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ORGANIC HALIDE-ETHYLENE GROWTH REACTION CATALYZED BY RUTHENIUM COMPLEXES

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Summary

$Ru(CO)_3(PPh_3)_2$ and a variety of other zero-valent ruthenium complexes promote the reaction of iodoalkanes with ethylene to produce higher molecular weight 1-iodoalkanes. The chemistry is best explained by the intermediacy of alkyl radicals generated by reaction of the ruthenium complexes with iodoalkanes. With the exception of α-chlorotoluene, organic bromides and chlorides do not undergo the growth reaction.

Introduction

Iodoethane reacts with ethylene in the presence of organic free radical initiators [1,2] to form a mixture of higher molecular weight iodoalkanes (eqn. 1). This reaction would be more useful if the molecular weight range of the product could be narrowed by further reaction of the lower molecular weight product iodides with ethylene. However, attempting to do this with organic radical initiators is subject to side reactions resulting from initiator attack on carbon—hydrogen bonds.

$$EtI + n\ CH_2{=}CH_2 \rightarrow Et(CH_2CH_2)_nI \qquad (1)$$

We have investigated transition metal complexes as catalysts for the ethylene-haloalkane growth reaction with the preconceived notion that these initiators would permit more control over the reaction because of the highly specific oxidative-addition attack of metal complexes on carbon—halogen bonds [3-5]. Many metal complex catalysts indeed have been found and their mode of catalytic behavior studied. In this paper, ruthenium catalysts and the scope of the haloalkane-ethylene growth reaction are reported. Subsequent papers will deal with catalysts of a variety of other metals. Most of the studies involve organic

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iodide substrates since organic bromides and chlorides were found to be considerably less reactive.

Results and discussion

The iodoalkane-ethylene growth reaction was achieved by placing 0.5 mmol of a zero-valent ruthenium complex, 20 mmol of the organic iodide and 30 ml of benzene in a small autoclave flushed with nitrogen. Ethylene was then introduced, the system heated (75°-150°C) and the solution stirred. The maximum pressure ranged from 1000-1500 psi. The reaction is usually complete in less than 60 minutes; longer reaction periods have little effect on the products, regardless of the ruthenium complex used.

The growth reaction of iodoethane with ethylene proceeds smoothly at 125°C in the presence of a variety of zero-valent ruthenium complexes (eqn. 1). The results are summarized in Table 1 where typical product compositions are listed as well as the moles of iodoethane and ethylene that reacted per mole of catalyst. The products consisted of mixtures of straight chain 1-iodoalkanes: secondary iodides were not formed. Iodides up to $C_{18}H_{37}I$ have been detected. No reaction occurred in the absence of a catalyst or in the presence of attendant ligands alone, such as Ph_3P. Considerable variation in catalyst effectiveness is indicated by the wide range of observed substrate conversion levels.

Iodoalkanes from iodomethane through 1-iodododecane all underwent the ethylene growth reaction in the presence of $Ru(CO)_3(Ph_3P)_2$ (Table 2). Thus, if higher molecular weight 1-iodoalkanes are preferred, the intermediate products from the iodoethane-ethylene reaction can be isolated and further converted with ethylene. A typical molar product composition obtained, for example,

TABLE 1

IODOETHANE-ETHYLENE GROWTH REACTION CATALYZED BY ZERO-VALENT RUTHENIUM COMPLEXES[a]

	IR ω(C=O) (cm^{-1})	Reaction time (h)	Conversion		
			C_2H_5I (%mol)	C_2H_5I (mol/mol catalyst)	C_2H_4 (mol/mol catalyst)
$Ru(CO)_3(n\text{-}Bu_3P)_2$	1820	2	35	14	19
$Ru(CO)_3(Cy_3P)_2$[c]	1830	3	42	17	21
$Ru(CO)_3Py_2$	1810	17	30	12	15
$Ru(Ph_3P)_4(CH_3CN)_2$[b]	—	6	76	30	73
$Ru(CO)_3(Ph_3P)_2$	1898	2	95	38	94
$Ru(CO)_3(Ph_3As)_2$	1892	2	5	2	2.4
$Ru(CO)_4(Ph_3P)$[b]	2060 1980 1940	48	75	30	67
$Ru(CO)_3(diphos)$	1880	1.5	33	13	19
$Ru(CO)_3(p\text{-}Tol_3P)_2$	1895	2	90	36	85

[a] Conditions: 0.5 mmol catalyst, 20 mmol iodoethane, 30 ml benzene, 1000-1500 psig ethylene, 125°C reaction temperature. [b] Kindly supplied by Dr. E.O. Sherman, Jr., Department of Chemistry, University of Ontario, London, Ontario, Canada. [c] Cy = cyclohexyl, Py = pyridine, diphos = bis(1,2-diphenylphosphine)ethane, p-Tol = p-tolyl.

