than chloro compounds directly (eq. 8).

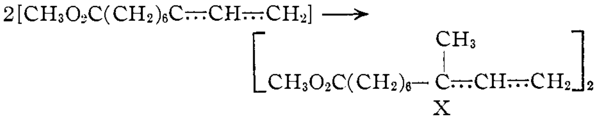
The reactivity of alkyl and allyl radicals toward cupric ion (reactions 6, 7 and 2) and cupric chloride (reactions 8 and 9) can be compared. Under conditions of the same copper concentrations it is shown that primary alkyl radicals (as exemplified by the ω-hexanoate radical) react more rapidly with cupric chloride than cupric ion since, in the presence of butadiene, cupric chloride traps radicals at the C_6-radical stage (I) whereas cupric sulfate reacts with radicals at the C_{10}-adduct (II) radical stage. Similarly, the allylic radical II is rather indiscriminate in its reaction with either cupric chloride or cupric ion, yielding in both cases the same product.

Some experiments were carried out in solvents other than methanol. The cyclohexanone–hydrogen peroxide adduct reacts with ferrous and cupric chloride in *acetic acid* solutions to produce ω-chlorohexanoic acid and ω-acetoxyhexanoic acid in 53% and 4% yields, respectively, based on input peroxide. With the addition of butadiene no allylic product could be isolated. Due to limited solubility in acetic acid the corresponding metal sulfates could not be used. Approximately 60–70% of the cyclohexanone is recovered. The reaction in *t*-butyl alcohol is similarly not encouraging. Approximately 30–40% yields of carboxylic acids are produced. These acids decompose readily on attempted distillation and presumably contain unreacted peroxides. They were not characterized further.

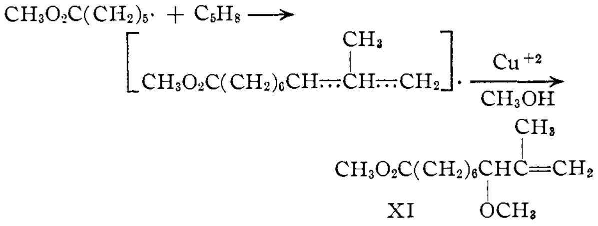
Isoprene.—5-(Methoxycarbonyl)-pentyl (I) adds to isoprene in a manner similar to butadiene. The mode of addition appears to be predominantly 1,2 to produce the allylic ether IXa (33%) and minor amounts of the isomer IXb (7%). In addition, the dimer ester X corresponding to the dimer III obtained with butadiene is produced in 20% yield. The C_6-esters VI and VII can also be isolated in 8% and 5% yields, respectively. The yields given are based on hydrogen peroxide charged. If calculated on the basis of cyclohexanone consumed the yields given above should be approximately doubled. These do not represent optimum yields of the C_{11}-esters IXa and IXb since no additional effort was made to vary the cupric ion and isoprene concentrations. There is no evidence that the 5-(methoxycarbonyl)-pentyl adds to the 4-position of isoprene. The terminally unsaturated esters IXa and IXb were examined by nuclear magnetic resonance spectroscopy and found to contain no propenyl groups expected from such 4,1- or 4,3-addition as in



$$\mathrm{CH_3O_2C(CH_2)_5\cdot + C_5H_8 \xrightarrow[CH_3OH]{Cu^{+2}} \underset{\text{IXa}}{CH_3O_2C(CH_2)_6\overset{\displaystyle CH_3}{\underset{\displaystyle OCH_3}{C}}CH{=}CH_2} + \underset{\text{IXb}}{CH_3O_2C(CH_2)_6\overset{\displaystyle CH_3}{C}{=}CHCH_2OCH_3}}$$



$$\mathrm{2[CH_3O_2C(CH_2)_6C{\cdots}CH{\cdots}CH_2] \longrightarrow \underset{\text{X}}{\left[CH_3O_2C(CH_2)_6{-}\overset{\displaystyle CH_3}{C}{\cdots}CH{\cdots}CH_2\right]_2}}$$



$$\mathrm{CH_3O_2C(CH_2)_5\cdot + C_5H_8 \longrightarrow \left[CH_3O_2C(CH_2)_6CH{\cdots}\overset{\displaystyle CH_3}{CH}{\cdots}CH_2\right]\cdot \xrightarrow[CH_3OH]{Cu^{+2}} \underset{\text{XI}}{CH_3O_2C(CH_2)_6CH\overset{\displaystyle CH_3}{\underset{\displaystyle OCH_3}{C}}{=}CH_2}}$$

These results are in accord with previous studies of free radical addition to isoprene.

Chloroprene.—The addition of 5-(methoxycarbonyl)-pentyl to chloroprene represents a potentially interesting route to produce olefinic ethers with chlorine functional groups. With the combination of cupric and ferrous sulfate the addition of the $C_6\cdot$ radical and methanol occurs by 1,2- and 1,4-addition. The chloroallylic ether XIV

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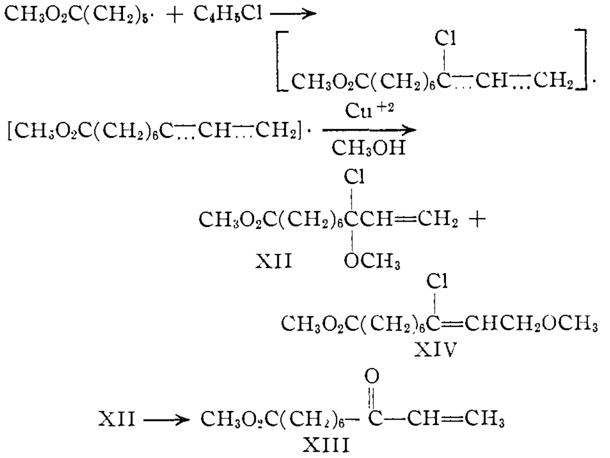
(6) J. K. Kochi, *J. Am. Chem. Soc.*, **78**, 4815 (1956); **79**, 2942 (1957); C. Bamford, A. Jenkins and R. Johnston, *Proc. Roy. Soc.* (*London*), **A239**, 214 (1957); J. Kumamoto, H. E. De La Mare and F. F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960).



