II. Kinetics of Ligand Transfer Oxidation of Alkyl Radicals. Evidence for Carbonium Ion Intermediates

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The rates of ligand transfer oxidation of alkyl radicals by copper(II) thiocyanate, chloride, and bromide approach the diffusion-controlled limit, having second-order rate constants at 25° of 3.6×10^8, 1.1×10^9, and 4.3×10^9 M^{-1} sec^{-1}, respectively. The kinetics were measured by comparing the first-order isomerization of 5-hexenyl and cyclopropylmethyl radicals as a function of the concentration of the copper(II) species. The cyclopropylmethyl radical can be trapped completely and without rearrangement at relatively low concentrations of copper(II) bromide. Oxidation of the cyclopropylmethyl radical by copper(II) thiocyanate and chloride, however, leads to a mixture of products involving partial rearrangement of the alkyl nucleus. The oxidation of the isomeric allylcarbinyl and cyclobutyl radicals was also examined. The extent of rearrangement observed in the products was independent of the concentration of copper(II) but varied with the structure of the copper(II) complex. Ligand transfer oxidation involves at least two simultaneous reactions, the major pathway being largely homolytic in nature and the other heterolytic.

A procedure for the study of ligand transfer oxidation of alkyl radicals by various copper(II) halides and pseudohalides was developed in the foregoing paper.[1] The method depended on the catalytic reaction of diacyl peroxide with halides or pseudohalides in the presence

$$(\mathrm{RCO_2})_2 + \mathrm{X^-} \xrightarrow{\mathrm{Cu^{I,II}}} \mathrm{RX} + \mathrm{CO_2} + \mathrm{RCO_2^-} \quad \mathrm{X} = \mathrm{Cl, Br, I, SCN, N_3, CN} \qquad (1)$$

of copper salts (eq 1).[2] The relevant steps in the process can be described according to eq 2–4.

$$(\mathrm{RCO_2})_2 + \mathrm{Cu^I} \longrightarrow \mathrm{R\cdot} + \mathrm{CO_2} + \mathrm{RCO_2Cu^{II}} \qquad (2)$$

$$\mathrm{RCO_2Cu^{II}} + \mathrm{X^-} \rightleftharpoons \mathrm{Cu^{II}X} + \mathrm{RCO_2^-} \qquad (3)$$

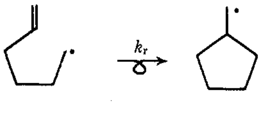
$$\mathrm{R\cdot} + \mathrm{Cu^{II}X} \longrightarrow \mathrm{RX} + \mathrm{Cu^I}, \text{ etc.} \qquad (4)$$

The excellent stoichiometry observed in most cases indicated that each step in the chain process (eq 2–4) occurred with great facility. The rates of step 4 in which the alkyl derivatives RX were efficiently produced by ligand transfer oxidation of alkyl radicals were of particular interest.

We sought to measure the kinetics of ligand transfer oxidation of alkyl radicals by comparing them directly with the rates of unimolecular rearrangement of 5-hexenyl and cyclopropylmethyl radicals. The study of these two alkyl radicals, especially the latter, also provided a sensitive probe for the role of carbonium ion intermediates[2c] in the ligand transfer process.

Results and Discussion

Ligand Transfer Oxidation of the 5-Hexenyl Radical.—Interest in the 5-hexenyl radical stems from the facile and irreversible intramolecular rearrangement (eq 5)



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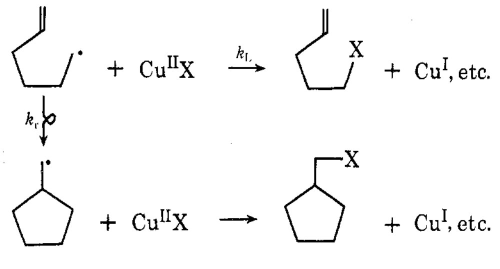
to the cyclopentylmethyl radical.[3] The isomerization occurs with a first-order rate constant k_r of 1×10^5 sec^{-1} at 25°.[4] It has been shown in a variety of systems[5] that the relative proportion of products derived from the 5-hexenyl radical or cyclopentylmethyl radical is dependent on the concentration of the chain transfer (trapping) agent. The following kinetic scheme provides the means of determining the rate constant k_L for ligand transfer with copper(II) complex (eq 6, 7). The ratio of the products derived from 5-



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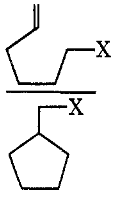
hexenyl and cyclopentylmethyl may be expressed as shown in eq 8. Equation 8 is applicable to the cata-



$$= \frac{k_L}{k_r}(\mathrm{Cu^{II}X}) \qquad (8)$$

lytic decomposition of peroxides if the steady state concentration of copper(II) can be determined. Thus, it was shown independently that copper(I) reacted instantaneously on mixing with peroxide.[2e] Furthermore, during the course of reaction its concentration relative to copper(II) was low, especially when the latter was present in amounts greater than 0.01 M. The steady-state concentration of copper(II) could also be measured by electron spin resonance spectroscopy and shown to be equal (within ±5%) to the total copper in solution.[2d]

The catalytic reaction of 6-heptenoyl peroxide (eq 2, R = 5-hexenyl) provided a convenient route to the 5-hexenyl radical. The irreversibility of the cyclization

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[1] C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, **36**, 3095 (1971).

[2] (a) J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963); (b) J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 1508 (1965); (c) J. K. Kochi and A. Bemis, *ibid.*, **90**, 4038 (1968); (d) J. K. Kochi, C. L. Jenkins, and A. Bemis, *ibid.*, **90**, 4616 (1968); (e) J. K. Kochi and A. Bemis, *Tetrahedron*, **24**, 5099 (1968).

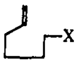
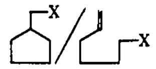
[3] R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Amer. Chem. Soc.*, **85**, 3483 (1963).

[4] D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

[5] (a) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *ibid.*, **88**, 5363 (1966); (b) G. F. Garst and F. E. Barton, *Tetrahedron Lett.*, 587 (1968); (c) J. Eastham, *Chem. Commun.*, 139 (1969); (d) J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, **92**, 137 (1970).

TABLE I

REACTION OF 5-HEXENYL AND CYCLOPENTYLMETHYL RADICALS WITH COPPER SALTS[a]

	Reactants, M				Products, mol %[f]		
Run	Peroxide[b]	Cu(II)[c]	Cu(I)[d]	Alkali salt[e]			
1	0.040 Hex	0.040 Cl	0.010 Cl	0.090 Cl	81	0	0
2	0.040 Hex	0.080 Cl	0.010 Cl	0.170 Cl	76	0	0
3	0.040 Hex	0.120 Cl	0.010 Cl	0.250 Cl	92	0	0
4	0.090 Hex	0	0.050 Cl	0.050 Cl	75	3.4	0.046
5	0.040 CP	0.040 Cl	0.010 Cl	0.090 Cl	0	74	
6	0.040 Hex	0.040 Br	0	0	75	0	0
7	0.040 Hex	0.080 Br	0	0	73	0	0
8	0.040 Hex	0.120 Br	0	0	52	0	0
9	0.040 CP	0.040 Br	0	0	0	105	
10	0.033 Hex	0.033 SCN	0	0.133 SCN	93	0	0
11	0.033 Hex	0.067 SCN	0	0.200 SCN	98	0	0
12	0.033 Hex	0.100 SCN	0	0.265 SCN	93	0	0
13	0.040 Hex	0.004 SCN	0.0016 SCN	0.080 SCN	64	20	0.320
14	0.040 Hex	0.010 SCN	0	0.080 SCN	94	5.5	0.058
15	0.040 Hex	0.010 SCN	0	0.160 SCN	87	4.4	0.050
16	0.040 Hex	0.020 SCN	0	0.080 SCN	92	1.3	0.014
17	0.040 CP	0.040 SCN	0	0.160 SCN	0	85	

[a] All reactions carried out in acetonitrile at 25°. [b] Hex = 6-heptenoyl peroxide; CP = cyclopentylacetyl peroxide. [c] Cl = $CuCl_2 \cdot 2H_2O$; Br = $CuBr_2$; SCN = $Cu(NCS)_2$. [d] Cl = CuCl; SCN = CuSCN. [e] Cl = LiCl; SCN = KSCN. [f] Products based on carbon dioxide yield.

