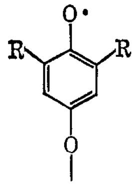
oratory[27] there have been no reports concerning the reactivities of phenoxy radicals although their possible physiological importance requires that they be highly selective in their reactions.

The complex, low molecular weight mixtures obtained on the oxidative polymerization of 2,6-diisopropylphenol[28] compared to the linear polymers obtained from 2,6-dimethylphenol may be due to the high selectivity of the intermediate phenoxy radicals IV. From



IV

the reactivity ratio for the 4-methoxyphenoxy radical, the relative rates of hydrogen abstraction from a tertiary $\geqslant$CH (isopropylbenzene) *vs.* a primary C–H (toluene) is calculated as 50.[29] Therefore, this reaction, leading to complex C–C and C–O compounds, would be of much greater importance in the case of the isopropyl compounds.

Kartesz and Zito[26] have reported that the relative rate of reaction of the reactive intermediate in the enzymatic oxidation of hydroquinone compared to phenol is 52. For the peroxy radical in the present study the ratio of rate constants for the same compounds in reaction 5 is 30. This result is not inconsistent then with the intervention of phenoxy radicals or semiquinones as intermediates in the reaction.

Experimental Section

Materials. The oxidizable hydrocarbon 9,10-dihydroanthracene was obtained from Henley and Co. (98% minimum). This material after three recrystallizations from ethanol had mp 109.5–110.0° (corrected) (lit.[8] 109–110.5°). Periodically during use, the hydrocarbon was subjected to iodometric analysis and contained less than 0.02% (limit of detection) hydroperoxide. Spectrophotometric analysis revealed an impurity of 0.08% anthracene.

2,2,3,3-Tetraphenylbutane was synthesized by the method of Müller and Roscheisen,[30] mp 122–123° (lit.[30] 122–123°).

9,10-Dihydro-9-anthryl hydroperoxide was prepared according to the procedure of Bickel and Kooyman.[5] Two recrystallizations from toluene–pentane yielded a material, mp 109–110°; iodometric analysis gave a value of 95% peroxide. The material contained a 4.8% impurity of anthracene as determined by spectrophotometric analysis.

3-Hydroxypyrene was prepared according to the procedure of Tietze and Bayer[31] and Vollman, *et al.*,[32] mp 180° (lit.[32] 179–180°). *Anal.* Calcd: C, 88.05; H, 4.62. Found: C, 88.03; H, 4.74.

The other phenols were obtained from commercial sources and purified by recrystallization and sublimation to yield materials which gave melting points which agreed with published literature values. Another criterion of purity was the single spot obtained by thin layer chromatography on silica plates on elution with benzene followed by 20% chloroform–benzene mixtures.

Rate measurements were carried out by means of the apparatus described in earlier publications from this laboratory.[2]

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(28) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959).

(29) Calculated on the basis that $(k_3)_{\text{cumene}}/(k_3)_{\text{toluene}}$ is 5.0; *cf.* G. A. Russell, *ibid.*, **78**, 1047 (1956).

(30) E. Müller and G. Roscheisen, *Ber.*, **90**, 543 (1957).

(31) E. Tietze and O. Bayer, *Ann.*, **539**, 207 (1939).

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Carbon Monoxide Reactions. II. The γ Radiation Initiated Chlorocarbonylation of Paraffins

Warren A. Thaler

Contribution from the Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey 07036. *Received December 15, 1966*

Abstract: The synthesis of acid chlorides by means of a radical chain reaction utilizing carbon tetrachloride and carbon monoxide as reagents has been extended to include a variety of hydrocarbons. The problems encountered when peroxide initiation was used have been traced to initiator-destroying products formed from the interaction of the metal reactor surface with acid chlorides. This difficulty has been circumvented by using γ radiation to initiate chlorocarbonylations. The γ radiation provides the added advantage of temperature-independent initiation. Acid chlorides have been produced from some representative paraffins ranging from ethane to hexadecane. Some approximate G values have been determined and used to estimate the magnitude of the kinetic chain length.

A novel route to acid halides, from paraffins *via* halogenation in the presence of carbon monoxide, is being investigated in this laboratory. The *peroxide-initiated* synthesis of cyclohexanecarboxylic acid chloride from cyclohexane, which was used as a model reaction to demonstrate the feasibility of this technique, was the subject of a previous communication.[1]

Our initial attempts to achieve this halocarbonylation with a variety of the more commonly used radical halogenating agents were unsuccessful and gave cyclohexyl halides exclusively. The synthesis of acid halide (eq 6) as opposed to alkyl halide (eq 5) involves a competition between CO and halogenating reagent for alkyl radi-

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(1) W. A. Thaler, *J. Am. Chem. Soc.*, **88**, 4278 (1966).

cals. In order to favor the reaction of alkyl radical with CO a high concentration of carbon monoxide to halogenating reagent is desirable.

N-Halo compounds such as N-bromosuccinimide (NBS) are sources of low concentration molecular halogen generated *in situ.*[2] With NBS, for example, the species which abstracts the hydrogen from a hydrocarbon has been shown to be a bromine atom,[3] while the alkyl radical appears to react with a low concentration of Br_2 to give alkyl bromide.[4] The abstraction of a hydrogen by bromine atom gives an alkyl radical and a molecule of HBr, which reacts rapidly with NBS to give a molecule of Br_2.

$$\mathrm{RH + Br\cdot \longrightarrow R\cdot + HBr}$$

$$\mathrm{{>}N{-}Br + HBr \longrightarrow {>}NH + Br_2}$$

The use of such a technique for *in situ* generation of low concentration halogen coupled with high CO pressures (6000 psi) should have resulted in exceedingly large ratios of CO to halogen. Despite this apparent advantage, the attempted halocarbonylations using NBS or N,N-dichlorobenzenesulfonamide produced only cyclohexyl halide without any trace of acid chloride.