TABLE 2

IODOALKANE-ETHYLENE GROWTH REACTION CATALYZED BY $Ru(CO)_3(Ph_3P)_2$[a]

	Reactant RI				
	CH_3I	C_2H_5I	n-C_4H_9I	n-$C_6H_{13}I$	n-$C_{10}H_{21}I$
Conversions:					
RI (mol/mol catalyst)	13	31	23	21	13
C_2H_4 (mol/mol catalyst)	42	70	40	32	18
Average mol C_2H_4/mol of RI converted	3.23	2.26	1.74	1.52	1.39

[a] Same conditions as listed in Table 1.

from 1-iodohexane is: 53% 1-iodooctane, 30% 1-iododecane, 14% 1-iodododecane and 4% 1-iodotetradecane. Secondary iodoalkanes tend to undergo olefin forming side reactions in addition to the usual growth reaction. 2-Iodo-2-methylbutane undergoes predominantly HI elimination to form isopentenes.

As shown in Table 3, difunctional iodocompounds, $I(CH_2)_nI$, $Cl(CH_2)_4I$, $NC(CH_2)_4I$ and $EtO_2C(CH_2)_3I$, also react with ethylene in the presence of $Ru(CO)_3(Ph_3P)_2$. The latter two substrates contained impurities and product identification was made by GLC only; however, it appears that they do undergo the ethylene growth reaction. Some cyclopropane also was formed from the substrates 1,3-diiodopropane and diiodomethane (vide infra).

Attempts to achieve ethylene growth of bromoalkanes and chloroalkanes in the presence of $Ru(CO)_3(Ph_3P)_2$ were largely unsuccessful. However, α-chlorotoluene was 28% converted: the chloride product consisted of 3-phenyl-1-chloropropane (44%), 5-phenyl-1-chloropentane (37%), 7-phenyl-1-chloroheptane

Product composition (mol %)							
C_4H_9I	$C_6H_{13}I$	$C_8H_{17}I$	$C_{10}H_{21}I$	$C_{12}H_{25}I$	$C_{14}H_{29}I$	$C_{16}H_{33}I$	$>C_{16}H_{33}I$
70	25	5	—	—	—	—	—
75	23	2	—	—	—	—	—
78	20	2	—	—	—	—	—
35	22	20	14	9	—	—	—
25	33	20	14	8	—	—	—
80	20	—	—	—	—	—	—
30	25	19	13	6	2	—	—
64	26	8	2	—	—	—	—
25	30	20	11	4	2	2	—

TABLE 3

DIFUNCTIONAL IODOALKANE-ETHYLENE GROWTH REACTION CATALYZED BY $Ru(CO)_3(Ph_3P)_2$[a]

	Reactant RI[b]						
	ICH_2I	$I(CH_2)_3I$	$I(CH_2)_4I$	$I(CH_2)_5I$	$Cl(CH_2)_4I$	$NC(CH_2)_4I$	$EtO_2C(CH_2)_3I$
Conversion (%) of RI, to products listed below	32[c]	5[c]	41	41	41	4	52
Product composition (mol %)							
$R(CH_2CH_2)_1I$	96	78	83	40	36	90	44
$R(CH_2CH_2)_2I$	4	22	16	33	44	10	36
$R(CH_2CH_2)_3I$	—	—	1	16	15	—	20
$R(CH_2CH_2)_4I$	—	—	—	11	5	—	—

[a] Same conditions as listed in Table 1, except the reaction temperature was 150°C for $I(CH_2)_5I$ and $Cl(CH_2)_4I$. [b] R is the functionalized alkyl group attached to a reactive iodine center, i.e., R = ICH_2, $I(CH_2)_3$, $Cl(CH_2)_4$, etc. [c] In addition to this conversion to products listed below, about 8% of the diiodoalkanes were converted to cyclopropane.