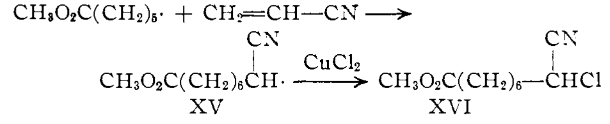
$$CH_3O_2C(CH_2)_5\cdot + C_4H_5Cl \longrightarrow \left[CH_3O_2C(CH_2)_6\overset{\overset{Cl}{|}}{C}\cdots CH\cdots CH_2\right]\cdot$$

$$[CH_3O_2C(CH_2)_6C\cdots CH\cdots CH_2]\cdot \xrightarrow[CH_3OH]{Cu^{+2}} \underset{\text{XII}}{CH_3O_2C(CH_2)_6\overset{\overset{Cl}{|}}{\underset{\underset{OCH_3}{|}}{C}}CH{=}CH_2} + \underset{\text{XIV}}{CH_3O_2C(CH_2)_6\overset{\overset{Cl}{|}}{C}{=}CHCH_2OCH_3}$$

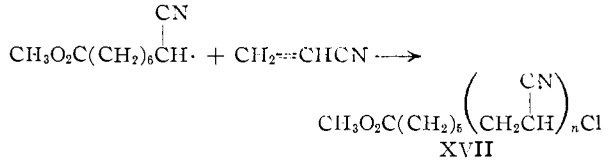
$$\text{XII} \longrightarrow \underset{\text{XIII}}{CH_3O_2C(CH_2)_6\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH{=}CH_3}$$

has been isolated in ~20% yield. The isomeric compound XII could not be isolated as such since its hydrolysis is too rapid. The hydrolytic product, the vinyl ketone XIII, is obtained as a polymer. Sufficient chloride ion is liberated in the hydrolysis to produce cupric chloride which traps 12% of the 5-(methoxycarbonyl)-pentyl as methyl ω-chlorohexanoate. Under scrupulously anhydrous conditions it should be possible to isolate the labile chloroallylic ether XII.

Acrylonitrile.—The addition of 5-(methoxycarbonyl)-pentyl to acrylonitrile occurs rapidly. In the presence of cupric (0.06 mole) and ferrous sulfate (1.0 mole), however, extensive polymerization of acrylonitrile takes place. If cupric (0.06 mole) and ferrous chloride (0.5 mole) are used to trap the intermediate radicals, methyl chlorohexanoate is the predominant product in addition to approximately 37% of the expected nitrile XVI. However, in a solution of cupric chloride (0.06 mole), ferrous chloride (0.25 mole) and ferrous sulfate (0.25 mole) a 46% yield of adduct is formed. The adduct XVII contains predominantly two acrylonitrile moieties ($n = 2$) associated with each hexanoate radical.

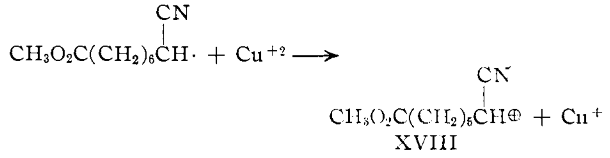


$$CH_3O_2C(CH_2)_5\cdot + CH_2{=}CH\text{—}CN \longrightarrow \underset{\text{XV}}{CH_3O_2C(CH_2)_6\overset{\overset{CN}{|}}{C}H\cdot} \xrightarrow{CuCl_2} \underset{\text{XVI}}{CH_3O_2C(CH_2)_6\text{—}\overset{\overset{CN}{|}}{C}HCl}$$



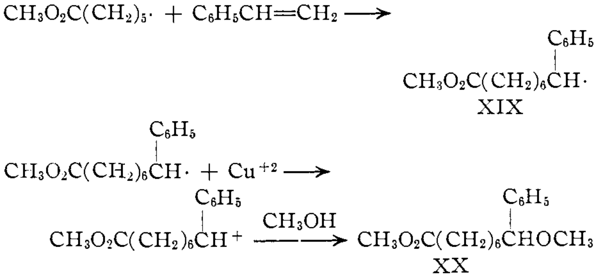
$$CH_3O_2C(CH_2)_6\overset{\overset{CN}{|}}{C}H\cdot + CH_2{=}CHCN \longrightarrow \underset{\text{XVII}}{CH_3O_2C(CH_2)_6\left(CH_2\overset{\overset{CN}{|}}{C}H\right)_nCl}$$

The adduct radical XV thus exhibits marked differences in selectivity to oxidation by cupric species. Oxidation by cupric ion to the carbonium ion intermediate XVIII appears to be an unfavorable process since extensive homopolymerization of the monomer occurs. Moreover, the same adduct radical adds to another acrylonitrile as readily as it reacts with cupric chloride.



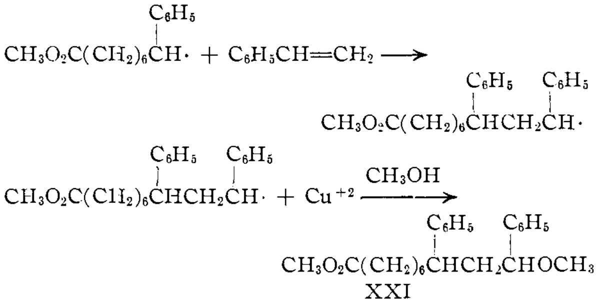
$$CH_3O_2C(CH_2)_6\overset{\overset{CN}{|}}{C}H\cdot + Cu^{+2} \longrightarrow \underset{\text{XVIII}}{CH_3O_2C(CH_2)_6\overset{\overset{CN}{|}}{C}H^{\oplus}} + Cu^{+}$$

Styrene.—Styrene can also be used as an acceptor for the 5-(methoxycarbonyl)-pentyl. The benzylic adduct radical XIX is easily oxidized by cupric ion to the benzyl carbonium ion which yields the ether XX in methanol. The benzylic ether is produced in 19% yield in addition to the product XXI formed in 28% yield corresponding to the incorporation of two molecules of styrene for each hexanoate radical. If the cupric sulfate concentration is increased and the styrene concentration decreased, the yields of XX and XXI are decreased.



$$CH_3O_2C(CH_2)_5\cdot + C_6H_5CH{=}CH_2 \longrightarrow \underset{\text{XIX}}{CH_3O_2C(CH_2)_6\overset{\overset{C_6H_5}{|}}{C}H\cdot}$$