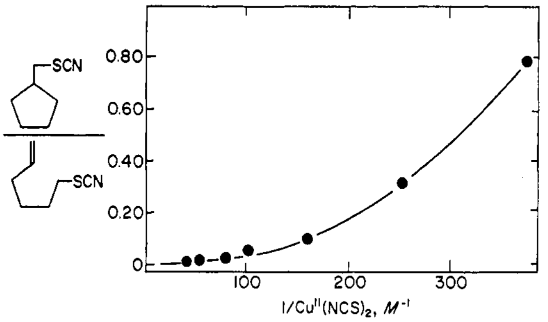


Figure 1.—The trapping of the 5-hexenyl radical by copper(II) thiocyanate.

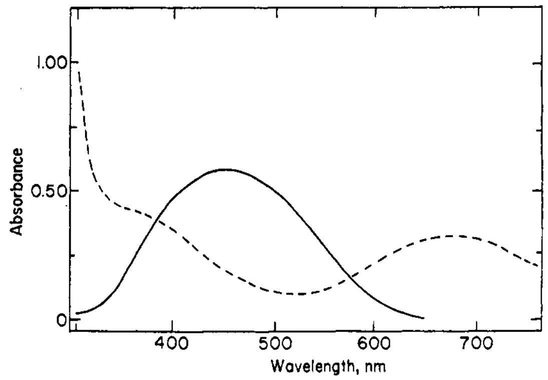
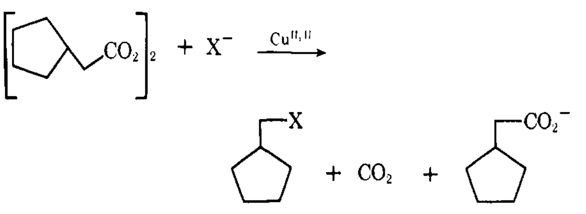


Figure 2.—Visible absorption spectrum of the decomposition of 0.040 M 6-heptenoyl peroxide by 0.010 M copper(II) thiocyanate and 0.080 M potassium thiocyanate in acetonitrile: ——, before reaction; - - - -, after reaction.

(eq 5) was tested by generating the cyclopentylmethyl radical from cyclopentylacetyl peroxide. As expected,[3] the catalytic reaction of cyclopentylacetyl peroxide with chloride, bromide, and thiocyanate afforded exclusively cyclopentylmethyl derivatives (runs 5, 9, 17, Table I) (eq 9).



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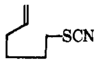
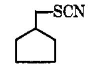
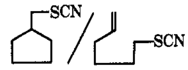
The reaction of 6-heptenoyl peroxide with copper(II) chloride, bromide, or thiocyanate gave *no* evidence of rearrangement in the range of copper(II) concentrations from 0.040 M to 0.12 M. We inferred from these results that the rates of ligand transfer to the 5-hexenyl radical were too fast for the cyclization to compete effectively. If an upper limit of a 1% yield of cyclopentylmethyl derivative was assumed, the rate constants k_L for chloride, bromide, and thiocyanate transfer were calculated to be at least $10^8\ M^{-1}\ sec^{-1}$.

Products of rearrangement were only observed when the concentration of copper(II) thiocyanate was reduced beyond 0.04 M as shown in Table II. The ratio of the yields of cyclopentylmethyl thiocyanate and 5-hexenyl thiocyanate was plotted according to eq 8 against the reciprocal of copper(II) thiocyanate concentration. The relationship, however, deviated significantly from linearity as shown in Figure 1 (runs 20–28, Table II).

The curvature in Figure 1 was attributed to the participation of several mixed ligand species of copper(II) reacting at significantly different rates. Thus, changes in the copper(II) species occurred even in the presence of excess thiocyanate as shown by the visible absorption spectrum in Figure 2, taken before and after reaction with 6-heptenoyl peroxide. It was also noted visually that the color of the solution of copper(II) thiocyanate in acetonitrile changed from deep red to yellow-green rapidly on the addition of the diacyl peroxide. The latter color could be reproduced in an independent experiment by the addition of potassium thiocyanate to copper(II) acetate.

The visible spectra of mixtures of potassium thiocyanate and copper(II) acetate were investigated over a

TABLE II
REACTION OF 5-HEXENYL RADICAL WITH COPPER(II) THIOCYANATE AND ACETATE IN ACETONITRILE AT 25°

	Reactants, *M*					Products, mol %		
Run	$Cu(NCS)_2$	$Cu(OAc)_2$	KSCN	6-Heptenoyl peroxide	1/Cu(II)			
20	0.0040	0	0.080	0.040	250	55.0	17.2	0.320
21	0.0100	0	0.080	0.040	100	81.2	4.7	0.058
22	0.0100	0	0.160	0.040	100	78.7	3.9	0.050
23	0.020	0	0.080	0.040	50	85.5	1.2	0.014
24	0.025	0	0.075	0.025	46	94.5	0.56	0.0059
25	0.0125	0	0.075	0.025	80	89.0	2.20	0.0247
26	0.00625	0	0.081	0.025	160	80.0	7.9	0.099
27	0.0025	0	0.070	0.025	400	35.9	27.8	0.780
28	0.0025	0	0.070	0.025	400	34.6	27.0	0.780
29	0.0100	0	0.080	0.0125	100	95.0	2.16	0.023
30	0.0125	0	0.088	0.0125	80	95.0	1.58	0.017
31	0.0143	0	0.093	0.0125	70	96.0	1.07	0.012
32	0.0175	0	0.102	0.0125	57	94.4	0.47	0.005
33	0.0200	0	0.110	0.0125	50	100.4	0.41	0.004
34	0	0.0020	0.0501	0.0125	500	20.8	32.4	1.565
35	0	0.0020	0.050	0.0125	500	19.5	32.6	1.670
36	0	0.0030	0.050	0.0125	333	31.2	33.3	1.065
37	0	0.0040	0.050	0.0125	250	42.6	29.4	0.695
38	0	0.0050	0.050	0.0125	200	52.6	26.6	0.510

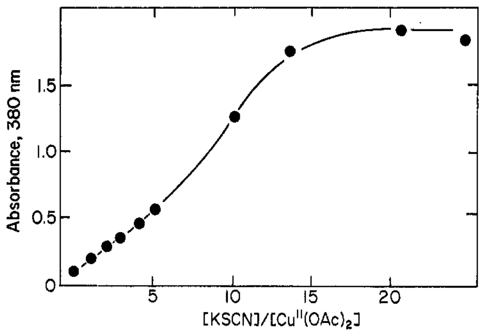


Figure 3.—The absorbance at 380 nm as a function of the molar ratio of potassium thiocyanate and copper(II) acetate.

