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ORGANOMERCURIALS. II.

SUBSTITUTION PROCESSES IN THE HOMOLYTIC CLEAVAGE OF DIALKYLMERCURY THE FORMATION OF ALKYLMERCURY(II) DERIVATIVES

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Abstract

Alkylmercuric benzoate and chloride formed in the benzoyl peroxide-initiated reaction of dialkylmercury in carbon tetrachloride solutions arise by homolytic displacements. Kinetic isotope effects demonstrate that any alkylmercuri radicals formed in the concurrent reductive elimination to metallic mercury cannot be intermediates leading to alkylmercuric chloride. Benzoyl peroxide and butyryl peroxide show widely divergent behavior as initiators owing to differences in the stabilities of the acyloxy radicals formed on homolysis, the relatively long-lived benzoyloxy radical being effective in S_H2 displacements on dialkylmercury in contrast to propyl radicals derived from the highly unstable butyryloxy radicals. The reactivity of oxygen-centered, chlorine and alkyl radicals are compared in homolytic displacements. A unified mechanism is presented for reductive elimination and the various substitution processes observed concurrently in dialkylmercury compounds, in which the radical intermediates are shared in common.

Introduction

The occurrence of a free radical chain process in the facile reductive elimination from dialkylmercury RHgR' by β-hydrogen abstraction was described in the previous paper.[1] The formation of alkene is accompanied by the concomitant reduction of mercury(II) to metallic mercury in carbon tetrachloride [illegible] of the dialkylmercurial to mercury(0) was made possible in these studies by the deliberate choice of appropriate alkyl groups to optimize reductive elimination.

In other studies, however, varying amounts of alkylmercury(II) derivatives such as RHgCl have been reported when analogous dialkylmercury compounds were subjected to similar treatment.[2,3] Unfortunately, the experimental basis in differentiating between processes leading to reductive elimination (Hg^o) and those leading to substitution (RHgX) is somewhat puzzling. On one hand, nearly quantitative yields of mercury metal have been reported, when the reaction between di-n-propylmercury and CCl_4 was induced thermally (150°C), photochemically or by di-t-butyl peroxide.[2] In contrast, Jensen and Guard[3] reported up to 25% yields of n-butylmercuric chloride in addition to mercury(0) from the reaction of di-n-butylmercury with CCl_4 initiated by benzoyl peroxide. An alkylmercuri radical RHg· was proposed as the key intermediate leading to reductive elimination and substitution in eqs. 1 and 2, respectively.

$$RHg\cdot \longrightarrow R\cdot + Hg(0) \quad \text{etc.} \tag{1}$$

$$RHg\cdot \xrightarrow{CCl_4} RHgCl + Cl_3C\cdot \quad \text{etc.} \tag{2}$$

It is difficult to reconcile such a formulation with the observation that the isomeric di-isopropylmercury affords i-propylmercuric chloride[2], since it requires that fragmentation in eq. 1 inexplicably occurs more rapidly with a primary n-propylmercury(I) species compared to the secondary i-propylmercury(I) which has a weaker CHg bond.[4] Moreover, our own results indicated that neopentylmercury(I) was not converted to NpHgCl.[1]

We conclude that many of these ambiguities arise from the absence of a clear delineation of the processes leading to the substitution products RHgX. In this regard, a major obstacle focusses on the different means which have been employed to initiate the reactions. Peroxides are commonly considered to serve only as an innocent source of chain-carrying radicals. For example, it has been suggested that trichloromethyl radicals are involved in the decomposition of dialkylmercury and arise from benzoyl peroxide by the following

$$(PhCO_2)_2 \longrightarrow 2Ph\cdot + 2CO_2 \qquad (3)$$

$$Ph\cdot + CCl_4 \longrightarrow PhCl + Cl_3C\cdot \text{ etc.} \qquad (4)$$

$$Cl_3C\cdot + R_2Hg \longrightarrow \text{Products} \qquad (5)$$

Since there are several studies of the reaction between dialkylmercury and benzoyl peroxide[5], we wish to scrutinize the assumptions embodied in eqs 3-5. The role of alkylmercuri radicals in the formation of alkylmercuric chloride in eq 2 is also examined in this report.

Results

The decomposition of dialkylmercury was studied in carbon tetrachloride solutions in the presence of peroxides as initiators.