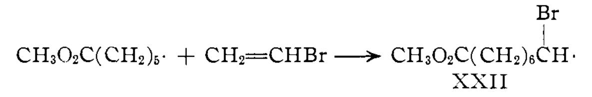
$$CH_3O_2C(CH_2)_6\overset{\overset{C_6H_5}{|}}{C}H\cdot + Cu^{+2} \longrightarrow CH_3O_2C(CH_2)_6\overset{\overset{C_6H_5}{|}}{C}H^{+} \xrightarrow{CH_3OH} \underset{\text{XX}}{CH_3O_2C(CH_2)_6\overset{\overset{C_6H_5}{|}}{C}HOCH_3}$$



$$CH_3O_2C(CH_2)_6\overset{\overset{C_6H_5}{|}}{C}H\cdot + C_6H_5CH{=}CH_2 \longrightarrow CH_3O_2C(CH_2)_6\overset{\overset{C_6H_5}{|}}{C}HCH_2\overset{\overset{C_6H_5}{|}}{C}H\cdot$$

$$CH_3O_2C(CH_2)_6\overset{\overset{C_6H_5}{|}}{C}HCH_2\overset{\overset{C_6H_5}{|}}{C}H\cdot + Cu^{+2} \xrightarrow{CH_3OH} \underset{\text{XXI}}{CH_3O_2C(CH_2)_6\overset{\overset{C_6H_5}{|}}{C}HCH_2\overset{\overset{C_6H_5}{|}}{C}HOCH_3}$$

Haloölefins.—Simple vinylic haloölefins are known to undergo free radical addition reactions.[7] Vinyl bromide reacts with 5-(methoxycarbonyl)-pentyl readily but similar to the adduct radical XV from acrylonitrile; extensive polymerization of the vinyl bromide occurs when only cupric sulfate is present. The indications are that the bromoalkyl radical XXII is not easily oxidized to the corresponding carbonium ion by cupric ion.



$$CH_3O_2C(CH_2)_5\cdot + CH_2{=}CHBr \longrightarrow \underset{\text{XXII}}{CH_3O_2C(CH_2)_6\overset{\overset{Br}{|}}{C}H\cdot}$$

When vinylidene chloride is allowed to react in the presence of the C_6-ester radical and cupric chloride it shows no indication of undergoing an addition reaction. The sole isolable product is methyl ω-chlorohexanoate (25% yield).

Methallyl chloride reacts readily with the 5-(methoxycarbonyl)-pentyl and cupric sulfate to form adducts in approximately 55% yield. The products boiling over a range were not completely identified, but elemental analysis and their infrared spectra suggest that the products do not include the ether product XXIV obtained by the oxidation of the chloroallyl radical XXIII to the corresponding carbonium ion. The product most compatible with the analysis is the unsaturated

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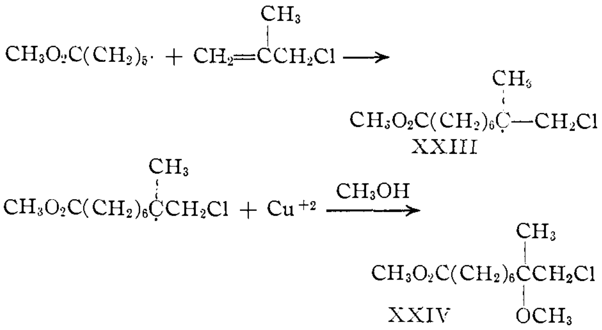
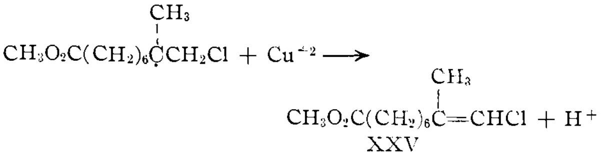
[7] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.



$$CH_3O_2C(CH_2)_5\cdot + CH_2{=}\overset{CH_3}{\overset{|}{C}}CH_2Cl \longrightarrow \underset{\text{XXIII}}{CH_3O_2C(CH_2)_6\overset{CH_3}{\overset{|}{\dot{C}}}{-}CH_2Cl}$$

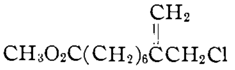
$$CH_3O_2C(CH_2)_6\overset{CH_3}{\overset{|}{\dot{C}}}CH_2Cl + Cu^{+2} \xrightarrow{CH_3OH} \underset{\text{XXIV}}{CH_3O_2C(CH_2)_6\underset{OCH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2Cl}$$

chloroester XXV. The vinyl chloride structure XXV is preferred to the alternative isomers XXVI



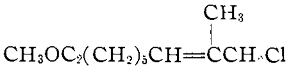
$$CH_3O_2C(CH_2)_6\overset{CH_3}{\overset{|}{\dot{C}}}CH_2Cl + Cu^{+2} \longrightarrow \underset{\text{XXV}}{CH_3O_2C(CH_2)_6\overset{CH_3}{\overset{|}{C}}{=}CHCl} + H^+$$

in which the double bond is allylic to the chlorine



$$CH_3O_2C(CH_2)_6\overset{CH_2}{\overset{\|}{C}}CH_2Cl$$

XXVIa

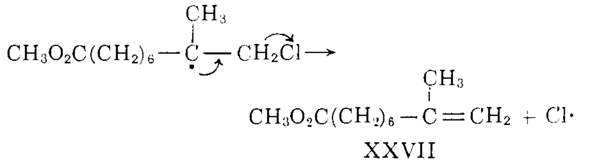


$$CH_3OC_2(CH_2)_5CH{=}\overset{CH_3}{\overset{|}{C}}CH_2Cl$$

XXVIb

because conditions under which the ester is saponified do not liberate chloride ions.

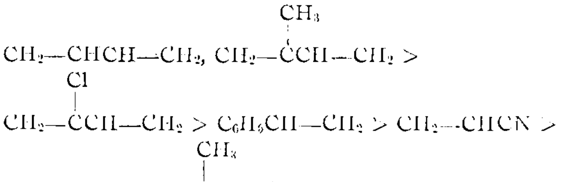
There is no indication that the unsaturated ester XXVII is formed which would result from the expulsion of the chlorine atom from the chloroallyl radical XXIII by a process similar to the free radical dimerization of methallyl chloride.[8]



$$CH_3O_2C(CH_2)_6{-}\overset{CH_3}{\overset{|}{\dot{C}}}{-}CH_2Cl \longrightarrow \underset{\text{XXVII}}{CH_3O_2C(CH_2)_6{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2} + Cl\cdot$$

Discussion

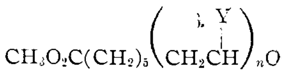
The addition of 5-(methoxycarbonyl)-pentyl to olefins of various structural types has been examined. The general reactivity sequence of olefins to addition by this radical is in the decreasing order



$$CH_2{=}CHCH{=}CH_2,\ CH_2{=}\overset{CH_3}{\overset{|}{C}}CH{=}CH_2 > CH_2{=}\overset{Cl}{\overset{|}{C}}CH{=}CH_2 > C_6H_5CH{=}CH_2 > CH_2{=}CHCN > CH_2{=}\overset{CH_3}{\overset{|}{C}}CH_2Cl > CH_2{=}CHBr >> CH_2{=}CCl_2$$

This order is based on the total yields of adduct products obtained by adding the 5-(methoxycarbonyl)-pentyl to the respective olefin under standard conditions of cupric ion and olefin concentration. This method is applicable since there is an independent alternative route by which the 5-(methoxycarbonyl)-pentyl can also react, *viz.*, to form the variety of C_6-ester products mentioned earlier.