wide range of ratios of SCN/Cu. As the thiocyanate concentration was increased, the absorption band for copper(II) acetate at 670 nm decreased and a new band appeared at 385 nm. The absorbance at 385 nm leveled off at high ratios (Figure 3). The absorption band at 450 nm attributed to tetrathiocyanatocopper(II) was not evident even up to ratios of thiocyanate to copper of 25:1. We concluded[6] that mixed ligand species I containing both thiocyanato and carboxylato ligands were formed on the addition of thiocyanate to copper(II) acetate (eq 10).

$$\underset{}{Cu^{II}OAc} + SCN^- \rightleftharpoons \underset{\text{I}}{Cu^{II}(OAc)(SCN)} \qquad (10)$$

The reactivity of the mixed ligand species I was investigated as a catalyst for the reaction of 6-heptenoyl peroxide. The ratio of the yields of cyclopentylmethyl and 5-hexenyl thiocyanates showed good linearity (Figure 4) over the range of copper(II) concentrations studied (runs 34–38, Table II). The rate constant for ligand transfer ($k_L = 2.5 \times 10^7\ M^{-1}\ sec^{-1}$) was smaller than that ($2.6 \times 10^8\ M^{-1}\ sec^{-1}$) obtained from a similar series of reactions (runs 29–33, Table II) using tetrathiocyanatocopper(II) as shown in Figure 5.

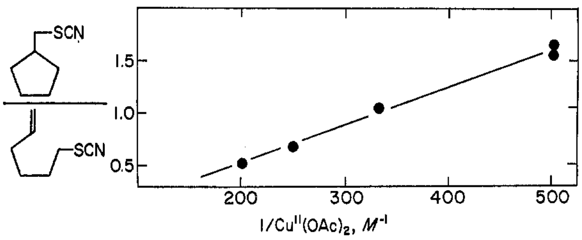


Figure 4.—The trapping of the 5-hexenyl radical by copper(II) acetate and potassium thiocyanate: $k = 2.5 \times 10^7\ M^{-1}\ sec^{-1}$.

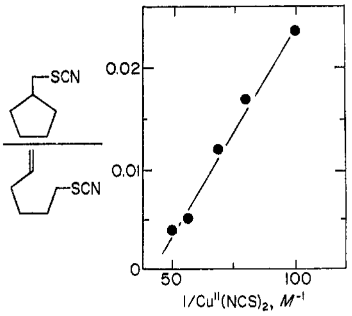


Figure 5.—Trapping of the 5-hexenyl radical by copper(II) thiocyanate and potassium thiocyanate: $k = 2.6 \times 10^8\ M^{-1}\ sec^{-1}$.

Due to the lability of these copper(II) complexes, however, it cannot be established unequivocally that these two rate constants are exclusively associated with pure I and tetrathiocyanatocopper(II) species, respectively.

The mixed ligand species I could be formed in the catalytic chain process by reaction 11 and equilibrated by reaction 12. If the latter was not rapid relative to

$$(RCO_2)_2 + Cu^I(SCN) \longrightarrow RCO_2Cu^{II}(SCN) + R\cdot + CO_2 \qquad (11)$$

$$RCO_2Cu^{II}(SCN) + SCN^- \rightleftharpoons Cu(SCN)_2 + RCO_2^- \qquad (12)$$

other steps or the equilibrium formed I, the ligand transfer process would be described by a composite of at least two rate constants. The contribution from the mixed ligand species would be favored at lower copper(II) concentrations in accord with the results shown in Fig-

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[6] Compare the spectra of related copper(II) complexes: W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, **5**, 47 (1969); H. Schmidtke, *Ber. Bunsenges. Phys. Chem.*, **71**, 1138 (1967).

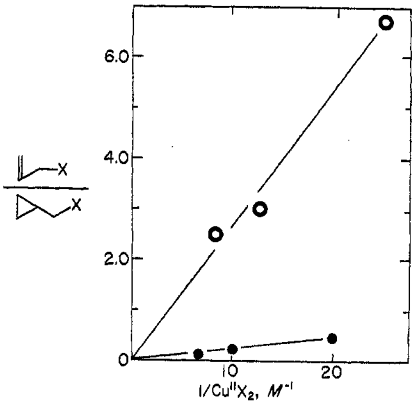
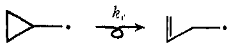


Figure 6.—The trapping of the cycloproplymethyl radical by copper(II) thiocyanate, O, and copper(II) bromide, ●.

ure 1. An alternative explanation involving the breakdown in the applicability of eq 8 in the region of low copper concentrations has not been rigorously discounted.

Oxidation of Homoallylic Radicals.—The term "homoallylic radicals" is used generically to denote the isomeric allylcarbinyl, cyclobutyl, and cyclopropylmethyl radicals.[2c] Each of these alkyl radicals was derived independently from the corresponding diacyl peroxide by reaction with copper species. Both cyclobutyl and allylcarbinyl radicals are relatively stable and do not undergo isomerization under these conditions.[2c] The cyclopropylmethyl radical, however, readily undergoes ring opening[7] to the allylcarbinyl radical with a first-order rate constant k_r estimated to be 1 × 10^8 M^{-1} $\sec^{-1}$ at 25°.[8] There is evidence that the rearrangement is reversible[9] but the equilibrium heavily favors the allylcarbinyl radical.[10] The kinetic scheme for the trapping of the cyclopropylmethyl radical (eq 14, 15) is analogous to that given earlier for the 5-hexenyl radical (eq 6, 7).



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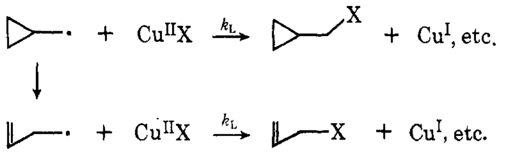

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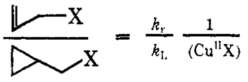
If we assume that k_L for allylcarbinyl and cyclopropylmethyl radicals are approximately the same, the relative yields of products may be expressed as shown[11] in eq 16. Since k_r for cyclopropylmethyl radical is 10^3 times larger than that for the 5-hexenyl radical, values of k_L substantially higher than 10^8 M^{-1} $\sec^{-1}$ should be attainable using this radical.



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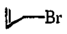
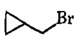
In the following study of homoallylic radicals with copper(II) halides and pseudohalides, the products of the reactions were examined first and the kinetics of the ligand transfer process then determined.

Ligand Transfer Oxidation of Homoallylic Radicals with Copper(II) Bromide.—The concentration of copper(I) bromide formed by the disproportionation of copper(II) bromide in acetonitrile was sufficient to catalyze[1] the decomposition of cyclobutanecarbonyl peroxide, allylacetyl peroxide, and cyclopropylacetyl peroxide effectively at 0° as shown in Table III.