(10%), 9-phenyl-1-chlorononane (6%) and 11-phenyl-1-chloroundecane (3%). The reaction was not a clean one as various alkenyl- and alkyl-benzenes also were produced. Ethylene and chloroalkanes, 1,2-dichloroethylene, chloroacetonitrile, chloropropionitrile, diethyl bromoacetal, 2-chloropyridine or γ-bromopropionitrile failed to react. If a small amount of LiI (~5 mmol) is added to the system containing bromoethane (20 mmol), a mixture of higher molecular weight bromoalkanes and iodoalkanes are obtained wherein the ratio of product bromoalkanes and iodoalkanes are roughly equivalent to the ratio of reactant bromide and iodide. Undoubtedly, halide exchange occurs in the system and only iodoalkanes produced in situ undergo the growth reaction.

Zero-valent ruthenium complexes most efficiently catalyze the topic reaction; e.g., $Ru(acac)_3$, $RuCl_3 \cdot 3H_2O$, $RuCl_2(CO)_2(PPh_3)_2$ and $RuI_2(CO)_2(PPh_3)_2$ are inactive. During the course of reaction, $Ru(CO)_3(Ph_3P)_2$ is gradually converted to the inactive $RuI_2(CO)_2(PPh_3)_2$. Similarly, other catalysts in Table 1 were converted to inactive diiodides. At first, the reaction was presumed to proceed by a three-step mechanism involving an oxidative-addition of RI to the metal complex (eqn. 2), a series of ethylene insertions into the resultant alkylmetal to increase the length of the alkyl group (eqn. 3), and finally a reductive-elimination step to produce the product $R(CH_2CH_2)_nI$ (eqn. 4)*. However, for a number of reasons (vide infra) we now believe the reaction occurs via a metal complex-initiated free radical pathway. The first step might be either an oxidative-addition or a simple coordination of the iodoalkane to the ruthenium (eqns. 2 and 5, respectively). In the proposed next step, an alkyl radical is generated either by homolytic scission of the metal—carbon (eqn. 6) or the carbon—iodine bond (eqn. 7). The generated alkyl radical grows with ethylene (eqn. 8) and, subsequently, chain transfers with the substrate iodide (EtI, etc.) to form the product iodoalkane and a new substrate alkyl radical (eqn. 9). Ruthenium diiodides probably are formed by attack of $RuIL_4$ on an iodoalkane (eqn. 10).

$$RI + RuL_5^{*} \rightarrow RuI(R)L_4 + CO \qquad (2)$$

$$RuI(R)L_4 + n\ CH_2{=}CH_2 \rightarrow RuI[(CH_2CH_2)_nR]L_4 \qquad (3)$$

$$RuI[(CH_2CH_2)_nR]L_4 \rightarrow [RuL_4] + R(CH_2CH_2)_nI \qquad (4)$$

$$RI + RuL_5 \rightarrow RI{\cdots}RuL_5 \qquad (5)$$

$$RuI(R)L_4 \rightarrow R\cdot + RuIL_4 \qquad (6)$$

$$RI{\cdots}RuL_5 \rightarrow R\cdot + RuIL_4 + CO \qquad (7)$$

$$R\cdot + n\ CH_2{=}CH_2 \rightarrow R(CH_2CH_2)_n\cdot \qquad (8)$$

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* Throughout this article L is CO or another ligand, such as Ph_3P. Many of the reactions may involve more than one step but are listed as single steps for simplicity. For example, losses or gains of ligands in the metal coordination sphere or the coordination of a substrate prior to reaction, etc., are not shown. Also, the number of ligands could deviate from that indicated in the equations.

$$R(CH_2CH_2)_n\cdot + RI \rightarrow R(CH_2CH_2)_nI + R\cdot \quad (9)$$

$$RuIL_4 + RI \rightarrow RuI_2L_4 + R\cdot \quad (10)$$

$$2R\cdot \rightarrow R{-}R + RH + \text{olefin}_{\text{(possible chain termination)}} \quad (11)$$

A radical mechanism would be in keeping with previous proposals that certain (non-ruthenium) metal carbonyls generate free radicals from polyhalomethanes. For example, Bamford et al. have initiated polymerizations in this way [6], and ethylene has been telomerized with polychloromethanes [7]. Also, free radical intermediates are believed to be involved in the oxidative addition, per se, of iodoalkanes to iridium(I) [8] and platinum(0) [9] complexes.