An alternate method of enabling the reaction of alkyl radical with CO to compete effectively against its reaction with halogenating reagent was the use of reagents which transfer a halogen slowly. Carbon tetrachloride was chosen as such a halogenating reagent[5] (which according to our reasoning[1] should have this attribute). The following series of chain-propagation steps were envisaged, where the sequence of steps 1 and 2 would give alkyl chloride and chloroform (eq 5) while

$$\mathrm{CCl_4 \xrightarrow{peroxide} Cl_3C\cdot}$$

$$\mathrm{RH + \cdot CCl_3 \longrightarrow R\cdot + HCCl_3} \tag{1}$$

$$\mathrm{R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3} \tag{2}$$

$$\mathrm{R\cdot + CO \rightleftharpoons R\underset{\cdot}{C}O} \tag{3}$$

$$\mathrm{R\underset{\cdot}{C}O + CCl_4 \longrightarrow RC(O)Cl + \cdot CCl_3} \tag{4}$$

1, 3, and 4 would lead to the desired acid chloride in the over-all reaction (eq 6).

$$\mathrm{RH + CCl_4 \longrightarrow RCl + CHCl_3} \tag{5}$$

$$\mathrm{RH + CCl_4 + CO \longrightarrow RCOCl + CHCl_3} \tag{6}$$

Successful chlorocarbonylations of cyclohexane using CCl_4 as the reagent could be achieved only after some serious obstacles were overcome. Initially, erratic results and low conversions were encountered, but an examination of the effect of steel (simulating the pressure reactor surface) and acid chloride on the "simple" CCl_4 chlorination of cyclohexane (eq 5) indicated that these two materials acted in concert to retard the chlorination and suggested that this was also the problem in the case of the chlorocarbonylation. The use of an epoxy-coated steel reactor solved this problem but presented new difficulties owing to the instability of the epoxy film. A double glass insert of a concentric tubular design was developed to minimize contact of liquid reactants with the steel surface of a rocked Aminco pressure reactor, while still permitting free access of gaseous CO. Using this liner good selectivities (up to 89%) and conversions were realized.[1] The selectivities were highly reproducible but the conversions were still somewhat variable presumably owing to variable traces of acid chloride–metal contaminant reentering the reaction zone. This problem has now been circumvented and the chlorocarbonylation reaction has been extended to several additional hydrocarbons.

Results and Discussion

The chlorination of cyclohexane by CCl_4 in sealed glass tubes to which metal and/or acid chloride had been added was reexamined with initiation by γ-radiation from a cobalt-60 source instead of the *t*-butyl peroxide used in our earlier work. Table I contrasts the effect of the two types of initiation. The peroxide-initiated chlorination was very sensitive to the combined presence of acid chloride and metal while the radiation-initiated reaction was essentially insensitive to these materials. These results suggest that the metal in conjunction with the acid chloride served as an efficient destroyer of the peroxide initiator and did not act as a radical chain inhibitor.

Table I. The Influence of Metal and Acid Chloride on the Peroxide- and γ-Initiated Chlorination of Cyclohexane by CCl_4[a]

Metal added, %[b]	Acid chloride added, %[c]	Conversion, % γ-ray initiation	 Peroxide initiation
None	None	76	97
3	None	. .	93
None	10	72	83
Trace	10	76	40–55
1	10	78	36
3	10	. .	8

[a] Mole ratio of cyclohexane:CCl_4 = 2. [b] Steel reactor filings, mole % based on CCl_4. [c] Cyclohexane carboxylic acid chloride, mole % based on CCl_4.

Using γ initiation, a 2:1 mole ratio of cyclohexane to carbon tetrachloride (130°) with 2900 psi carbon monoxide pressure gave 69% selectivity to the acid chloride (31% chlorocyclohexane) compared to 67% selectivity for a peroxide-initiated reaction[1] at the same pressure. No special precautions were required regarding contact with the metal reactor surface, but a glass insert was retained in subsequent experiments since the reaction mixture appeared to develop less color when prolonged contact of the acid chloride product with metal was avoided. Cyclopentane was also found to behave in essentially the same fashion as cyclohexane.

Since no difference in the course of the chlorocarbonylation was evident, a reexamination of the chlorocarbonylation of cyclohexane using γ initiation was postponed. Instead we chose to first gain some information on the scope of this acid chloride synthesis. Some low molecular weight hydrocarbons whose simple structure permitted identification of the isomeric products were examined first, followed by higher molecular weight paraffins. Reactions were run using a 2–2.5:1

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(2) (a) J. Adams, P. A. Gosselain, and P. Goldfinger, *Nature*, 171, 704 (1953); (b) F. L. J. Sixma and R. H. Riem, *Koninkl. Ned. Akad. Wetenschap. Proc., Ser. B.*, 61, 183 (1958); (c) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961).

(3) (a) R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354, 3141 (1963); (b) G. A. Russel, C. De Boer, and K. M. Desmond, *ibid.*, **85**, 365 (1963); G. A. Russel and K. M. Desmond, *ibid.*, **85**, 3139 (1963); (c) C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963).