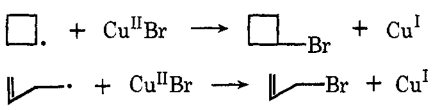
TABLE III

REACTION OF HOMOALLYLIC RADICALS WITH COPPER(II) BROMIDE[a]

	Reactants, M		Products, mol %			
Run	$CuBr_2$	Peroxide[b]	CO_2			
40	0.100	0.065 CB	98		97	
41	0.150	0.065 CB	97		97	
42	0.050	0.055 AA	100	93		
43	0.100	0.055 AA	95	90		
44	0.150	0.055 AA	93	83		
45	0.050	0.0575 CP	99	30	2.8	65
46	0.100	0.0575 CP	98	1.7	3.2	83
47	0.150	0.0575 CP	100	0.8	4.6	85

[a] Reactions were carried out in 20 ml of propionitrile at 0°. [b] CB = cyclobutyl carbonyl peroxide; AA = allyl acetyl peroxide; CP = cyclopropyl acetyl peroxide.

The oxidation of cyclobutyl (runs 40 and 41, Table III) and allylcarbinyl (runs 42–44) radicals afforded no products of rearrangement in significant amounts (eq 17, 18). On the other hand, the oxidation of cyclopropylmethyl radicals produced a mixture of homoallylic bromides whose composition varied with the concentration of copper(II) bromide (runs 45–47, Table III). Cyclopropylmethyl bromide was the predominant product, and its yield relative to the yield of allylcarbinyl bromide increased linearly with the concentration of copper(II) bromide according to eq 16 as shown in Figure 6. We calculated the second-order rate constant k_L for ligand transfer of bromine as 4.3 × 10^9 $M^{-1}\sec^{-1}$. All products were stable and the formation of small but discrete amounts of cyclobutyl bromide from the oxidation of cyclopropylmethyl radicals will be discussed further.



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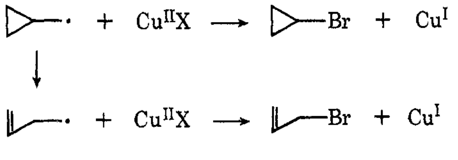

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Ligand Transfer Oxidation of Homoallylic Radicals by Copper(II) Thiocyanate.—The disproportionation of copper(II) thiocyanate in acetonitrile formed copper(I) in sufficient concentrations to catalyze the smooth decomposition of the three diacyl peroxides.[1] These reactions were complete within 30–60 min at 0°. Under

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[7] For a review, see C. Walling, "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 440 ff.

[8] A lower limit based on the isocholesteryl to cholesteryl rearrangement; see ref 4.

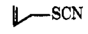
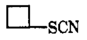
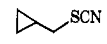
[9] L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Amer. Chem. Soc.*, **89**, 923 (1967); **89**, 3050, 6556 (1967).

[10] P. J. Krusic, D. R. Eaton, and J. K. Kochi, *ibid.*, **91**, 1877 (1969).

[11] The kinetic scheme also assumes that the cyclopropylmethyl–allylcarbinyl rearrangements is not significantly reversible under these conditions. Studies represented in Tables III–VI support the validity of this assumption.

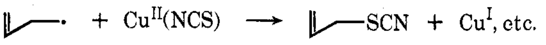
Table IV

Homoallylic Radicals with Copper(II) Thiocyanate[a]

Run	Reactants, M: $Cu(NCS)_2$	KSCN	Peroxide[b]	Products, mol %: CO_2			
50	0.040[c]	0	0.040 CB	103	2.8	79	15
51	0.040	0.080	0.040 CB	103	3.7	87	12
52	0.040	0.120	0.040 CB	100	1.5	96	4.2
53	0.040	0.200	0.040 CB	100	0.9	98	3.9
54	0.020	0.080	0.040 CB	100	1.9	95	4.5
55	0.080	0.200	0.040 CB	100	1.5	98	5.0
56	0.040[c]	0	0.040 AA	104	72	0	0
57	0.040	0.080	0.040 AA	95	76	0	0
58	0.080	0.200	0.040 AA	99	98	0	0
59	0.120	0.280	0.040 AA	102	99	0	0
60	0.040[c]	0	0.040 CP	106	79	0.8	5.6
61	0.040	0.120	0.040 CP	98	79	1.2	11.6
62	0.080	0.200	0.040 CP	95	68	2.3	22
63	0.120	0.280	0.040 CP	96	64	2.5	25

[a] Reactions were carried out in duplicate in 25 ml of acetonitrile at 0°. [b] CB = cyclobutyl carbonyl peroxide; AA = allylacetyl peroxide; CP = cyclopropyl acetyl peroxide. [c] Heterogenous.

these conditions allylcarbinyl radicals gave allylcarbinyl thiocyanate exclusively as shown in runs 56–59 in Table IV (eq 20). Cyclobutyl radicals reacted with copper(II) thiocyanate to afford predominantly, but not exclusively, cyclobutyl thiocyanate (eq 21). The best yields were obtained at the highest concentrations of thiocyanate (runs 52–55, Table IV). Smaller amounts of both allylcarbinyl and cyclobutyl thiocyanates were also produced and their proportion appeared to increase at lower concentrations of thiocyanate (runs 50 and 51, Table IV).



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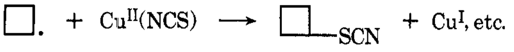
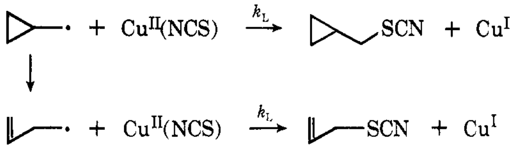


(21)

Each of the corresponding homoallylic isothiocyaates was also prepared by independent methods. The analyses of reaction mixtures were carried out under conditions in which all six isomers could be readily identified by gas chromatography. Control experiments showed that none of these homoallylic isothiocyanates was a product of the reaction nor were they isomerized under reaction conditions.

In the absence of copper the reaction of cyclobutanecarbonyl peroxide with potassium thiocyanate generated less than 1% carbon dioxide at 0° for 3 hr. After 12 hr, reanalysis indicated the presence of no homoallylic thiocyanates.

The reaction of cyclopropylmethyl radical with copper(II) thiocyanate afforded principally a mixture of allylcarbinyl and cyclopropylmethyl thiocyanates (runs 60–63, Table IV). A small amount of cyclobutyl thiocyanate was also formed. The variation in the composition of the product with the concentration of copper(II) thiocyanate was plotted in Figure 6, according to eq 16 from which we calculated the value of k_L as $3.6 \times 10^8 M^{-1} sec^{-1}$ at 25° (eq 22).



(22)

(20)

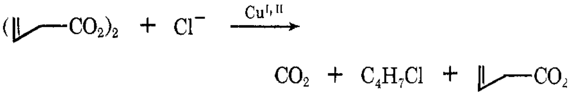
The decomposition of cyclobutanecarbonyl peroxide was also carried out with a mixed carboxylatothiocyanatocopper(II) complex I prepared *in situ* from copper(II) carboxylate and potassium thiocyanate (Table V). The relative amounts of the isomeric homoallylic thiocyanates were somewhat similar to those obtained with tetrathiocyanato copper(II). It is possible that rearranged products may have been derived *via* these mixed ligand species (*vida infra*).

At relatively low levels of thiocyanate, appreciable amounts of cyclobutene were formed (runs 71 and 72, Table V) (eq 23). The latter is characteristic of electron transfer oxidation of cyclobutyl radicals by copper(II) carboxylates.[2c] There is some ambiguity, however, whether cyclobutene found under these conditions was due to copper(II) carboxylate formed by dissociation of the mixed ligand complex given in eq 24 or by I itself.