There are two variables which must be considered in determining the products of the reaction; (1) copper ion concentration and (2) olefin concentration. At high cupric ion concentrations the reaction is terminated at the initial free radical stage [$CH_3O_2C(CH_2)_5\cdot$]. The products are methyl 5-hexenoate and methyl ω-methoxyhexanoate when cupric sulfate is used and methyl ω-chlorohexanoate when cupric chloride is present. At high olefin concentrations the telomers of the general structure



$$CH_3O_2C(CH_2)_5\left(CH_2\overset{Y}{\overset{|}{C}}H\right)_nOCH_3$$

XXVIII

$$CH_2{=}CHY$$

XXIX

XXVIII are formed from olefins XXIX in addition to diesters of type III.

It is apparent from the pattern of reactions presented earlier that there are at least two main considerations to be made with reference to the receptivity of the olefin to 5-(methoxycarbonyl)-pentyl addition: (a) the capacity for free radical addition and (b) the oxidation by cupric ion of the resulting adduct radical. With respect to the former, olefins show the same behavior to the 5-(methoxycarbonyl)-pentyl as they do to other free radicals. Thus, conjugated dienes are the most reactive followed by olefins conjugated to unsaturated groups such as phenyl, carbonyl and cyano, and alkyl substituted olefins and followed lastly by halogenated vinyl compounds. In this respect it should be mentioned that 5-(methoxycarbonyl)-pentyl, like alkyl radicals in general, exhibits electrophilic properties[9] in that it adds relatively slowly to olefins possessing electron-withdrawing groups.

The ease of oxidation of the adduct radical is also a function of the substituents on the olefins. In olefin XXIX if Y is an electron-withdrawing group such as cyano, carbonyl or halogen, oxidation by cupric sulfate involving an electron transfer reaction does not occur. If the olefin is prone to homopolymerization, extensive polymerization will occur. This seems reasonable in view of the general observation that positions alpha to these substituents do not tolerate a positive charge[10] (*e.g.*, slow solvolysis of α-haloketones, nitriles, etc.). However, if the adduct radical can undergo an oxidation without generation of a positive charge as, for example, in the chloride ligand transfer reaction[11] (eq. 8) alluded to earlier,[6] the reaction proceeds smoothly to produce the corresponding chloride, without polymerizing the olefin. These phenomena have been observed with acrylonitrile, acrolein[12] and vinyl bromide. In the cases where Y is an alkyl, vinyl, aryl or a similar moiety capable of stabilizing an adjacent positive charge, oxidation by cupric sulfate[13] as well as cupric chloride, occurs quite readily.

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(8) Reference 7, p. 269.

(9) F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

(10) J. Hine, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y.

(11) Even in ligand transfer reactions there is a modicum of positive charge generated in the free radical moiety. This is borne out by the fact that oxy and thiyl radicals are not oxidized by cupric chloride (see refs. 1,13).

(12) J. K. Kochi, unpublished observations.

(13) In the previous sections the oxidation of free radicals by cupric sulfate (see results) was written as a two-step process involving the formation of carbonium ions as intermediates. The presentation was made for the sake of clarity and did not intend to convey a mechanistic

The implication from these results is that the structural requirements of the free radicals toward oxidation by electron transfer differs from that by ligand transfer. The ligand transfer process and the electron transfer process can be considered as two extreme forms of the oxidation mechanisms of free radicals by metal salts. In many cases they are competing reactions and the slight alterations in the structural features of the radicals which contribute to the variation in the rates of the oxidation reactions leads us to postulate that these oxidation processes can be formally represented as proceeding through similar and related transition states. These transition states (XXX) can be represented as consisting of resonance contributions from ligand transfer and electron transfer forms. The degree to which each contributes to

$$\underset{\text{XXX}}{\left[\underset{(a)}{\mathrm{R}\cdot\ \mathrm{XM}^{+n}} \longleftrightarrow \underset{(b)}{\mathrm{R}^{+}\ \mathrm{XM}^{+n-1}} \longleftrightarrow \underset{(c)}{\mathrm{R{-}XM}^{+n-1}} \longleftrightarrow \underset{(d)}{\mathrm{R\cdot X\cdot M}^{+n-1}}\right]}$$

the transition state will depend not only on the electronic requirements of the free radical as discussed earlier but also on the metal species and its associated ligand. The importance of the latter, especially in the ligand transfer process, is demonstrated by the reaction between negatively substituted radicals and cupric sulfate. Although the oxidation reactions can be carried out with alkyl radicals in water and alcohol solvents to yield substitution products in which OH and OR are the groups transferred (X in formula XXX), they cannot be carried out with negatively substituted radicals. The latter, which cannot easily accommodate a positive charge, undergoes, however a facile oxidation by cupric chloride in a ligand, transfer process. The difference in reactivity of chlorides and bromides, compared to such oxyanions as hydroxides and alkoxides, is tentatively attributed to the importance of the oxidation potential[14] of the ligand (from d in formula XXX).

Acknowledgment.—We wish to thank Mr. Kenneth Kuykendall for technical assistance and Dr. Harold E. De La Mare for helpful discussions.