(4) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2850 (1963).

(5) J. P. West and L. Schmerling, *ibid.*, **72**, 3525 (1950).

Table II. Reaction of Ethane with CO and CCl_4[a]

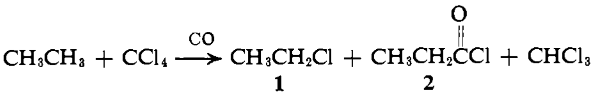
Temp, °C	Conversion[b] based on CCl_4, %	Selectivity, % Propionyl chloride[c]	Selectivity, % Ethyl chloride[d]
250	51	73	27
250	54	68	32
190	9.3	79	21
160	6.6	73	27

[a] 5300 psi at 25°, 16 hr. [b] Determined by $CHCl_3$ formed. [c] Determined as its ester derivative. [d] Determined by difference between $CHCl_3$ and C_2H_5COCl.

mole ratio of hydrocarbon to CCl_4 and radiation from a 6000-curies cobalt-60 source. After reaction, the acid chlorides were converted to their corresponding esters by treatment with an appropriate alcohol. The products derived from lower hydrocarbons were then analyzed by vapor phase chromatography (vpc) and the products identified by comparison with authentic samples. The products from the higher molecular weight hydrocarbons were isolated by fractional distillation.

An additional advantage which could be gained by the use of radiation was the ability to run reactions with essentially temperature-independent initiation. This made possible reactions at higher temperatures, where peroxide initiators have half-lives which are too small to permit their effective use.

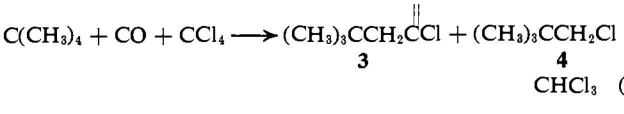
Ethane was the simplest hydrocarbon examined (Table II) and could give only two possible products, ethyl chloride (**1**) and propionyl chloride (**2**).



$$\underset{}{CH_3CH_3} + CCl_4 \xrightarrow{CO} \underset{\mathbf{1}}{CH_3CH_2Cl} + \underset{\mathbf{2}}{CH_3CH_2\overset{\overset{O}{\|}}{C}Cl} + CHCl_3 \qquad (7)$$

The volatility of the ethyl chloride did not permit its direct analysis since considerable loss occurred on venting carbon monoxide after termination of the reaction. The selectivities were determined instead by assuming ethyl chloride to be equal to the difference between the yields of chloroform and propionyl chloride. The chlorocarbonylation of ethane required a temperature greater than 200° to effect reasonable conversions in a 16-hr reaction period. The primary hydrogen atoms of ethane were found considerably less reactive toward hydrogen abstraction than the secondary hydrogens of cyclohexane. This is partly explained by the 3.5 kcal/mole greater bond dissociation energy of primary C–H bonds than that of the secondary. The other factor in this difference in reactivity is the relatively high degree of stability of the abstracting reagent, the trichloromethyl radical. At 250°, 73% selectivity to propionyl chloride at about 50% conversion of the carbon tetrachloride could be realized.

Neopentane which also contains only primary hydrogens required high temperatures to achieve a reasonable rate of conversion (Table III). The selectivity to acid chloride was still quite good at these temperatures. In addition to the chloroform, the only products which were observed by vpc analysis were neopentanecarboxylic acid chloride (**3**) and neopentyl chloride (**4**). Some carbonization was apparent at the 250° reaction temperature.



$$C(CH_3)_4 + CO + CCl_4 \longrightarrow \underset{\mathbf{3}}{(CH_3)_3CCH_2\overset{\overset{O}{\|}}{C}Cl} + \underset{\mathbf{4}}{(CH_3)_3CCH_2Cl} + CHCl_3 \qquad (8)$$

Table III. Reaction of Neopentane with CCl_4 and CO[a]

Initial CO pressure at 25°	Temp, °C	Time, hr	Conversion, %[b] $CHCl_3$[c]	Conversion, %[b] Products[d]	Selectivity, % Acid chloride	Selectivity, % Alkyl chloride
5300	190	16	6.6	7.0	100	..
5300	190	16	7.2	7.9	100	..
5300	190	64	19	25	100	..
4400	250	16	39	45	74	26

[a] Mole ratio $C(CH_3)_4:CCl_4 = 2$. [b] Calculated on basis of initial CCl_4. [c] $CHCl_3$:initial CCl_4. [d] Sum of neopentyl products:initial CCl_4.

The abstraction of a hydrogen atom from propane by trichloromethyl radical produces both a secondary and a primary alkyl radical. The primary alkyl radical can give rise to *n*-propyl chloride (**5**) and *n*-butyryl chloride (**6**), while the secondary alkyl radical would give isopropyl chloride (**7**) and isobutyryl chloride (**8**).

$$CH_3CH_2CH_3 + \cdot CCl_3 \longrightarrow CH_3CH_2CH_2\cdot \qquad (9)$$

$$CH_3CH_2CH_2\cdot + CCl_4 \xrightarrow{CO} \underset{\mathbf{5}}{CH_3CH_2CH_2Cl} + \underset{\mathbf{6}}{CH_3CH_2CH_2COCl} \qquad (10)$$

$$CH_3CH_2CH_3 + \cdot CCl_3 \longrightarrow CH_3\underset{\cdot}{C}HCH_3 \qquad (11)$$

$$CH_3\underset{\cdot}{C}HCH_3 + CCl_4 \xrightarrow{CO} \underset{\mathbf{7}}{CH_3CH(Cl)CH_3} + \underset{\mathbf{8}}{CH_3CH(CH_3)COCl} \qquad (12)$$