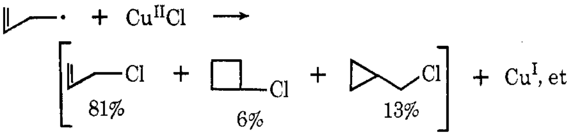
(23)

$$\underset{\mathrm{I}}{Cu^{II}(O_2CR)(NCS)} \rightleftharpoons Cu^{II}(O_2CR) + SCN^- \qquad (24)$$

Ligand Transfer Oxidation of Homoallylic Radicals with Copper(II) Chloride.—The copper-catalyzed reaction of allylacetyl peroxide and chloride in acetonitrile was initiated by the deliberate addition of small amounts of copper(I) chloride at 0°. Carbon dioxide and homoallylic chlorides were formed according to eq 25 as shown in Table VI. Although allylcarbinyl chloride was the principal product formed from the oxidation of allylcarbinyl radical by copper(II) chloride, significant amounts of other isomeric chlorides were also formed (eq 26). *The composition of the mix-*



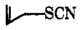
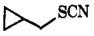
(25)



(26)

TABLE V

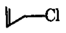
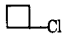
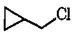
REACTION OF CYCLOBUTYL RADICALS WITH COPPER(II) CARBOXYLATES AND POTASSIUM THIOCYANATE[a]

	Reactants, *M*				Products, mol %					
Run	$Cu^{II}(OCR)_2$[b]	$Cu^{I}SCN$	KSCN	Peroxide	CO_2					
64	0.040 CB	0	0.040	0.040	105	1.7	60	5.1	[c]	[c]
65	0.040 CB	0	0.060	0.040	104	1.3	49	3.7	[c]	[c]
67	0.040 CB	0	0.080	0.040	98	2.2	82	4.7	[c]	[c]
68	0.040 CB	0	0.160	0.040	97	1.1	92	3.5	[c]	[c]
69	0.020 CB	0	0.160	0.040	101	0.06	93	3.7	[c]	[c]
70	0.020 CB	0	0.400	0.040	101	0.8	93	2.9	[c]	[c]
71	0.040 M	0.0148	0.020	0.040	104	2.9	75	9	20	0
72	0.040 M	0.0108	0.040	0.050	98	2.6	73	9	12	0

[a] Reactions were carried out in 25 ml of acetonitrile at 0°. [b] CB, R = cyclobutyl; M, R = methyl. [c] Not determined.

TABLE VI

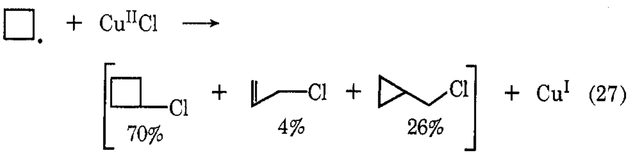
REACTION OF HOMOALLYLIC RADICALS WITH COPPER(II) CHLORIDE[a]

	Reactants, *M*				Products, mol %		Distribution, %		
Run	Peroxide[b]	$CuCl_2$	CuCl	LiCl	CO_2	C_4H_7Cl			
75	0.040 CB	0.020	0.013	0.013	95	91	4	71	25
76	0.040 CB	0.040	0.013	0.013	90	92	4	70	26
77	0.040 CB	0.040	0.013	0.013	90	92	4	70	26
78	0.040 CB	0.080	0.013	0.013	93	96	4	70	26
79	0.040 CB	0.120	0.013	0.013	91	94	4	70	26
80	0.040 CB	0.194	0.057	0.057	99	92	5	70	25
81	0.040 CB	0.230	0.057	0.057	100	93	5	70	25
82	0.040 AA	0.040	0.013	0.013	89	89	81	6	13
83	0.040 AA	0.080	0.013	0.013	99	98	81	6	13
84	0.040 AA	0.120	0.013	0.013	95	92	82	5	13
85	0.040 CP	0.020	0.013	0.013	75	75	68	6	26
86	0.040 CP	0.040	0.013	0.013	83	76	59	7	34
87	0.040 CP	0.080	0.013	0.013	90	74	47	9	44
88	0.040 CP	0.160	0.010	0.330	93	90	35	8	57
89	0.040 CP	0.194	0.010	0.390	97	91	32	8	60
90	0.040 CP	0.240	0.010	0.490	97	88	29	9	62
91	0.040 CP	0	0.020	0.020	95	65	80	6	14

[a] Reactions carried out in acetonitrile at 0°. [b] CB = cyclobutylcarbonyl peroxide; AA = allylacetyl peroxide; CP = cyclopropylacetyl peroxide.

ture of homoallylic chlorides was independent of the concentration of copper(II) chloride employed (runs 82–84, Table VI).

The reaction of cyclobutanecarbonyl peroxide under similar conditions also led to a mixture of homoallylic chlorides, in which cyclobutyl chloride predominated. The distribution of isomeric chlorides given in eq 27



(27)

was, furthermore, independent of the concentrations of copper(II) chloride and lithium chloride (see runs 75–81, Table VI).

On the other hand, the relative amounts of homoallylic *chlorides* resulting from the oxidation of cyclopropylmethyl radical with copper(II) chloride were highly dependent on the concentration of copper(II) chloride present. Thus, the yield of cyclopropylmethyl chloride increased and the yield of allylcarbinyl chloride decreased with increasing copper(II) chloride concentrations (runs 85–90, Table VI). When only copper(I) chloride was added to cyclopropylacetyl peroxide [*i.e.*, the initial concentration of copper(II) was zero], and the copper(II) species was only formed by reduction of the peroxide, the mixture of homoallylic chlorides was the same as that obtained from the oxidation of allylcarbinyl radical derived from allylacetyl peroxide (*cf.* run 91 and 82, Table VI).

Since considerabe amounts of rearranged products were formed during the oxidation of these homoallylic radicals with copper(II) chloride, the analytical methods were carefully examined to ensure that the products were not isomerized. The analytical results of reaction mixtures on standing for several days were the same as those obtained shortly after completion of the reaction (several hours). The same analyses were obtained from the crude reaction mixtures as those from which all the copper species had been removed. Each homoallylic chloride was prepared by an independent procedure and shown to be stable to conditions employed in gas chromatographic analysis. Finally, in order to test the stability of the products under reaction conditions a known amount of cyclopropylmethyl chloride (the most reactive chloride) was added to a mixture of valeryl peroxide, copper(II) and (I) chlorides and lithium chloride. After the reaction of valeryl peroxide was complete, analysis of the reaction mixture indicated a quantitative yield of *n*-butyl chloride. A quantitative recovery (reanalysis) of the cyclopropylmethyl chloride was effected with no evidence of isomerization. Cyclobutyl chloride was subjected to the same procedure and no loss or isomerization was noted. It was concluded, therefore, that the product distribution shown

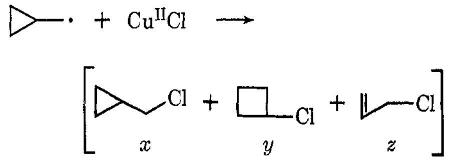
Table VII
Rates of Ligand Transfer Oxidation

Radical	Copper(II)	k_r/k_L	k_L[a]	k_L (relative)
5-Hexenyl	$Cu^{II}(NCS)$	3.9×10^{-4}	2.6×10^{8}	
Cyclopropylmethyl	$Cu^{II}(NCS)$	2.7×10^{-1}	3.6×10^{8}	1
5-Hexenyl	$Cu^{II}Cl$	$<4 \times 10^{-4}$	$>2 \times 10^{8}$	
Cyclopropylmethyl	$Cu^{II}Cl$	9.2×10^{-2}	1.1×10^{9}	3
5-Hexenyl	$Cu^{II}Br$	$<4 \times 10^{-4}$	$>2 \times 10^{8}$	
Cyclopropylmethyl	$Cu^{II}Br$	2.3×10^{-2}	4.3×10^{9}	12