Experimental

Materials.—Ferrous chloride, $FeCl_2{\cdot}4H_2O$, General Chem., Allied Chem. and Dye reagent; Ferrous sulfate, $FeSO_4{\cdot}7H_2O$, same source; Cupric chloride, $CuCl_2{\cdot}2H_2O$, Baker analyzed reagent, J. T. Baker Chemical Co., $CuCl_2$ obtained by heating hydrate at 100° *in vacuo;* Cupric sulfate, $CuSO_4{\cdot}5H_2O$, Baker analyzed reagent; Cyclohexanone, Eastman Kodak Co., reagent grade; Hydrogen peroxide, 30% aqueous solution, Shell Chemical Co.; Butadiene, Phillips Petroleum Co., reagent grade; Isoprene, Phillips Petroleum Co., reagent grade; Chloroprene, Monomer Polymer Lab., distilled from solution immediately before use; Acrylonitrile, Eastman Kodak reagent grade, distilled before use; Vinyl bromide, The Matheson Co., 99% purity distilled from cylinder; Styrene, Eastman Kodak Co., redistilled before use; Vinylidene chloride, Dow Chemical Co.. redistilled before use; Methallyl chloride, Shell Chemical Co., redistilled before use.

5-(Methoxycarbonyl)-pentyl with Cupric Sulfate.—Cyclohexanone (19.6 g.) and 30% hydrogen peroxide (11.5 g.) were stirred at room temperature for 0.5 hour. Solutions of 10 ml. of concentrated sulfuric acid in 150 ml. of methanol and 3 g. of cupric sulfate ($CuSO_4{\cdot}5H_2O$) in 150 ml. of methanol were added and the homogeneous solution cooled to 0° with stirring and nitrogen flushing. A solution of 41.7 g. of ferrous sulfate ($FeSO_4{\cdot}7H_2O$) in 400 ml. of methanol was added dropwise. The solution was then stirred for 1 hour and poured into excess water. The aqueous solution was extracted with chloroform three times. The chloroform extract was washed with water once and dried over sodium sulfate. Distillation yielded unchanged cyclohexanone (10.0 g.); methyl 5-hexenoate (6.0 g., 47%) boiling at 75–76° (50 mm.) $n^{20}{}_{\mathrm{D}}$ 1.4204; and methyl ω-methoxyhexanoate (4.3 g., 27%) boiling at 58–61° (2 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4213; and residue (1.1 g.).

Anal. Calcd. for methyl 5-hexenoate ($C_7H_{12}O_2$): C, 65.59; H, 9.44; sapon. equiv., 128.2; Br no., 71. Found: C, 65.6; H, 9.3; sapon. equiv., 128; Br no., 72. Calcd. for methyl ω-methoxyhexanoate ($C_8H_{16}O_3$): C, 59.98; H, 10.1; sapon. equiv., 160.2; methoxy (Zeisel), 85.1. Found: C, 60.0; H, 10.0; sapon. equiv., 165; methoxy (Zeisel), 82.

5-(Methoxycarbonyl)-pentyl with Cupric Chloride.—To a stirred mixture of 19.1 g. of cyclohexanone and 11.5 g. of 30% hydrogen peroxide was added a solution of 10 ml. of concd. sulfuric acid and 3.0 g. of cupric chloride ($CuCl_2{\cdot}2H_2O$) in 30 ml. of methanol. The solution was cooled to 0° and a solution of 35 g. of ferrous chloride ($FeCl_2{\cdot}4H_2O$) in 400 ml. of methanol was added dropwise with stirring. The mixture after stirring an additional half-hour was poured into excess water and extracted with chloroform three times. The chloroform extract after washing with water and drying over sodium sulfate was distilled to yield cyclohexanone (8.6 g.) and methyl ω-chlorohexanoate (11.3 g., 69%) boiling at 56–58° (1 mm.), $n^{25}{}_{\mathrm{D}}$ 1 4388, and residue (0.7 g.).

Anal. Calcd. for methyl ω-chlorohexanoate ($C_7H_{13}O_2Cl$): C, 51.1; H, 7.96; Cl, 21.5; sapon. equiv., 164. Found: C, 51.3; H, 8.0; Cl, 21.2; sapon. equiv. (cor. for hydrolyzed chloride), 177.

5-(Methoxycarbonyl)-pentyl with Butadiene and Cupric Sulfate.—A mixture of 19.6 g. of cyclohexanone and 11.5 g. of hydrogen peroxide (30%) was stirred at room temperature for 0.5 hour. Chilled solutions of 20 ml. of concd. sulfuric acid in 150 ml. of methanol and 1.5 g. of cupric sulfate in 150 ml. of methanol then were added. The solution was cooled to 0°, 85 ml. of butadiene was added and the homogeneous solution briefly flushed with nitrogen. A solution of 41.7 g. of ferrous sulfate ($FeSO_4{\cdot}7H_2O$) in 400 ml. of methanol was added dropwise to the stirred solution at such a rate as to maintain the butadiene refluxing in the Dry Ice condenser, approx. 1.5 hours. The mixture was stirred at room temperature to allow the butadiene to distil off and the mixture then poured into 1.5 liters of water. It was extracted with 100-ml. portions of chloroform three times. The chloroform extract was dried with sodium sulfate and distilled to yield methyl ω-hexenoate (0.8 g., 6%), methyl ω-methoxyhexanoate (0.3 g., 2%), methyl 7-methoxy-9-decenoate (9.7 g., 45%, b.p. 89–90° (1 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4397), methyl 10-methoxy-7-decenoate (3.5 g., 16%, b.p. 107–108° (1 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4462) and 7-methoxy-9-decenoic acid (1.6 g., 8%, b.p. 134–136° (1 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4509).

Anal. Calcd. for methyl 7-methoxy-9-decenoate ($C_{12}H_{22}O_3$): C, 67.25; H, 10.4; sapon. equiv., 214; Br no. (eq./100 g.), 74.8. Found: C, 67.3; H, 10.5; sapon. equiv., 215; Br no. (eq./100 g.), 73.

Methyl 7-methoxydecenoate absorbs in the infrared at 10.1 and 10.8 μ characteristic of the vinyl group. The nuclear magnetic resonance spectrum also exhibits proton resonances characteristic of the vinyl group centered at 211 c.p.s. relative to tetramethylsilane internal reference.

Anal. Calcd. for methyl 10-methoxy-7-decenoate ($C_{12}H_{22}O_3$): C, 67.25; H, 10.4; sapon. equiv., 214; Br no. (eq./100 g.), 74.8. Found: C, 67.0; H, 10.4; sapon. equiv., 213; Br no. (eq./100 g.), 74.

The infrared spectrum of methyl 10-methoxy-7-decenoate shows a prominent absorption at 10.3 μ characteristic of an unsubstituted *trans*-olefin. Similarly the nuclear magnetic resonance spectrum shows proton resonances of the hydrogens of internal olefins centered at 222 c.p.s. relative to tetramethylsilane.