Statistically, three times more primary than secondary radicals would be formed; however, the stability of the trichloromethyl radicals and the lower bond energy of the secondary hydrogens should result in a lower activation energy for the abstraction of the secondary hydrogens. Examination of the isomer distribution of the primary- and secondary-substituted products from the chlorocarbonylation of propane (Table IV) reveals that the ratio of secondary to primary intermediate alkyl radicals is about 4, which represents a relative reactivity per hydrogen for secondary:primary hydrogen of approximately 12. Acid chlorides are the principal reaction products but an increase in reaction temperature or a decrease in CO pressure decreased the selectivity for acid chlorides and favored alkyl chloride formation.

Table IV. Chlorocarbonylation of Propane[a]

CO pressure, psi[b]	Temp, °C	Time, hr	Conversion, %[c] $CHCl_3$[d]	Conversion, %[c] Products[e]	Selectivity, % Acid chloride *sec* (**8**)	Selectivity, % Acid chloride *n* (**6**)	Selectivity, % Alkyl chloride *sec* (**7**)	Selectivity, % Alkyl chloride *n* (**5**)
5300	160	16.0	27	26	53	14	28	5
5300	190	15.8	46	36	42	16	38	4
5300	190	20.3	42	41	43	18	37	3
4100	190	16.3	40	34	34	16	46	4

[a] Mole ratio initially 2.5, propane:CCl_4. [b] Measured at 25°. [c] Calculated on basis of initial CCl_4. [d] $CHCl_3$ produced:CCl_4 initial. [e] Sum of alkyl chlorides and acid chlorides produced:CCl_4 initial.

The reaction of butane was quite similar to that of propane. Four products were possible: *n*-butyl chloride (**9**) and *n*-valeryl chloride (**10**) from reaction at the primary position, along with *sec*-butyl chloride (**11**) and α-methylbutyryl chloride (**12**) from the secondary position.

Again the isomer distribution of primary and secondary substitution products indicated that a secondary hydrogen of *n*-butane was about 12 times as reactive at 160° toward $\mathrm{Cl_3C\cdot}$ as a primary hydrogen.

$$\mathrm{CH_3CH_2CH_2CH_3 + CCl_4 \xrightarrow{CO} CHCl_3 + \underset{\textbf{9}}{CH_3CH_2CH_2CH_2Cl} +}$$

$$\underset{\textbf{10}}{\mathrm{CH_3CH_2CH_2CH_2COCl}} + \underset{\textbf{11}}{\mathrm{CH_3CH_2CHClCH_3}} + \underset{\textbf{12}}{\mathrm{CH_3CH_2CH(CH_3)COCl}} \tag{13}$$

As expected the presence of secondary hydrogens imparted enhanced reactivity, and good conversions could be obtained with *n*-butane (Table V) at lower temperatures than those required for ethane or neopentane. This was quite favorable since increased temperature was found to have a deleterious effect on the formation of acid chloride. Although good selectivities to acid chloride were obtained with neopentane and ethane at the high temperatures necessary for their reaction, hydrocarbons with secondary hydrogens were less selective in the formation of acid chloride at high temperatures. Carbonylation of secondary alkyl radicals appears to be more difficult than that of primary radicals and is favored by lower temperatures. Indeed the decrease in acid chloride from 78% of the total product at 130° to 50% at 190° is mainly at the expense of the secondary acid chloride with corresponding increase in secondary chloride.

Table V. Chlorocarbonylation of *n*-Butane[a]

CO pressure, psi[b]	Temp, °C	Time, hr	Conversion, %[c] $\mathrm{CHCl_3}$[d]	Conversion, %[c] Products[e]	Acid chloride, % *sec* (**12**)	Acid chloride, % *n* (**10**)	Alkyl chloride, % *sec* (**11**)	Alkyl chloride, % *n* (**9**)
5300	130	15.7	22	24	70	8	22	...
5200	160	15.8	37	38	58	11	31	...
4300	160	17.3	36	39	52	10	38	...
5300	160	64.1	75	75	41	15	44	...
5300	160	4.1	16	16	59	8	33	...
5300	190	15.7	49	46	37	16	47	...
5300	190	15.9	54	53	34	16	50	...

[a] Mole ratio initially 2.1:1, *n*-butane:$\mathrm{CCl_4}$. [b] Measured at 25°. [c] Calculated on basis of initial $\mathrm{CCl_4}$. [d] $\mathrm{CHCl_3}$ produced: $\mathrm{CCl_4}$ initial. [e] Sum of alkyl chlorides and acid chlorides:$\mathrm{CCl_4}$ initial.

Unlike the other hydrocarbons which were examined, isobutane which contains a tertiary hydrogen did not give acid chloride in high selectivity, instead *t*-butyl chloride (**13**) was the principal reaction product with less than 10% pivalyl chloride (**14**) being formed. The attack by $\mathrm{Cl_3C\cdot}$ appeared quite selective since no primary substitution products such as isobutyl chloride or β-methylbutyryl chloride could be detected.

$$\mathrm{(CH_3)_3CH + CCl_4 \xrightarrow{CO} \underset{\textbf{13}}{(CH_3)_3CCl} + \underset{\textbf{14}}{(CH_3)_3CCOCl} + CHCl_3} \tag{14}$$

These results indicate that reactions with hydrocarbons containing a significant number of tertiary hydrogens will not be favorable for acid chloride production, and suggest that hydrocarbons which produce radicals that are of lower energy than *t*-butyl radical cannot be suitable substrates for chlorocarbonylation.