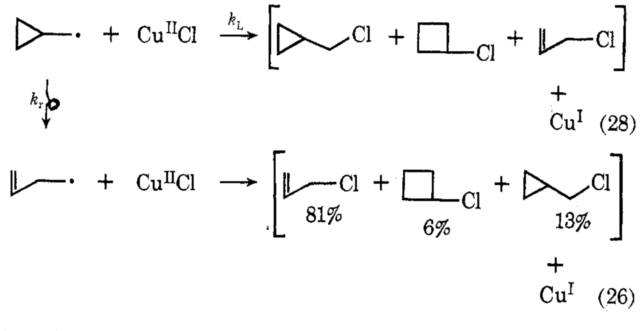
[a] At 25° assuming $k_r = 1 \times 10^5$ sec^{-1} for the 5-hexenyl radical and 1×10^8 sec^{-1} for the cyclopropylmethyl radical.

in Table VI was indeed the result of reactions carried out under kinetic control.

Rate of Ligand Transfer Oxidation with Copper(II) Chloride.—Since a single product was not formed from the oxidation of either the allylcarbinyl or cyclopropylmethyl radical by copper(II) chloride, the rate constant for ligand transfer k_L could not be simply evaluated from eq 16. We assumed for the kinetic analysis, however, that oxidation of cyclopropylmethyl radical by copper(II) chloride produced a unique mixture of homoallylic chlorides (eq 28, where x, y, and z represent mole fractions). The composition of such a single mixture would be invariant with copper(II) concentration in the *absence of isomerization of the radical*, as was the oxidation of allylcarbinyl radical given in eq 26 or cyclobutyl radical given in eq 27. The following scheme then applies (eq 28). If α represented the fraction of products derived from oxidation of the allylcarbinyl radical then



+ Cu^I, etc. (28)



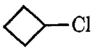
(28)

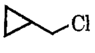
(26)

$$\frac{k_r}{k_L}\frac{1}{(Cu^{II}Cl)} = \frac{\alpha}{1-\alpha} \tag{29}$$

which is the modified form of eq 16. At a given concentration of copper(II) chloride the yields of each homoallylic chloride are given as shown in eq 30–32.


$= 0.81A + x(1 - \alpha)$ (30)


$= 0.06A + y(1 - \alpha)$ (31)


$= 0.13A + z(1 - \alpha)$ (32)

The fourth equation is supplied by the material balance (eq 33). The coefficients for the distribution of homo-

$$1.0 = x + y + z \tag{33}$$

allylic chlorides from the oxidation of the cyclopropylmethyl radical were then evaluated by solving the four simultaneous equations for each concentration of copper(II) chloride using the normalized total yield of each chloride. As a result, a distribution for x, y, and z was found, which, like the oxidation of allylcarbinyl and cyclobutyl radicals, was invariant with the copper(II) concentration (eq 34). The value of α at each concentration of copper(II) chloride was obtained from eq 30–32 (Table VI) and plotted in Figure 7. If a value for the rate of isomerization[8] of the cyclopropylmethyl radical was taken as 10^8 sec^{-1}, the rate of ligand transfer of chlorine from copper(II) was 1×10^9 M^{-1} sec^{-1} at 25° in acetonitrile.

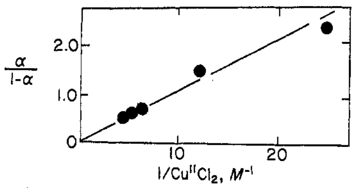
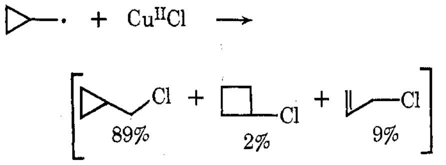


Figure 7.—The trapping of the cyclopropylmethyl radical by copper(II) chloride. See text.



+ Cu^I, etc. (34)

Rates of Ligand Transfer Oxidation by Copper(II).—Studies based on the isomerization of 5-hexenyl and cyclopropylmethyl radicals provide results which are in remarkable agreement with one another, considering a variation in rates of rearrangement by a factor of 10^3. The second-order rate constants k_L for the ligand transfer oxidation of copper(II) radicals by copper(II) thiocyanate, chloride, and bromide are summarized in Table VII.

The values of k_L represent a composite of a number of individual rate constants k_i for various copper(II) species (eq 35). Thus, copper(II) complexes generally

$$k_L(CuCl_2) = k_1(CuCl^+) + k_2(CuCl_2) + k_3(CuCl_3^-) + k_4(CuCl_4^{-2}) \tag{35}$$

are highly substitution labile, and equilibria involving a number of species must be taken into account. For example, copper(II) chloride in acetonitrile solution participates in a number of exchanges[12] tabulated in Table VIII. All of the chlorocopper(II) species are extant in appreciable amounts in acetonitrile solutions.

---

[12] (a) S. E. Manahan and R. T. Iwamoto, *Inorg. Chem.*, **4**, 1409 (1965); (b) J. Bjerrum, *Kem. Maanedsbl. Nord. Handelsblad Kem. Ind.*, **26**, 24 (1945); (c) see also R. P. Eswein, *et al.*, *J. Inorg. Nucl. Chem.*, **29**, 437 (1967); C. Furlani and G. Morpurgo, *Theor. Chim. Acta*, **1**, 103 (1963); C. C. Hinckley, *Inorg. Chem.*, **7**, 396 (1968); W. G. Hatfield and T. S. Piper, *ibid.*, **3**, 841 (1964); R. D. Willet, *et al.*, *ibid.*, **6**, 1666, 1885 (1967).

TABLE VIII
EQUILIBRIA INVOLVING COPPER(II) CHLORIDE IN SOLUTION

Equilibrium	Formation constant CH$_3$CN^a	Formation constant H$_2$O^b
$Cu^{II} + Cl^- \rightleftharpoons Cu^{II}Cl^+$	$K_1 = 10^{9.7}$	1.0
$Cu^{II}Cl^+ + Cl^- \rightleftharpoons Cu^{II}Cl_2$	$K_2 = 10^{7.9}$	0.2
$Cu^{II}Cl_2 + Cl^- \rightleftharpoons Cu^{II}Cl_3^-$	$K_3 = 10^{7.1}$	0.04
$Cu^{II}Cl_3^- + Cl^- \rightleftharpoons Cu^{II}Cl_4^{2-}$	$K_4 = 10^{3.7}$	0.01

[a] From ref 12a. [b] From ref 12b.

However, the formation constants for chlorocopper(II) species are substantially smaller in aqueous solutions.

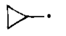
At this juncture it is impossible to separate the rate constant k_i by which each of these chlorocopper(II) species oxidize alkyl radicals. If the value of k_L listed in Table VII includes all of these species, it is reasonable to expect that some values of k_i (particularly for Cu-Cl_4^{-2}) may actually be at the diffusion-controlled limit since the value of k_e for oxidative elimination by Cu^{II} is in the range 10^7–10^8 M^{-1} sec^{-1}.[13]

Carbonium Ions as Intermediates.—The predominant product obtained from the oxidation of each homoallylic radical by copper(II) chloride was that isomeric chloride resulting from the radical with the structure intact. That is, cyclobutyl radical afforded principally cyclobutyl chloride, allylcarbinyl radical gave largely allylcarbinyl chloride. Even cyclopropylmethyl radical produced mainly cyclopropylmethyl chloride, provided the copper(II) chloride concentration was sufficiently high. In each case the by-product from the oxidation was a mixture of the other two homoallylic chlorides.