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implication. For a discussion of substitution reactions which accompany electron transfer processes, see ref. 1.

[14] Although the difference in reactivity is attributed mostly to the oxidation potential of the anion, the importance of such factors as atom and bond polarizabilities cannot be overlooked. These considerations bear further investigation.

Anal. Calcd. for 7-methoxy-9-decenoic acid ($C_{11}H_{20}O_3$): C, 66.0; H, 10.1; neut. equiv., 200.3; Br no. (eq./100 g.), 80. Found: C, 65.9; H, 10.2; neut. equiv., 212; Br no. (eq./100 g.), 74.

5-(Methoxycarbonyl)-pentyl with Butadiene and Cupric Chloride.—The 5-(methoxycarbonyl)-pentyl was added to butadiene in the presence of varying amounts of chloride ion (cupric chloride). In each of the following cases, to a mixture of 40 g. of cyclohexanone and 23 g. of 30% hydrogen peroxide was added: (a) 40 ml. concd. sulfuric acid, 2 g. of cupric chloride, 400 ml. of butadiene in 600 ml. of methanol. The reducing agent consisted of a solution of 28 g. of ferrous sulfate and 20 g. of ferrous chloride in 800 ml. of methanol; yields: recovered cyclohexanone, 12.1 g.; methyl methoxydecenoate, 30.2 g.; residue, 2.6 g. (b) 40 ml. of concd. sulfuric acid, 2 g. of cupric chloride, 400 ml. of butadiene and 600 ml. of methanol. The reducing agent was 40 g. of ferrous chloride in 800 ml. of methanol; yields: recovered cyclohexanone, 14.5 g.; methyl methoxydecenoate, 27.2 g.; methyl ω-chlorohexanoate, 2 g.; residue, 3.4 g. (c) 80 ml. of concd. hydrochloric acid, 20 g. of cupric chloride, 400 ml. of butadiene in 600 ml. of methanol. The reducing agent was 40 g. of ferrous chloride in 800 ml. methanol; yields: methyl methoxydecenoate, 1.5 g.; methyl 10-chloro-7-decenoate, 1.2 g.; methyl ω-chlorohexanoate, 18 g.; residue, 1 g.

5-(Methoxycarbonyl)-pentyl with Isoprene and Cupric Sulfate.—To a stirred mixture of 59 g. cyclohexanone and 46 g. of 30% hydrogen peroxide was added a solution of 20 ml. of concd. sulfuric acid, 4.5 g. of cupric sulfate ($CuSO_4 \cdot 5H_2O$) and 255 ml. of isoprene in 580 ml. of methanol. After cooling the solution to 0° a solution of 83 g. of ferrous sulfate in 800 ml. of methanol was added. The workup following the earlier procedure yielded cyclohexanone (29.2 g.), methyl ω-hexenoate (5.1 g., 10%), methyl ω-methoxyhexanoate (3.7 g., 5%), methyl 8-methoxy-8-methyl-9-decenoate (23.0 g., 27%, b.p. 103–104° (2 mm.), n^{20}_D 1.4469), methyl 10-methoxy-8-methyl-7-decenoate (6.2 g., 7.2%, b.p. 114–118° (2 mm.), n^{20}_D 1.4512), 8-methoxy-8-methyl-9-decenoic acid (5.5 g., 6.5%, b.p. 140–144° (2 mm.), n^{20}_D 1.4604) and residue (14.8 g.) which was primarily the diesters of dimethyleicosadienedioic acids. The infrared spectrum of this compound shows a characteristic absorption band at 10.0 and 10.85 μ of the vinyl group. The nuclear magnetic resonance spectrum shows a group of proton resonances centered at 210 c.p.s. relative to tetramethylsilane internal reference diagnostic of the vinyl group.

Anal. Calcd. for methyl 8-methoxy-8-methyl-9-decenoate ($C_{13}H_{24}O_3$): C, 68.4; H, 10.6; sapon. equiv., 228.3; Br no., 70. Found: C, 68.5; H, 10.6; sapon. equiv., 230; Br no., 78. Calcd. for methyl 10-methoxy-8-methyl-7-decenoate ($C_{13}H_{24}O_3$): C, 68.4; H, 10.6; sapon. equiv., 228.3; Br no., 70. Found: C, 68.9; H, 10.7; sapon. equiv., 226; Br no., 73,74. Calcd. for 8-methoxy-8-methyl-9-decenoic acid ($C_{12}H_{22}O_3$): C, 67.3; H, 10.3; neut. equiv., 214.3. Found: C, 68.5; H, 10.5; neut. equiv., 221. Calcd. for residue (dimethyl ester of dimethyleicosadienedioic acid, $C_{24}H_{21}O_4$): C, 73.0; H, 10.75; sapon. equiv., 197. Found: C, 72.2; H, 10.3; sapon. equiv., 198.

5-(Methoxycarbonyl)-pentyl with Chloroprene and Cupric Sulfate.—To a stirred mixture of 19.6 g. of cyclohexanone and 11.5 g. of 30% hydrogen peroxide was added a chilled solution of 10 ml. of concd. sulfuric acid and 3 g. of cupric sulfate in 300 ml. of methanol. This was followed by the addition of 100 ml. of freshly distilled chloroprene. The dropwise addition of a solution of 41.7 g. of ferrous sulfate in 400 ml. of methanol was regulated to maintain a reaction temperature of 0° with an ice-bath. The homogeneous reaction mixture was worked up in the usual manner to yield methyl ω-chlorohexanoate (2.0 g., 12%) and methyl chloromethoxydecenoate (b.p. 111–118°, 5.1 g., 20%) in addition to polymeric residues.

Anal. Calcd. for methyl chloromethoxydecenoate ($C_{12}H_{21}O_3Cl$): C, 57.9; H, 8.52; Cl, 14.24; sapon. equiv., 248.8. Found: C, 58.2; H, 8.5; Cl, 12.7; sapon. equiv. (cor. for saponified chloride), 212.