The relation between hydrocarbon structure and selectivity to acid chloride formation is related to the ease with which acyl radicals lose carbon monoxide. The acyl radicals which lose CO most readily are those which give the most stable alkyl radicals (tertiary > secondary > primary), therefore, the selectivity to acid chloride should decrease with the stability of the alkyl radical involved. The rate at which acyl radicals lose carbon monoxide (eq 3) compared to their rate of reaction with carbon tetrachloride, as in eq 4, has been measured

$$\mathrm{R\underset{\cdot}{C}O \longrightarrow R\cdot + CO} \tag{3}$$

recently by Applequist and Kaplan[6] who generated the acyl radicals from aldehydes in $\mathrm{CCl_4}$ solution. Using *n*-butyraldehyde, isobutyraldehyde, and pivaldehyde, they found at 135° k_{-3}/k_4 was 0.14, 1.14, and 12.3 when $\mathrm{R\cdot}$ was *n*-propyl, isopropyl, and *t*-butyl, respectively.

Apparently, secondary acyl radicals lose CO an order of magnitude faster than primary acyl radicals, and tertiary acyl radicals two orders of magnitude faster than primary. Our findings in the chlorocarbonylation reaction are consistent with these results. In a primary system where the acyl radicals have relatively little tendency to lose carbon monoxide, we observe a high selectivity to acid chloride, while with a tertiary system where loss of CO from acyl radical occurs readily, very poor selectivity is observed. Secondary radical systems are intermediate, giving high selectivities only under favorable conditions.

An attempt to chlorocarbonylate methyl chloride to chloroacetyl chloride was unsuccessful.

$$\mathrm{CH_3Cl + CCl_4 + CO \not\longrightarrow CH_2Cl_2 + ClCH_2COCl + CHCl_3} \tag{15}$$

Even at 250° no conversion of $\mathrm{CCl_4}$ to $\mathrm{CHCl_3}$ could be detected, demonstrating that $\mathrm{Cl_3C\cdot}$ was incapable of abstracting a hydrogen from $\mathrm{CH_3Cl}$. Bond dissociation energies indicate that ethyl radical ($\mathrm{CH_3CH_2\cdot}$) and chloromethyl radical ($\mathrm{ClCH_2\cdot}$) are of comparable stability; however, data on the chlorination of methane, methyl chloride, and ethane[7] (at 100°) show that their reactivities are in the ratio of 1:3:170. Thus, the deactivation by the electronegative inductive effect of the chloride substituent makes methyl chloride only 0.018 as reactive as ethane toward chlorine atom. $\mathrm{Cl_3C\cdot}$ and $\mathrm{Cl\cdot}$ have the same bond moment, so a similar deactivation by the chloride substituent can be expected. Furthermore, considerably greater differences in reactivity would be anticipated when the less reactive trichloromethyl radical is involved instead of a chlorine atom. Since the chlorocarbonylation of ethane has been shown to require a 250° reaction temperature to achieve significant conversions, it is reasonable that methyl chloride is unreactive at this temperature. Another implication of this finding is that the chlorocarbonylation of methane with $\mathrm{CCl_4}$ will not be possible.

The chlorocarbonylation of several higher molecular weight *n*-paraffins was examined to determine if these could be successfully converted to secondary acid chlorides. Before turning to preparative-scale runs, which would necessitate the use of a large, heavy-walled reactor with the resultant decrease in the absorption of

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(6) D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, 87, 2194 (1965).

(7) H. O. Pritchard, J. B. Pyke, and A. C. Trotman-Dickenson, *ibid.*, 77, 2629 (1955).

γ radiation, several small-scale reactions with the same Aminco microbomb and 20 g of reaction mixture as used with the light hydrocarbons were examined for purposes of comparison. The conversion of CCl_4 to $CHCl_3$ was measured at several reaction temperatures (Table VI). The results at 130° were similar to those obtained with cyclohexane.

Table VI. Chlorocarbonylation of n-C_{11} Paraffin[a]

Temp, °C	Initiator	Conversion, %[b]
190	γ rays (Co^{60})	70
160	γ rays (Co^{60})	66
130	γ rays (Co^{60})	47
100	γ rays (Co^{60})	31
130	Peroxide[c]	67

[a] 5300 psi CO at 25°; 16 hr; 2:1 undecane:CCl_4 (mole). [b] Over-all conversions measured from $CCl_4 \longrightarrow CHCl_3$. [c] Protected from contact with metal surface during reaction.

The preparative-scale (1 mole) chlorocarbonylations were run in a 3-l. Aminco bomb equipped with a conventional glass insert. Reactions at 130° had to be irradiated for about 48 hr to get conversions equivalent to those obtained in 16 hr in the microbomb. After the reactions were terminated the conversions of CCl_4 to $CHCl_3$ were determined by adding a known quantity of 1-chloro-3-fluorobenzene to a small aliquot and analyzing for $CHCl_3$ by vpc. These values were in excellent agreement with conversions determined from the sum of the weights of the acid chlorides (isolated as esters) and alkyl chlorides obtained after distillation.