Effect of Peroxides on Di-alkylmercury

1. Benzoyl Peroxide

Di-neopentylmercury Np_2Hg which has no β-hydrogen cannot undergo reductive elimination. Indeed, no mercury(0) is observed when Np_2Hg is heated in CCl_4 at 100°C in the presence of benzoyl peroxide. The formation of neopentylmercury benzoate and neopentyl chloride in more or less equimolar amounts occurs in a rather slow stoichiometric (i.e., non-chain) reaction as summarized in Table I.

Table I. **Benzoyl Peroxide-Initiated Cleavage of Di-neopentylmercury in Carbon Tetrachloride.**[a]

$(PhCO_2)_2$	Neopentyl Chloride		$NpHgO_2CPh$
(mmol)	(mmol)	(%)[b]	(mmol)[c]
0.030	0.050	83	0.042
0.044	0.075	85	0.062
0.059	0.088	75	0.083

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[a] In 1ml solution of 0.29M Np_2Hg at 100°C for 7 hrs. [b] Based on total equivalents of benzoyloxy radicals. [c] Approximate yield, see Experiment Section.

The first-order thermal decomposition of benzoyl peroxide alone in CCl_4 proceeds by the rate-limiting homolysis of the O-O bond in eq 6.[6] If the subsequent unimolecular decarboxylation of the benzoyloxy radical (k_c in eq 7) occurs more rapidly than any other bimolecular reaction, a yield of 2.0 mole

$$(PhCO_2)_2 \xrightarrow{k_i} 2PhCO_2\cdot \qquad (6)$$

$$PhCO_2 \xrightarrow{k_c} Ph\cdot + CO_2 \qquad (7)$$

of carbon dioxide would be obtained from each mole of peroxide. The observation of 1.88 mole of CO_2 indeed suggests that radical dimerization and induced decomposition are not major complications at 100°C.

The yield of CO_2 is diminished, however, when the decomposition of benzoyl peroxide is carried out in the presence of dialkylmercury. The extent of CO_2 diminution depends to a marked degree on the alkyl groups as shown in Table II.

Table II. Yield of Carbon Dioxide for the Decomposition of Peroxides in the Presence of Dialkylmercury[a]

Dialkylmercury RHgR	Yield of CO_2 from Peroxide (%)[b] $(PhCO_2)_2$	$(n\text{-}C_4H_9CO_2)_2$
none	100[c]	100[d]
i-Propyl	5	78
n-Butyl	17	96
neo-Pentyl	30	101
Methyl	93	100

[a] In 2ml t-butylbenzene solution containing 0.047 mmol peroxide and 0.23 mmol R_2Hg [b] Yields based on CO_2 observed in the absence of R_2Hg [c] 1.88 mol CO_2 per mol $(PhCO_2)_2$ [d] 1.92 mol CO_2 per mol $(C_4H_9CO_2)_2$

The rate of peroxide disappearance is not highly dependent on the presence of the mercurial. For example, the first order rate constant for decomposition of benzoyl peroxide (k_i = 4.9×10^{-4} sec^{-1}) at 100°C in carbon tetrachloride the rate constant only increased to 7.2×10^{-4} $\sec^{-1}$ in the presence of 0.12 M Np_2Hg. In this case, no more than a quarter of the 70% decrease in CO_2 yield (Table II) can be ascribed to any process associated with the induced decomposition of the mercurial. The unaccounted CO_2 must be due to the trapping of benzoyloxy radicals by dialkylmercury (Np_2Hg), which leads to alkylmercuric benzoate as shown later.

2. Butyryl Peroxide

In contrast to the foregoing results, not only the rate but also the yields of carbon dioxide from the decomposition of di-n-butyryl peroxide are singularly unaffected by various dialkylmercury compounds listed in Table II. Indeed, the nearly quantitative yields of CO_2 indicate that any possible complication due to the induced decomposition of butyryl peroxide is not important.

A further illustration of the difference between benzoyl peroxide and butyryl peroxide is obtained from the cleavage of dineopentylmercury. Thus, neopentyl chloride is observed is 34% yield when 0.029 M Np_2Hg in CCl_4 is treated with 0.18 M benzoyl peroxide for 40 hours at 80°C. but only 1.5% of NpCl is obtained from di-n-butyryl peroxide under the same conditions.