Oxidation of each homoallylic radical by copper(II) bromide and by copper(II) thiocyanate gave similar results, although the amount of rearrangement varied appreciably with the copper(II) oxidant.

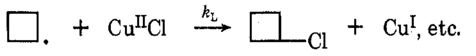
The approximate extent of rearrangement accompanying ligand transfer oxidation of each homoallylic radical by various copper(II) complexes in acetonitrile is summarized in Table IX which appears below.

TABLE IX
REARRANGEMENT RESULTING FROM LIGAND TRANSFER OXIDATION OF HOMOALLYLIC RADICALS BY COPPER(II) COMPLEXES[a]

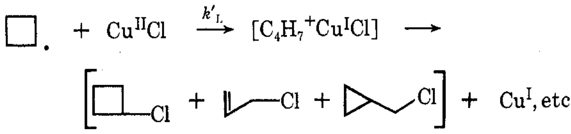
	Radical, %			
$Cu^{II}X$				Relative rate
$Cu^{II}Br$	0	0	<1	12
$Cu^{II}Cl$	20	50	15	3
$Cu^{II}NCS$	0	5	3	1

[a] Extent of arrangement extrapolated from Tables III–VI.

Since isomerization of the reactants and products can be ruled out, we interpret these results as indicating the rearrangement of an alkyl moiety *during* the oxidation step. The pattern of products obtained suggests a carbonium ion intermediate. One such scheme which would accommodate these results is given in eq 36, 37.



(36)



(37)

For example, the oxidation of cyclobutyl radical by copper(II) chloride would proceed as shown. In this scheme, two simultaneous reactions are represented by rate constants k_L and k_L' for processes which are largely homolytic and heterolytic in nature, respectively. Further evidence for the duality of mechanisms in ligand transfer oxidation of alkyl radicals will be presented.[14]

Experimental Section

Materials.—Reagents and chemicals used in the previous study have been described[1] and others are given below.

6-Chlorohexene-1.—To 5 g of lithium aluminum hydride (0.132 mol) in 250 ml of ethyl ether was added 19 g of 5-hexenoic acid (0.166 mol). After work-up, the product was distilled at 22 mm pressure, bp 76–78°, to yield 11 g of hex-5-en-1-ol. To 14.3 g of thionyl chloride (0.12 mol) was added 8 g of hex-5-en-1-ol (0.08 mol) at 50–60°. Distillation yielded 2.5 g of 6-chlorohexene-1, bp 55° (32 mm). Ir and pmr spectra were consistent with the structure of 6-chlorohexene-1.

Cyclopentylmethyl Chloride.—To 14.3 g of thionyl chloride (0.12 mol) was added 6 g of cyclopentylcarbinol (0.06 mol) at 50–60°. Distillation yielded 4.2 g of cyclopentylmethyl chloride, bp 55° (32 mm). The ir and pmr spectra were consistent with cyclopentylmethyl chloride.

Homoallylic Chlorides.—Samples of allylcarbinyl, cyclobutyl, and cyclopropylcarbinyl chlorides were generously donated by Dr. H. Lin.[15]

Cyclopentylmethyl Bromide.—To 47.5 g of phosphorous tribromide (0.175 mol) was added 50 g of cyclopentylcarbinol (0.50 mol). The reaction was maintained at 80° for 2 hr. The reaction was poured into water and extracted with ethyl ether. The ether extract was washed with water, 10% sodium bicarbonate, and water, then dried over magnesium sulfate, filtered, concentrated, and distilled to yield 31 g of material, bp 75° (15 mm). The infrared and pmr spectra confirmed the product to be cyclopentylmethyl bromide.

Homoallylic Bromides.—Samples of allylcarbinyl, cyclobutyl, and cyclopropylcarbinyl bromides were also generously donated by Dr. H. C. Lin.[15]

5-Hexenylthiocyanate.—To 12.1 g of potassium thiocyanate (0.125 mol) in 150 ml of reagent grade acetone was added 16.3 g of 6-bromohexene-1 (Columbia Co.) and the reaction refluxed for 5 hr. The precipitated potassium bromide was filtered and the acetone removed by rotary evaporation. The product and excess potassium thiocyanate were mixed with water and the product was extracted with ethyl ether. The ether extract was dried and concentrated. The crude product was distilled to yield 3 g of 5-hexenyl thiocyanate, bp 102° (9 mm). The infrared and pmr spectra confirmed the structure to be 5-hexenyl thiocyanate.

Cyclopentylmethyl Thiocyanate.—To 12.1 g of potassium thiocyanate (0.125 mol) in 150 ml of reagent grade acetone was added 16.3 g of cyclopentylmethyl bromide and the reaction mixture refluxed for 5 hr. The work-up was the same as that for 5-hexenyl thiocyanate. Distillation yielded 3 g of cyclopentylmethyl thiocyanate, bp 102° (9 mm). The infrared and pmr spectra were consistent with cyclopentylmethyl thiocyanate.

Allylcarbinyl Thiocyanate.—To 15.6 g of toluenesulfonyl chloride (0.083 mol) in 30 ml of pyridine was added 4 g of allylcarbinyl alcohol at 0°. The reaction was stirred for 3 hr and then poured into an ice–water mixture and extracted with methylene chloride. After, the extract was washed successively with dilute sulfuric acid, sodium bicarbonate, and water. After drying, the solvent was removed at room temperature by rotary evaporation to yield 10.2 g of yellow oil (allylcarbinyl tosylate). This yellow oil (10.1 g) was added to 15 g of potassium thiocyanate in 200 ml of reagent grade acetone and refluxed for 2 hr. After the work-up described for 5-hexenyl thiocyanate, distillation yielded 1.5 g of allylcarbinyl thiocyanate, bp 82–83° (25 mm). The product was confirmed by its infrared and pmr spectra.

Cyclopropylcarbinyl thiocyanate.[16]—By the procedure de-

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(14) C. L. Jenkins and J. K. Kochi, *ibid.*, in press.

(15) *Cf.* G. A. Olah and C. H. Lin, *ibid.*, **90**, 6468 (1968).

(16) L. A. Spurlock and P. E. Newallis, *Tetrahedron Lett.*, **3**, 303 (1966).

scribed for allylcarbinyl thiocyanate, 10 g of cyclopropylcarbinyl alcohol reacted with 40 g of toluenesulfonyl chloride to yield 27 g of cyclopropylcarbinyl tosylate. Reaction of 20 g of cyclopropylcarbinyl tosylate with 43 g of potassium thiocyanate was carried out at room temperature. After the work-up (see 5-hexenyl thiocyanate), distillation resulted in a mixture boiling over a wide range [45–90° (22 mm)]. Approximately 1 g of material boiling 89–90° (22 mm) was collected, and the pmr spectrum indicated that it was predominately of cyclopropylcarbinyl structure. By means of preparative gc on a 9-ft 20% FFAP column at 100°, 53 mg of material was obtained which was confirmed by pmr and infrared spectroscopy to be cyclopropylcarbinyl thiocyanate.