Tables VII–IX give the results of the chlorocarbonylations of C_{11}, C_8, and C_{16} n-paraffins. Analysis of the ester fraction from n-undecane by vpc and comparison with n-butyl n-dodecanoate, which had a longer retention time than the secondary esters, demonstrated that no reaction took place at the primary position. No attempt was made to separate the isomeric secondary acid esters.

Table VII. Preparative-Scale Chlorocarbonylation of Undecane (n-C_{11})[a]

Product[b]	CCl₄ conversion[c] Mole	Mole % (select.)	Product distribution Mole	Mole %
n-Butyl dodecanoates	0.373	69.0	0.373	74.3
Di-n-butyl tridecandioates	0.030	5.5	0.015	3.0
Chloro-n-butyl dodecanoate	0.036	6.7	0.018	3.5
Chloroundecanes	0.102	18.8	0.102	20.1
Total	0.541[c]	100.0	0.508	100.0

[a] 2 moles of undecane; 1 mole of CCl_4; 5200 psi CO at 25°; γ initation; 130°. [b] Acid chloride products esterified with n-butyl alcohol. [c] 54.1% of CCl_4 *converted.*

In order to get an estimate of the γ radiation available to initiate reaction chains the energy absorbed by 20 g of a ferrous–ferric dosimeter solution[8] was used to calibrate the microbomb reactor for conditions simulating chlorocarbonylation runs. The dose was shown to be a linear function of time (see Experimental Section) and was found to be 1.24×10^{17} 100 ev/g hr. Using this value, G values (molecules/100 ev) for several chlorocarbonylations were determined for 20-g reaction samples containing a 2:1 molar ratio of hydrocarbon to CCl_4. The data are summarized in Table X. It should be emphasized that these are rough values and do not represent any attempt at efficient utilization of radiation. Nevertheless, the values are quite informative since they permit a direct comparison of chlorocarbonylation and chlorination of cyclohexane by CCl_4. Such a comparison was not possible using peroxide initiation because of the difficulties encountered with the metal–acid chloride destruction of the initiator and the resulting lack of reproducibility in determining conversions for chlorocarbonylations.

Table VIII. Preparative-Scale Chlorocarbonylation of Octane (n-C_8)[a]

Product[b]	CCl₄ conversion[d] Mole % (select.)	Mole	Product distribution Mole %	Mole
Butyl nonanoate	78.8	0.278	81.4	0.278
Disubstituted products[c]	6.4	0.023	3.3	0.011
Chlorooctane	14.8	0.053	15.3	0.053
Total	100.0	0.354[d]	100.0	0.342

[a] 2 moles of octane; 1 of mole CCl_4; 5600 psi CO at 25°; γ initiation; 130°. [b] Acid chloride products esterified with n-butyl alcohol. [c] Chlorinated ester and diester. [d] 35.4% of CCl_4 *converted.*

Table IX. Preparative-Scale Chlorocarbonylation of Hexadecane (n-C_{16})[a]

Product[b]	CCl₄ conversion[c] Mole % (select.)	Mole	Product distribution Mole %	Mole
Ethyl heptadecanoate	70.5	0.404	77.0	0.404
Diethyl octadecandioate	11.9	0.068	6.5	0.034
Ethyl chloroheptadecanoate	5.2	0.030	3.0	0.015
Chlorohexadecane	12.4	0.071	13.5	0.071
Total	100.0	0.573[c]	100.0	0.524

[a] 2 moles of hexadecane; 1 of mole CCl_4; 7200 psi CO at 25°; γ initiation; 130°. [b] Acid chloride products esterified with ethanol. [c] 57.3% of CCl_4 *converted.*

Table X. Radiation Dose Determination for the Chlorocarbonylations of Some Hydrocarbons[a]

Hydrocarbon reacted	G values, moles/100 ev	Reaction time, hr	Conversion, %[b]
n-Undecane	3.80×10^2	8.67	30.9
Cyclohexane	4.59×10^2	8.67	26.5
Cyclohexane	5.15×10^2	4.33	14.7
Cyclohexane[c]	1.24×10^3	4.33	35.5

[a] Dose rate 1.24×10^{17} 100 ev/g hr (20 g). [b] 6000 psi CO at 25°; 130° reaction. [c] Chlorination of cyclohexane with CCl_4.

The peroxide-initiated chlorination of cyclohexane by CCl_4 (Table XI) revealed that over 500 moles of product was formed per mole of peroxide. Each peroxide molecule gives two radicals, indicating a minimum chain length of 250, assuming each radical initiates a

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[8] S. C. Lind, "Radiation Chemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1961, pp 57–61.

chain (longer chains if initiator is less than 100% efficient). The G value for the chlorocarbonylation of cyclohexane was about 40% of the value for chlorination, indicating that over 100 molecules of product are formed in the chlorocarbonylation for each radical generated.

Table XI. Peroxide-Initiated Chlorination of Cyclohexane by Carbon Tetrachloride[a]

Initiator, %[b]	Conversion, %[c]	Moles/mole of peroxide
2.51	99.9	39.8
1.00	99.0	99.0
0.527	96.5	183
0.246	86.5	351
0.120	70.0	583
0.000	11.1	...

[a] 2:1 molar ratio cyclohexane:CCl_4, 130°. [b] *t*-butyl peroxide; per cent of initial CCl_4 concentration. [c] *Ca.* four half-lives of initiator.