5-(Methoxycarbonyl)-pentyl with Acrylonitrile.—To 19.6 g. of cyclohexanone and 11.5 g. of 30% hydrogen peroxide at 0° was added a solution of 10 ml. of concd. sulfuric acid, 3 g. of cupric chloride and 100 ml. of acrylonitrile in 300 ml. of methanol. A solution of 20 g. of ferrous sulfate and 20 g. of ferrous chloride in 400 ml. of methanol was added at 0° with stirring. The reaction became slightly opaque. After dilution with water and extraction with chloroform, the chloroform extract was washed with water, dried with sodium sulfate and distilled. With a maximum pot temperature of 80° and 1 mm. pressure, the residue remaining after distillation of the unreacted cyclohexanone (13 g.) is a viscous oil (18 g.). The infrared spectrum shows absorption bands at 4.45 (CN), 5.8 (carbonyl), 8–8.5 (ester) and 13–13.5 μ (Cl). The absorption band at 9–9.2 μ for methoxyl is absent.

Anal. Calcd. for $C_{13}H_{19}ClN_2O_2$: C, 57.7; H, 7.1; N, 10.3; Cl, 13.1; ester value (eq./100 g.), 0.37; acidity, O; nitrile value (eq./100 g.), 0.74. Found: C, 57.9; H, 7.3; N, 8.63; Cl, 12.0; ester value (eq./100 g.), 0.786; acidity, 0.06; nitrile value (eq./100 g.), 0.57.

If the reaction is carried out using 50 ml. of acrylonitrile and 35 g. of ferrous chloride (as reducing agent), the non-distillable residue remaining is 2.6 g. There is formed in addition methyl ω-chlorohexanoate (3.3 g., 20%) and methyl 8-chloro-8-cyanoöctanoate (8 g., 37%, b.p. 123–124° (2 mm.), n^{25}_D 1.4532).

Anal. Calcd. for methyl 8-chloro-8-cyanoöctanoate ($C_{10}H_{16}ClO_2N$): C, 55.4, H, 7.38; N, 6.40; Cl, 16.2; sapon. equiv., 218.7. Found: C, 55.9; H, 7.6; N, 5.88; Cl, 15.2; sapon. equiv. (cor. for chloride), 232.

5-(Methoxycarbonyl)-pentyl with Styrene and Cupric Sulfate.—The mixture of cyclohexanone (19.6 g.) and hydrogen peroxide (11.5 g., 30%) was treated with a solution of 20 ml. of concd. sulfuric acid, 1.5 g. of cupric sulfate ($CuSO_4 \cdot 5H_2O$) and 100 ml. of styrene in 300 ml. of methanol at 0°. The reducing agent consisted of a solution of ferrous sulfate (41.7 g. $FeSO_4 \cdot 7H_2O$) in 400 ml. of methanol. The distillation of the chloroform extract consisted of 18 g. of higher boiling residues. Vacuum distillation of this material yielded methyl hexanoate (1.0 g., 7.8%), methyl ω-methoxyhexanoate (0.6 g., 3.8%), methyl 8-methoxy-8-phenyloctanoate (5.1 g., 19%, b.p. 138–142° (2 mm.), n^{25}_D 1.4394) and non-distillable residue (10.2 g., 28%) which is methyl 10-methoxy-8,10-diphenyldecanoate.

Anal. Calcd. for methyl 8-methoxy-8-phenyloctanoate ($C_{16}H_{24}O_3$): C, 72.69; H, 9.15; sapon. equiv., 264.4. Found: C, 73.6, 72.7[15]; H, 9.5, 9.0[15]; sapon. equiv., 260, 256.[15] Calcd. for methyl 10-methoxy-8,10-diphenyldecanoate ($C_{24}H_{32}O_3$): C, 78.4; H, 8.78; sapon. equiv., 368.5. Found: C, 79.5, 76.5[15]; H, 8.4, 8.6[15]; sapon. equiv., 389.

5-(Methoxycarbonyl)-pentyl with Vinyl Bromide and Cupric Sulfate.—A 100-ml. portion of vinyl bromide was added to a mixture consisting of 19.6 g. of cyclohexanone 11.5 g. of 30% hydrogen peroxide, 20 ml. of concd. sulfuric acid, 1.5 g. of cupric sulfate in 300 ml. of methanol at 0°. The addition of a solution of 41.7 g. of ferrous sulfate in 400 ml. of methanol caused the solution to become viscous and precipitate a colorless solid (58 g.) consisting of polymeric vinyl bromide. The crude reaction was filtered and the filtrate examined in the usual manner. The distillation of chloroform from the extract yielded 18 g. of residue which consisted primarily of cyclohexanone (10.5 g.) and methyl ω-methoxyhexanoate (2.7 g., 16%). The residue on standing several days gave a colorless solid precipitate. Recrystallization twice from chloroform (very soluble in *n*-hexane) yielded dense prisms, m.p. 83–86°. The absence of a carbonyl stretching band in the infrared spectrum indicates that the compound is not derived from 5-(methoxycarbonyl)-pentyl. Elemental analyses were difficult to obtain reproducibly on this solid.

Anal. Calcd. for $C_{15}H_{25}Br_2$: C, 49.4; H, 6.91; Br no., 43.9; mol. wt. (ebull., C_6H_6), 365. Found: C, 50.7, 51.1, 63.7; H, 7.0, 7.5, 8.9; Br no., 49.1, 44.9, 40.1; mol. wt. (ebull., C_6H_6), 344 ± 10.

5-(Methoxycarbonyl)-pentyl with Vinylidene Chloride and Cupric Chloride.—The reaction carried out in the usual manner consisted of 19.6 g. of cyclohexanone, 11.5 g. of 30% hydrogen peroxide, 10 ml. of concd. sulfuric acid, 3 g. of cupric chloride hydrate, 58 ml. of vinylidene chloride in 300 ml. of methanol which was treated with a solution of 20 g. of ferrous sulfate and 20 g. of ferrous chloride in 400 ml. of methanol. The products consisted of 9.7 g. of re-

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(15) Sample from a duplicate experiment.

covered cyclohexanone, 6.8 g., 42%, of methyl ω-chlorohexanoate and 5.6 g. of non-distillable residue.

5-(Methoxycarbonyl)-pentyl with Methallyl Chloride and Cupric Sulfate.—The charge consisted of 19.6 g. of cyclohexanone, 11.5 g. of 30% hydrogen peroxide, 10 ml. of concd. sulfuric acid, 3 g. of cupric sulfate hydrate, 84 ml. of freshly redistilled methallyl chloride in 300 ml. of methanol and 41.7 g. of ferrous sulfate hydrate in 400 ml. of methanol. Methyl chlorodecenoate boiling at 146–151° (2 mm.) (n^{20}D 1.4698–1.4703) was obtained in 8.1 g. yield together with a mixture of methyl 5-hexenoate and methyl ω-methoxyhexanoate (3.0 g.) and 3.2 g. of high boiling residue.