Cyclobutyl Thiocyanate.[16]—Cyclobutanol (10.5 g) was prepared from cyclopropylcarbinol and allowed to react with 40 g of toluenesulfonyl chloride in 80 ml of pyridine at 0° by the procedure described for allylcarbinyl thiocyanate to afford 31 g of cyclobutyl tosylate. To 26 g of potassium thiocyanate in 150 ml of reagent grade acetone was added 26 g of cyclobutyl tosylate and refluxed for 12 hr. After the work-up (see 5-hexenyl thiocyanate), 5 g of crude material was obtained. Analysis by gas chromatography (11-ft XF1150 at 150°) gave the following composition of products: allylcarbinyl isothiocyanate, 1.4%; cyclobutyl isothiocyanate, 7.5%; cyclopropylmethyl isothiocyanate, 8.3%; allylcarbinyl thiocyanate, 14.5%; cyclobutyl thiocyanate, 23.5%; cyclopropylmethyl thiocyanate, 44.5%. A pure sample of cyclobutyl thiocyanate was obtained by preparative gas chromatography on a 9-ft XF1150 column at 130°. The structure was confirmed by infrared and pmr analysis.

Homoallylic Isothiocyanates.—Each of the homoallylic isothiocyanates was prepared by reaction of the corresponding amine with carbon disulfide by the method of Hodgkins and Ettlinger.[17] Cyclobutyl amine was generously donated by Dr. L. Friedman. Each of the amines gave isomerically pure material by gas chromatography and pmr and infrared analysis.

6-Heptenoic Acid.—To 4.5 g of magnesium metal in 400 ml of dry tetrahydrofuran was added 30 g of 6-bromohexene-1 (Columbia Co.) After the magnesium metal was consumed the reaction was poured onto approximately 200 g of carbon dioxide. A solution of 6% hydrochloric acid was added at 3° until the resulting solution was acidic. The solution was then extracted with ethyl ether; the ether solution was then extracted with a 10% NaOH solution and reacidified and extracted once again with ethyl ether. The ethyl ether solution was dried over magnesium sulfate, filtered, and concentrated by rotary evaporation. The crude acid was distilled to yield 15.4 g (65%) of 6-heptenoic acid, bp 120° (12 mm) [lit.[18] 125° (15 mm)]. Gas chromatography showed it to be isomerically pure.

Allylacetic, cyclobutanecarboxylic, and cyclopropylacetic acids were as described previously.[20]

General Procedure for Preparation of Acid Chlorides.—The acid (1 equiv) was added slowly to purified thionyl chloride (1.5 equiv) at 50–60°. After all the acid was added, the solution was refluxed for approximately 1 hr. The excess thionyl chloride was distilled off at atmospheric pressures. The acid chloride was distilled at either reduced pressure or atmospheric pressure. The following acid chlorides were prepared by this method: 6-heptenoyl chloride, cyclobutylcarbonyl chloride, valeryl chloride, 2-methylbutyryl chloride, allylacetyl chloride, and cyclopropylacetyl chloride.

Preparation of Diacyl Peroxides. General Method A.—A solution of 1.1 equiv of pyridine and 50 ml/mol of diethyl ether were cooled to −10°. Then 0.55 equiv of 30% hydrogen peroxide were added portionwise so that the temperature did not exceed 0°. The solution was stirred rapidly and the acid chloride, 1.0 equiv, added dropwise, maintaining the temperature between −5 and −10°. The reaction was then stirred an additional 2 hr at 0°. The reaction was then neutralized by the addition of a small amount of chilled 10% H_2SO_4 (throughout the work-up the solution is *not allowed to warm above* 10°). The reaction was then diluted with ethyl ether and the peroxide extracted. The solution was diluted further with pentane and washed with chilled 10% sulfuric acid, 10% sodium bicarbonate, and distilled water. The pentane ether extract was dried and concentrated on a rotary evaporator using a water aspirator. Final traces of solvent were removed by use of a vacuum pump. (The flask was *never warmed* and was always maintained in an ice bath throughout the evaporation).

General Method B.—The diacyl peroxide was made directly from the carboxylic acid and anhydrous hydrogen peroxide in the presence of dicyclohexyl carbodiimide by the method of Greene and Kazan.[19]

Analysis of Diacyl Peroxides.—Diacyl peroxides were analyzed by infrared spectroscopy and showed a characteristic doublet at 5.55 and 5.61 μ. The purity was further determined by iodometeric titration using ferric chloride (0.02% solution) as a catalyst. Peroxides were not used unless their purity exceeded 98%.

Reaction Procedure.—The copper(II) complex and any other additives were dissolved in the appropriate solvent contained in a 125-ml erlenmeyer flask. The diacyl peroxide was then added from a standard solution by means of a pipet. The flask was capped with a rubber septum and flushed with a stream of helium for approximately 15 min to remove any oxygen from the system. The appropriate copper(I) species in solution was then added by means of a hypodermic syringe through the rubber septum. The reactions were then run until carbon dioxide was literated completely.

General Reaction Procedure for Copper(II) Bromide and Thiocyanate.—The copper(II) complex and additives, if any, were dissolved in the appropriate solvent. The 125-ml erlenmeyer flask was then capped with a rubber septum and the solution flushed with helium for approximately 15 min to remove oxygen. A solution of the diacyl peroxide was added by means of a hypodermic syringe. The reaction was then run until carbon dioxide was no longer evolved.

Analysis.—All gaseous and liquid products were analyzed by standard gas chromatographic procedures using the internal standard method.[2] In all cases standard solutions or standard gas samples were prepared and calibrations of products *vs.* internal standard determined under reaction conditions.

Gases.—Carbon dioxide and ethane were determined by gas chromatography on a 2-ft Porapax Q (150–200 mesh) column at room temperature using thermal conductivity detectors. Gaseous hydrocarbons were determined on a 15-ft 15% Dowtherm A on firebrick or a 20-ft 20% silver nitrate–15% benzonitrile column on Chromosorb W.

Liquid Products.—The analyses for liquid products were performed by removing an aliquot of the reaction mixture and an aliquot of the internal standard solution to a separatory funnel. Excess water was added and the organic products were extracted with an appropriate solvent, usually ethyl ether or pentane. The extract was then washed several times with water and 10% sodium bicarbonate to remove the solvents (usually acetonitrile). In those cases where the products were soluble in water, the reaction mixture was analyzed directly by adding an aliquot of the internal standard to an aliquot of the reaction mixture. Possible interference in the analysis from the presence of copper salts was carefully checked.

Registry No.—Cyclopentylmethyl, 23907-66-6; copper(II) thiocyanate, 15192-76-4; copper(II) chloride 7447-39-4; copper(II) bromide, 7789-45-9; copper(II) acetate, 142-71-2; copper(II) cyclobutylcarboxylate, 31280-78-1; 5-hexenyl, 16183-00-9; cyclopropylmethyl, 2154-76-9; allylcarbinyl, 2154-62-3; cyclobutyl, 4548-06-5; copper(I) chloride, 7758-89-6; copper(I) thiocyanate, 1111-67-7; 6-heptenoyl peroxide, 26841-80-5; potassium thiocyanate, 333-20-0; lithium chloride, 7447-41-8; allylcarbinyl thiocyanate, 764-49-8; 6-chlorohexene-1, 928-89-2; cyclopentylmethyl chloride, 13988-39-1; cyclopentylmethyl bromide, 3814-30-0; cyclopentylmethyl thiocyanate, 31280-81-6; 5-hexenyl thiocyanate, 31246-84-1.

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