A detailed investigation of the effect of reaction variables on rates and selectivities in hydrocarbon chlorocarbonylations is in progress. This information should provide more insight into the reaction mechanism and permit optimization of rates and yields.

Experimental Section

Chlorocarbonylation of Cyclohexane. In a typical experiment, a mixture of 16.8 g (0.2 mole) of cyclohexane, 15.4 g (0.1 mole) of CCl_4, and 6.5 g (0.05 mole) of 1-chloro-3-fluorobenzene was prepared. A 20-ml portion of this solution was placed in a glass insert which in turn was placed into a 300-ml, chrome-vanadium steel Aminco microbomb. The bomb was placed into a rocker assembly, which had been modified by affixing holders along the horizontal axis to accommodate the cobalt-60 source. The vessel was pressured to 2900 psi with CO at ambient (~25°). The vessel was then heated to 130°, and the CO pressure rose to about 4000 psi. The γ source which consisted of four stainless steel plates, of about 1500 curies each, with cobalt-60 slugs imbedded inside were then lowered into the holders by remote control.

The reaction vessel was rocked in front of these plates for 18 hr, after which time the source was removed and the bomb cooled and vented. An excess of ethanol was added to the reaction mixture which was allowed to stand for several hours before analysis.

Analysis was accomplished using an F & M 810 vpc equipped with a 9-ft column, 2-ft D.C. 200 silicone oil and 7-ft Ucon LB550X, 20% on 60–80 mesh, acid-washed Chromosorb W. The unit was programmed at 6°/min from 75 to 176° with a 10-min upper limit hold. Area ratios of the product peaks to the internal standards were determined and multiplied by the appropriate correction factor, determined by calibration with weighed mixtures of authentic samples, to determine the molar ratios.

In this reaction the results were 47% conversion based on $CHCl_3$, and 52% conversion based on chlorocyclohexane + cyclohexanecarboxylic acid chloride (determined as the ethyl ester). Selectivity to acid chloride: [acid chloride/(alkyl chloride + acid chloride)] = 69%.

The Chlorocarbonylation of Undecone. In a typical preparative-scale reaction, 312.6 g (2.0 moles) of *n*-undecane and 153.8 g (1.0 mole) of CCl_4 were placed in a glass insert for a 3-l. Aminco pressure bomb. The bomb, which fit a large rocker assembly equipped to accommodate the radiation source, was pressured to 5200 psi at ambient, and then the reactor was maintained at 127–129° for 48 hr while being irradiated.

After cooling and venting, a 4.66-g aliquot of the reaction mixture was removed and 0.652 g of 1-chloro-3-fluorobenzene added. Vpc analysis indicated about 50% conversion of CCl_4 to chloroform. Then 74.12 g (1.0 mole) of *n*-butyl alcohol was added to the rest of the reaction mixture which became quite warm and evolved HCl. After standing overnight, the mixture was treated carefully with $NaHCO_3$ until no more CO_2 evolution occurred. The solution was filtered and the solid washed with CCl_4. The washings were combined with the filtrate, and the liquid mixture was distilled. The distillation could be followed by vpc using a 4-ft column of 20% silicone gum rubber on Chromosorb W. The fractions are summarized in Table XII.

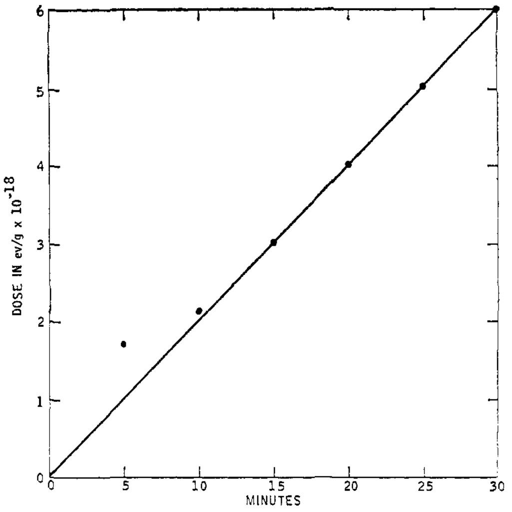

Figure 1. Calibration of absorbed dosage in a 300-ml steel reactor.

Table XII

Fraction no.	Bp, °C (mm)	Wt, g	Products	Anal., %
3	94–99 (32)	180.0	Undecane	100
4	70 (12)	31.7	Undecane	92.6
			Chloroundecanes	7.4
5	60–80 (1)	20.4	Undecane	16.6
			Chloroundecanes	83.4
6	114–120 (0.4)	95.5	Butyl dodecanoates (trace of chloride)	99
7	113–144 (0.005)	10.4	Chloro ester	50
			Diester	50
Residue		3.6		

Fractions 1 and 2 contained the low boilers CCl_4, $CHCl_3$, and n-C_4H_9OH. Fractions 3–6 were analyzed by vpc; fraction 7 gave an infrared spectrum essentially the same as fraction 6, but it could not be eluted from the vpc column. The boiling point suggested that it was a disubstituted undecane and elemental analysis and molecular weight confirmed this.

Elemental Analysis. Fraction 6. *Anal.* Calcd for $C_{16}H_{32}O_2$ (butyl dodecanoates): C, 74.94; H, 12.58; Cl, 0; mol wt, 256.4. Found: C, 73.56; H, 12.55; Cl, 0.89; mol wt, 252, 255. After redistillation C, 74.99; H, 12.66; Cl, <0.2.