3. Differences between Benzoyl and Butyryl Peroxides

In accounting for the divergent behavior of benzoyl peroxide and butyryl peroxide, it is important to note there is no significant difference in the strengths of the O–O bonds in these two peroxides. Thus, butyryl peroxide undergoes a first-order homolysis of the O–O bond at more or less the same rate as benzoyl peroxide.[7] However,

$$(n\text{-}PrCO_2)_2 \xrightarrow{k_i} 2n\text{-}PrCO_2\cdot \qquad (8)$$

$$n\text{-}PrCO_2\cdot \xrightarrow{k_c} n\text{-}Pr\cdot + CO_2 \qquad (9)$$

the difference between these peroxides lies in the thermal stability of the resultant acyloxy radicals. The unimolecular rate of decarboxylation of the aliphatic acyloxy radicals is so fast [$k_c > 10^9$ $\sec^{-1}$ at 65°C in eq 9] that they have never been trapped outside of cage processes.[8] In other words, for all practical purposes the rate-limiting homolysis of butyryl peroxide leads directly to propyl radicals (eq 10).

$$(n\text{-}PrCO_2)_2 \xrightarrow{k_i} 2n\text{-}Pr^{\cdot} + 2CO_2 \qquad (10)$$

Benzoyloxy and other radicals, on the other hand, decarboxylate at significantly slower rates [$k_c = 2.4 \times 10^4\ sec^{-1}$ at 80°C] and have been intercepted by various radical traps.[8,9] Thus, benzoyl peroxide and butyryl peroxide differ significantly in the types of radical produced on homolysis and not on the rates of radical production.

This difference is also apparent in the selectivity observed in the cleavage of an unsymmetrical dialkylmercury compound in the presence of the two peroxides. For example, the foregoing study[1] showed that isobutylneopentylmercury undergoes reductive elimination with high selectivity to neopentyl chloride according to eq 11.

$$(CH_3)_2CHCH_2HgNp + CCl_4 \rightarrow (CH_3)_2C{=}CH_2 + NpCl + Hg + HCCl_3 \qquad (11)$$

The extent to which isobutyl chloride is formed reflects an alternative cleav-

Table III. Effect of Initiators on the Formation of Neopentyl and Isobutyl Chlorides From Isobutylneopentylmercury in CCl_4[a]

Initiator	Conditions		Equivalent of RCl[b]		$\frac{i\text{-}BuCl}{NpCl}$
	Temp(°C)	Time(hr)	i-BuCl	NpCl	
none	100	300[c]	0.01	0.77	0.013
$(PhCO_2)_2$	100	7	0.08	0.75	0.11
$(PhCO_2)_2$	80	50	0.08	0.81	0.099
$(n\text{-}C_4H_9CO_2)_2$	80	20	0.02	0.94	0.021
hν(3500Å)	30	10	0.10	0.92	0.11
AIBN[d]	80	10	<0.01	0.07	

age of an alkyl-mercury bond arising from either an inefficient initiation step or the presence of other chain-carrying radicals.[1] Up to 10% of such side reactions observed with benzoyl peroxide in Table III is in contrast to 2% obtained from butyryl peroxide. [The low selectivity in photochemical initiation was discussed earlier.[1]]

Reductive Elimination and Substitution as Competing Processes.

1. Alkylmercuric Benzoate and Chloride from Benzoyl Peroxide

Our concern that the peroxidic initiator might play a role different from that presented in eqs 3-5, led us to reexamine the alkylmercuric chloride reported earlier.[3] The identification of this product was of particular interest since the reported method of analysis (involving its isolation as the iodide derivative) would not have distinguished alkylmercuric chloride from the benzoate analog.

A solution of 0.45 M di-n-butylmercury and 0.056 M benzoyl peroxide in carbon tetrachloride was heated at 100°C for 7 hours. The formation of n-butyl chloride, chloroform, butene-1 (as the adduct, 1, 1, 1, 3 - tetrachloropentane) and mercury metal in the amounts previously reported[3] was confirmed in Table IV. The formation of these products are generally in accord with the stoiochio-

Table IV. Di-n-butylmercury in Carbon Tetrachloride with Benzoyl Peroxide and Butyryl Peroxide as Initiators[a]

Peroxide Initiator	BuCl	Products (mol %)[b] Bu(-H)[c]	Hg	$CHCl_3$	BuHgX	Recovered Bu_2Hg
$(PhCO_2)_2$[d]	53	52	64	67	25	
$(PhCO_2)_2$	44	41	55	59	20[e]	12
$(n\text{-}BuCO_2)_2$	26	26	29	31	10[f]	48

[a] In solutions containing 0.45 M $(n\text{-}Bu)_2Hg$ and 0.056 M peroxide at 100° for 7 hours, except as noted [b] based on the stoichiometry in eq 12. [c] Butene-1 and

metry in eq 12, which has been established for reductive elimination (eq 11).

$$Bu_2Hg + CCl_4 \longrightarrow BuCl + Bu(-H) + Hg + CHCl_3 \qquad (12)$$

The other nonvolatile products, however, were found to consist of roughly equimolar quantities of n-butylmercuric chloride and n-butylmercuric benzoate as determined by the proton nmr spectrum and confirmed with authentic materials using thin layer chromatography. Furthermore, fractional crystallization of the crude product mixture at -20°C allowed the isolation of the pure crystalline n-butylmercuric chloride and the liquid n-butylmercuric benzoate (contaminated with small amounts of the chloride).