Information about the initial step of the iodoethane-ethylene growth reaction was obtained from infrared spectra of the reaction media obtained under actual reaction conditions. With passage of time, carbonyl bands due to the catalyst, $Ru(CO)_3(PPh_3)_2$, decreased in intensity as those due to $RuI_2(CO)_2(PPh_3)_2$ and an intermediate increased (see IR data in Table 4). Subsequently, bands due to the catalyst and the intermediate gradually disappeared and only those due to $RuI_2(CO)_2(PPh_3)_2$ remained, at which time, the growth reaction ceased (determined by GLC analyses). When ethylene was omitted and $Ru(CO)_3(PPh_3)_2$ heated with a solution of iodoethane, a transient intermediate also was detected having somewhat different carbonyl adsorptions than those of the intermediate mentioned above. The intermediate could not have been $RuIL_4$ since this transient metal species would be identical with and without ethylene present. It seems more likely that the detected intermediate was $RuI(R)(CO)_2(PPh_3)_2$, where R is Et in the absence of ethylene and a higher molecular weight alkyl group with ethylene present.

Support for an alkylruthenium precursor to the formation of radicals, was obtained by using a hydride complex, $RuI(H)(CO)(PMe_2Ph)_3$ or $RuI(H)(CO)_2(PPh_3)_2$ as the catalyst. These materials behaved catalytically the same as $Ru(CO)_3(PPh_3)_2$. Since ruthenium hydrides are known to add to olefins [10,11],

TABLE 4

HIGH RESOLUTION INFRARED DATA[a] OF RUTHENIUM COMPLEXES

	ν(C=O) (cm^{-1})	Adsorptivity ($l\ mol^{-1}\ cm^{-1}$)
$Ru(CO)_3(Ph_3P)_2$	1898	6000
$RuI_2(CO)_2(PPh_3)_2$	2052	1660
	1993	1400
Intermediate with EtI and $CH_2{=}CH_2$ present $RuI(R)(CO)(PPh_3)_2$ (?)	2022[b] 1958[b]	(equivalent)
Intermediate with EtI only present $RuI(Et)(CO)_2(PPh_3)_2$ (?)	2028[c] 2060[c]	— —

[a] Obtained with a Cary Model 90 double beam spectrometer operating at 3 cm^{-1} resolution over the spectral region 1500-2100 cm^{-1}. [b] Spectra obtained under actual reaction conditions of 125°C and 1000-1500 psig of ethylene. [c] Spectra obtained at 125°C in the absence of ethylene.

addition to ethylene in the present case would be expected to produce the same alkylruthenium intermediate as is obtained from EtI and $Ru(CO)_3(PPh_3)_2$ (eqns. 12 and 13).

$$Ru(CO)_3(PPh_3)_2 + EtI \rightarrow RuI(Et)(CO)_2(PPh_3)_2 + CO \quad (12)$$

$$RuI(H)(CO)_2(PPh_3)_2 + CH_2{=}CH_2 \rightarrow RuI(Et)(CO)_2(PPh_3)_2 \quad (13)$$

As noted earlier, s-iodoalkanes and especially t-iodoalkanes produced substantial amounts of olefins from the iodide under the reaction conditions employed for the ethylene growth reaction. This also is consistent with the intermediacy of alkylruthenium species since s-alkyl- and t-alkyl-ruthenium compounds would tend to undergo the competing olefin elimination reaction more easily than would primary alkylruthenium compounds (e.g., eqns. 14 and 15).

$$Ru(CO)_3(PPh)_2 + \text{iodocyclohexane} \rightarrow RuI(\text{cyclohexyl})(CO)_2(PPh_3)_2 \quad (14)$$

$$RuI(\text{cyclohexyl})(CO)_2(PPh_3)_2 \rightleftharpoons RuI(H)(CO)_2(PPh_3)_2 + \text{cyclohexane} \quad (15)$$

While the metal hydride can re-add to the olefin, it might also terminate by reaction with another iodoalkane to give the inactive diiodide complex (eqn. 16).

$$RuI(H)(CO)_2(PPh_3)_2 + RI \rightarrow RuI_2(CO)_2(PPh_3)_2 + RH \quad (16)$$

The differences encountered in the conversion of iodoethane by the various ruthenium complexes (Table 1) might be explained by an olefin elimination reaction like eqn. 15, with consequent formation of inactive ruthenium diiodide complexes (eqn. 16), which competes favorably in some cases with the normal production of radicals (eqn. 6). The difference might also be due to the influence of ligands on the rate of complex deactivation (eqn. 10) relative to chain transfer with iodoethane (eqn. 9). Furthermore, metal complexation of alkyl radicals could have a significant effect.