Fraction 7. *Anal.* Calcd for $C_{16}H_{31}O_2Cl$ [$C_{11}H_{22}Cl(CO_2C_4H_9)$]: C, 66.07; H, 10.74; Cl, 12.19; mol wt, 290.9. Calcd for $C_{21}H_{40}O_4$ [$C_{11}H_{22}(CO_2C_4H_9)_2$]: C, 70.74; H, 11.31; Cl, 0; mol wt, 356.5. Found: C, 68.69; H, 11.03; Cl, 6.04; mol wt, 320. Calcd for a 50:50 mixture of these two anticipated disubstitution products: C, 68.04; Cl, 6.09; mol wt, 323.7.

The results of the chlorocarbonylation of undecane are tabulated in Table VII.

Dosimetry. The microbomb reactor was calibrated using a 20-g sample of a Fe^{2+}–Fe^{3+} dosimeter solution.[8] The reaction was limited to 30-min irradiation time, since excessive conversions of Fe^{2+} to Fe^{3+}, which became difficult to measure, occurred if longer times were used. The radiation absorbed for the time required to affix and remove the four cobalt-60 source plates was determined and substracted from the total radiation absorbed. Small variations in the time required for manipulation of the source introduced a small error into the calibration at short irradiation times (5 min), but a linear absorption of radiation with time (Figure 1) was demonstrated and the average dose rate of 1.24×10^{17} (100 ev/g hr) was used to calculate G values.

To determine G values (molecules of product formed per 100 ev absorbed), 20-g samples of solutions containing 2 moles of hydrocarbon/mole of CCl_4 were irradiated in the same reactor. The product formed was determined by vpc analysis. G values were calculated by dividing the number of molecules of product produced by the number of 100 ev [$(1.24 \times 10^{17})(20)$(reaction time, hr)] absorbed.

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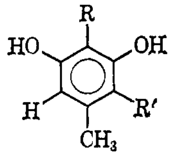
Nuclear Magnetic Resonance. Influence of Substituents on the Long-Range Spin–Spin Coupling Constant between Benzylic and Ring Protons in the Orcinol Series[1a]

Donald T. Witiak, Dhun B. Patel,[1b] and Youlin Lin

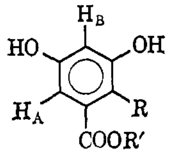
Contribution from the Laboratories of Medicinal Chemistry, College of Pharmacy, University of Iowa, Iowa City, Iowa 52240. *Received October 24, 1966*

Abstract: Long-range spin–spin coupling between benzylic *ortho* and *para* ring protons in a number of substituted orcinol derivatives is discussed. The data show that coupling of methyl to *ortho* ring protons is not affected by the nature of the substituent introduced *para* to the methyl group. Introduction of CHO *ortho* to the methyl group causes an increase in the *ortho* coupling constant, a reflection of increased π-bond order between the carbons holding the methyl and *ortho* protons. Utilization of electron-withdrawing groups larger than CHO does not increase the π-bond order and the *ortho* coupling constant in this series because of steric inhibition of resonance.

Desire to obtain orcinol derivatives of the general structure I for metabolism studies prompted investigation of these compounds by means of nuclear magnetic resonance in order to confirm the direction of the substitution reaction utilized in their synthesis. During the course of these investigations long-range spin–spin coupling was observed between the Ar–CH_3 group and ring protons.



I, R = R′ = H
II, R = $COOCH_3$; R′ = H
III, R = COOH; R′ = H
IV, R = NO_2; R′ = H
V, R = $COOCH_3$; R′ = CHO
VI, R = H; R′ = CHO
VII, R = H; R′ = COOH
VIII, R = H; R′ = $COOCH_3$
IX, R = H; R′ = NO_2



X, R = R′ = H
XI, R = CHO; R′ = CH_3

Long-range coupling has been studied extensively in other systems but only during recent years has benzylic coupling received much attention.[2] Generally, side-chain ring coupling involving sp^3-hybridized carbon atoms has been observed in heterocyclic[2a,3] and some polycyclic[2a,4] aromatic ring systems. While Hoffman[5] was able to observe splitting of the proton and methyl resonances in mesitylene, spectra of *p*- and *o*-xylenes showed only single lines. Freeman[6] also reported that the methyl proton resonance of 3,5-di-*t*-butyl-4-hydroxytoluene exists as a triplet with $|J| = 0.60$ cps. This is in agreement with observations reported by Rottendorf and Sternhell[7] who studied a series of three isomeric tetrachlorotoluenes. The resonance assigned to the methyl group in the tetrachlorotoluene series indicated *ortho* and *para* coupling of methyl to ring protons to be equal ($|J| = 0.63$ cps), while *meta* coupling was considerably smaller (0.36 cps).

Hoffman[8] and others[9] have suggested such long-range couplings, presumably involving σ–π configuration interactions,[2a,10] are evidence of hyperconjugation between the methyl group and π-electron orbitals. While hyperconjugation seems to be necessary for benzylic coupling, studies with polycyclic[2a,4,7] and heterocyclic[2a,3] compounds indicated the magnitude of the *ortho* coupling constant to be dependent upon the π-bond order between the carbons holding the methyl and *ortho* protons. Orcinol (I) derivatives are particularly suitable to a study of the magnitude of such long-range couplings relative to their dependence upon π-bond order since (1) hydroxyl groups prevent ad-

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