Anal. Calcd. for $C_{11}H_{19}ClO_2$: C, 60.2; H, 8.7; Cl, 16.2; ester value, 0.456. Found: C, 59.7; H, 9.0; Cl, 17.2; ester value, 0.52.

Cyclohexanone–Hydrogen Peroxide with Butadiene in Acetic Acid.—The usual mixture of 19.6 g. of cyclohexanone and 11.5 g. of 30% hydrogen peroxide was stirred for 30 minutes and 300 ml. of acetic acid and 3 g. of cupric chloride were added. After stirring for 30 minutes at room temperature the reaction was cooled to 15°, 200 ml. of butadiene was added and the reaction cooled further to 0°. A solution of 20 g. of ferrous chloride in 200 ml. of acetic acid and 50 ml. of water was added. The mixture was added to excess water and extracted three times with chloroform. Distillation yielded, in addition to acetic acid and cyclohexanone, 8.0 g. of ω-chlorohexanoic acid, a 53% yield based on H_2O_2. The infrared spectrum matched that of an authentic sample.[4]

Cyclohexanone–Hydrogen Peroxide and Butadiene in *t*-Butyl Alcohol.—A charge of 40 g. of cyclohexanone and 24 g. of 30% hydrogen peroxide after stirring for 15 minutes was cooled to 5° and a chilled solution of 40 ml. of concd. sulfuric acid in 100 ml. of water was added. A mixture of 3 g. of cupric sulfate, 400 ml. of *t*-butyl alcohol and 340 ml. of butadiene was added at 0°. To the chilled solution was added dropwise a solution of 84 g. of ferrous sulfate hydrate in 125 ml. of water. A total of 500 ml. of gas was given off. The reaction was worked up in the usual manner to yield 50 g. of material after the chloroform was distilled off. Further distillation yielded 35 g. of cyclohexanone and 15 g. of non-distillable material. The infrared spectrum indicated it to be a carboxylic acid. However, attempts to distil the acid *in vacuo* (bath temp. 50–60°) led to its rapid decomposition with the evolution of heat. The material was not further characterized.

When the aqueous mother liquor was titrated for ferrous ion with a standard ceric sulfate solution, it was found that only 30% of the ferrous ion equivalent to the hydrogen peroxide was consumed. It is believed that the lability of the acidic products is due to unreacted peroxidic materials.

NOTE ADDED IN PROOF.—The addition of free radicals to conjugated olefins in the presence of copper salts has also been reported recently by Minisci, *et al.*, *Gazz. Chim. Ital.*, 91, 1023, 1031 (1961).

[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE, BRYN MAWR, PENNA.]

The Bromination of Fluorene in Aqueous and Glacial Acetic Acid[1]

BY UN-JIN P. ZIMMERMAN[2] AND ERNST BERLINER[3]

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The bromination of fluorene by bromine in 75% aqueous acetic acid and in the presence of an excess of bromide ion has been found to have the same kinetic characteristics as the reaction in 50 and 60% aqueous acetic acid.[8,10] The reactions in glacial acetic acid, 90 and 75% aqueous acetic acid, without added bromide ion, are of an order higher than one in bromine. The separate second- and third-order rate constants in the two aqueous solvents have been evaluated, and the results are discussed in terms of the accepted bromination mechanism. In 75% acetic acid, fluorene is brominated to an extent of 97.0 ± 0.8% in the 2-position, as determined by the isotopic dilution method.

In glacial acetic acid and other solvents of low polarity the bromination of aromatic compounds is often of an order higher than one in bromine. According to the work of Robertson, de la Mare and their co-workers,[4] the reaction is best described as a composite one of the kinetic form

$$-dx/dt = k_2(\mathrm{ArH})(\mathrm{Br_2}) + k_3(\mathrm{ArH})(\mathrm{Br_2})^2 + k_4(\mathrm{ArH})(\mathrm{Br_2})^3 \quad (1)$$

where the contributions of each term to the total rate depend on various experimental factors. Later workers,[5] notably Keefer and Andrews,[6] have confirmed the presence of high-order terms and the general form of the rate equation, and the latter evaluated spectrophotometrically the separate constants k_2 and k_3 for bromination of various hydrocarbons in pure and in 90% aqueous acetic acid. Bradfield and co-workers[7] did the same for the reaction of phenol ethers in 75% acetic acid.

Following the observation of Robertson, *et al.*, that water and a low concentration of bromine favor low-order brominations, it was found that in 50% aqueous acetic acid, and in the presence of an excess of bromide ion, the bromination of naphthalene is strictly second order over-all, first order in each reactant.[8] The presence of bromide ion, in addition to reducing the free bromine concentration, also simplifies the kinetics, because the excess is much larger than the amount of bromide ion formed during reaction, and the latter can therefore be neglected. The occurrence of second-order kinetics under those conditions has since been confirmed for bromination of some other hydrocarbons and appears to be quite general.[9] It also holds for reaction in 60% aqueous acetic acid when bromide ion is present.[10]

It seemed of interest to find out whether in these latter reactions the increased water content, the bromide ions, or both, contribute to the lowering

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(1) Kinetics of Aromatic Halogenation. X.

(2) Taken from the Ph.D. thesis of Mrs. U. P. Zimmerman, Bryn Mawr College, June, 1961.

(3) To whom inquiries should be addressed.

(4) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); P. B. D. de la Mare and P. W. Robertson, *ibid.*, 100 (1948); P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, Chapter 9.

(5) G. Illuminati and G. Marino, *J. Am. Chem. Soc.*, **78**, 4975 (1956); S. F. Mason, *J. Chem. Soc.*, 4329 (1958); L. M. Yeddanapalli and N. S. Gnanapragasam, *J. Indian Chem. Soc.*, **36**, 745 (1959).

(6) R. M. Keefer, A. Ottenberg and L. J. Andrews, *J. Am. Chem. Soc.*, **78**, 255 (1956); R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 3637 (1956).

(7) A. E. Bradfield, G. I. Davies and E. Long, *J. Chem. Soc.*, 1389 (1949).

(8) E. Berliner and M. C. Beckett, *J. Am. Chem. Soc.*, **79**, 1425 (1957).

(9) E. Berliner and J. C. Powers, *ibid.*, **83**, 905 (1961).

(10) E. Berliner and B. J. Landry, *J. Org. Chem.*, **27**, 1083 (1962).