Although there is reason to believe that alkylruthenium compounds are radical precursors for the growth reaction, it is possible that some radicals may be generated by direct attack of the metal complex on the iodoalkane (eqns. 5 and 7).

While not unequivocal, the total fabric of observations seems consistent with free radical steps (eqns. 8 and 9) following the initiation steps just discussed. The low reactivity of bromoalkanes and chloroalkanes is supportive of a radical mechanism since the chain propagating transfer reaction (eqn. 9 with Br or Cl in place of I) is expected to be slow relative to that of iodoalkanes. $Ru(CO)_3(PPh_3)_2$ was converted by 1-bromobutane to $RuBr_2(CO)_2(PPh_3)_2$ and typical free radical products, n-octane (45% yield), n-butene and n-butane (10-15% yield). Of the chlorides, only α-chlorotoluene gave higher chlorides. The benzylic chloride, being more reactive than other chloroalkanes, apparently could cause chain transfer (eqn. 9); however, some alkenyl- and alkyl-benzenes were found in the product, presumably from radical disproportionation reactions. An effort was not made to identify the many possible chain-termination products (eqn. 11) from the ethylene growth of iodoethane.

The organic free radical initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) and $Ru(CO)_3(PPh_3)_2$ were compared as catalysts at 75°C and 800 psig of ethylene. Identical molar concentration of catalysts were injected directly into the autoclave at reaction temperature. Two different concentrations of iodoethane were employed in two sets of experiments. With 23.7% of the iodoethane converted in all cases, the same product profiles were obtained for AIBN and $Ru(CO)_3(PPh_3)_2$. With both catalysts, increasing the concentration of iodoethane increased the amount of the shorter chain iodoalkanes in the products. These coincidental results could be fortuitous but they are suggestive that $Ru(CO)_3(PPh_3)_2$ also generates free radicals. With higher iodoethane concentrations, chain transfer rates are increased (eqn. 9), thus higher yields of the shorter chain iodides result. This concentration effect would tend to rule against the discounted mechanism depicted by eqns. 2-4, unless, in the unlikely case, the reductive elimination step (eqn. 4) were bimolecular (eqn. 17). $Ru(CO)_3(PPh_3)_2$ behaving as does AIBN indicates that chain transfer involving an intermediate or product metal iodide (eqn. 18) is not important, otherwise the products would not have been identical in both cases.

$$RuI[(CH_2CH_2)_nR]L_4 + EtI \rightarrow RuI(Et)L_4 + R(CH_2CH_2)_nI \qquad (17)$$

$$R\cdot + RuIL_4 \rightarrow RI + [RuL_4] \qquad (18)$$

The characteristics of the growth reaction of iodoethane and 1-pentene also are very similar for AIBN and $Ru(CO)_3(PPh_3)_2$. 1-Pentene participates in the growth reaction less readily than does ethylene.

In keeping with the postulate of a radical reaction, solvents which are more easily attacked by radicals tend to give lower conversions of iodoethane. For example, for several solvents the following conversions were observed with $Ru(CO)_3(PPh_3)_2$: benzene 78%, cyclohexane 69%, and toluene 33%.

In the presence of an organic free radical initiator (benzoyl peroxide, etc.), 1,3-diiodopropane is readily converted to cyclopropane [12]. This reaction proceeds by a free radical mechanism as do other cyclopropane forming reactions where incipient γ-iodopropyl radicals are formed [13]. $Co(CN)_5^{3-}$ also converts 1,3-diiodopropane to cyclopropane via γ-iodopropyl radicals [4,14]. In the presence of an olefin and a radical initiator, diiodomethane likewise is converted to cyclopropane, presumably, via the intermediacy of γ-iodopropyl radicals [15]. The formation of cyclopropane during the $Ru(CO)_3(PPh_3)_2$-catalyzed ethylene growth reactions of diiodomethane and 1,3-diiodopropane (Table 3), adds weight to our proposal that the present growth reaction proceeds by a free radical mechanism: γ-iodopropyl radicals being formed directly from 1,3-diiodopropane and from diiodomethane by the addition of $ICH_2\cdot$ to ethylene.

In summary, the sum total of the observations reported above seem quite consistent with a free radical mechanism for the zero-valent ruthenium-catalyzed ethylene-iodoalkane growth reaction. Some participation of other reaction paths, such as those of eqns. 3-5, although unlikely, are not rigorously excluded.

Experimental

Materials. High purity organic iodides, solvents and ethylene were used as purchased. Two organic iodides, $NC(CH_2)_4I$ and $EtO_2C(CH_2)_3I$, had significant impurities present; however, they were suitable for obtaining the qualitative observation that they do undergo the ethylene growth reaction. $Ru(CO)_3(PPh_3)_2$, $Ru(CO)_3(AsPh_3)_2$, $RuI_2(CO)_2(PPh_3)_2$, $RuBr_2(CO)_2(PPh_3)_2$ and $RuCl_2(CO)_2(PPh_3)_2$ have been described elsewhere and were prepared accordingly [16]. $Ru(CO)_3(n\text{-}Bu_3P)_2$, $Ru(CO)_3[(cyclohexyl)_3P]_2$, $Ru(CO)_3(Ph_2PCH_2CH_2PPh_2)$ and $Ru(CO)_3[(p\text{-}tolyl)_3P]_2$ were prepared analogously. Significant IR bands are listed in Tables 1 and 4. $RuCl_2(CO)_2(Py)_2$ was prepared by known procedures [17] and converted to $Ru(CO)_3(Py)_2$ via the reduction procedure used by Collman and Roper [16]. $Ru(CO)_3(Py)_2$ was only 85% pure and contained about 15% of the starting material, $RuCl_2(CO)_2(Py)_2$. $Ru(CO)_4(PPh_3)$ was prepared as described by Piacenti et al. [18]. The preparation of $RuI(H)(CO)(PMe_2Ph)_3$ has been reported by Shaw et al. [19]. $Ru(CH_3CN)_2(Ph_3P)_4$ was donated by E.O. Sherman, Jr. $RuI(H)(CO)_2(PPh_3)_2$ was prepared by placing 0.9 g of $RuI_2(CO)_2(PPh_3)_2$, 30 ml of benzene and 10 mmol of triethylamine in an autoclave and heating at 50°C for 17 hours under 400 psig of H_2. The oil obtained upon concentration of the solution was crystallized from methanol. The IR spectrum of the compound had a band due to Ru—H at 1868 cm^{-1} and carbonyl bands at 1930 and 2055 cm^{-1}.

The reaction of organic halides and ethylene. In an 80-ml Hastelloy B autoclave flushed with N_2 were placed 30 ml of benzene, 20 mmol of the organic halide and 0.5 mmol of the ruthenium catalyst. Ethylene was introduced under pressure (~1000 psig) and the system heated at 75 to 150°C as the solution was stirred by means of an internal magnet bar set in motion by an external magnetic stirrer. The various reaction times and temperatures are listed in the tables. The liquid products were analyzed by GLC using an appropriate column (usually SE30, silicone) temperature programmed from 75 to 250°C at 6°/min. The product iodides were compared with authentic compounds and found to be identical. Various spectroscopic techniques, such as mass spectrometry, IR and NMR, were employed for this purpose. In certain cases the iodides were converted to alcohols for further structure confirmation. The structures of some of the higher molecular weight iodoalkanes, such as $C_{16}H_{33}I$ and $C_{18}H_{37}I$, were assumed by analogy with the structures found for the lower molecular weight iodoalkanes and their GLC emergence times. As described in the text, 1-iodoalkanes were the usual products. Cyclopropane formed from diiodomethane and 1,3-diiodopropane was distinguished from propane and propylene by GLC emergence times and confirmed unequivocally from its unique mass spectrometric fragmentation pattern.

Techniques and equipment employed to obtain the IR spectra under actual reaction conditions have been described previously [20].

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