Reductive elimination as represented in eq 12 is the principal route by which di-n-butylmercury reacts with carbon tetrachloride in a radical chain process The formation of n-butylmercuric benzoate and chloride accounts mostly for the remainder (~ 25%) of the di-n-butylmercury consumed. The origin of n-butylmercuric benzoate is clearly associated with the trapping of benzoyloxy radicals.

2. Alkylmercuric Chloride from Butyryl Peroxide.

To obviate the formation of benzoate, di-n-butyryl peroxide was used as the initiator in the reaction of di-n-butylmercury in CCl_4. The results in Table IV show that reductive elimination is again the predominant mode of reaction. The formation of n-butylmercuric chloride is generally in accord with the results obtained with benzoyl peroxide. Significantly, no n-butylmercuric butyrate is formed.

Kinetic Isotope Effects in the Formation of Alkylmercuric Chloride

The formation of alkylmercuric chloride during the course of the free radical chain reaction of di-alkylmercury has been ascribed to the chain transfer reaction of the alkylmercuri radical with CCl_4 in eq 2.[3] Deuterium isotope studies[1] have shown that reductive elimination of di-n-heptylmercury-β_1,β-d_2 favors cleavage of the n-heptyl bond to mercury in eq 14 by a factor of 4.9 over that of n-heptyl-β,β-d_2 in eq 13.

$$C_5H_{11}CD_2CH_2\text{-}Hg\text{-}CH_2CH_2C_5H_{11} + \breve{C}Cl_3 \left\{ \begin{array}{ll} \xrightarrow{17\%} \dot{H}gCH_2CH_2C_5H_{11} + CDCl_3 + C_5H_{11}CD{=}CH_2 & (13) \\ \xrightarrow{83\%} \dot{H}gCH_2CD_2C_5H_{11} + CHCl_3 + C_5H_{11}CH{=}CH_2 & (14) \end{array} \right.$$

Therefore, if alkylmercuric chloride does arise by way of the alkylmercuri radical, a five-fold deuterium enrichment in n-heptylmercuric chloride should obtain. Heptylmercuric chloride derived from di-n-heptylmercury-β,β-d_2 was isolated from the reaction mixture by fractional crystallization -20°C. It was subsquently cleaved with bromine in ether solution, and the resultant mixture of n-heptyl bromide and n-heptyl-β,β-d_2 bromide subjected to mass spectral analysis. The observed ratio of deuterated and non-duterated bromides was 1.1 ± 0.2, consistent with little or no isotope effect in the formation of n-heptylmercuric chloride. Control experiments showed no significant exchange between alkylmercuric chloride and dialkylmercury.

Chlorinolysis of Dialkylmercury with Hexachloroethane

The isotopic studies indicate that the alkylmercuri radical is not the precursor for alkylmercuric chloride. This conclusion is in accord with the ready fragmentation of these species discussed earlier.[4] The formation of alkylmercuric chloride must then arise via a competing chlorinolysis of dialkylmercury under reaction conditions. A number of converging lines of evidence (vide infra), suggested that hexachloroethane, formed by the dimerization of chain-carrying trichloremethyl radicals, might be one of the agents active in such a chlorinolysis.

Indeed, the treatment of di-neopentylmercury (0.15 M) with hexachloroethane (1 M) in benzene solution at 80°C resulted in a 90% conversion to neopentyl chloride and neopentylmercuric chloride in equal amounts, together with tetrachloroethylene after 5000 minutes. No peroxidic initiator was required.

$$Np_2Hg + C_2Cl_6 \longrightarrow NpCl + NpHgCl + C_2Cl_4 \qquad (15)$$

A similar treatment of di-t-butylmercury resulted in the quantitative conversion to t-butyl chloride and t-butylmercuric chloride within 20 minutes.[10] On further exposure the t-butylmercuric chloride was completely converted to t-butyl chloride and mercuric chloride after 100 minutes.

$$t\text{-BuHgCl} + C_2Cl_6 \longrightarrow t\text{-BuCl} + HgCl_2 + C_2Cl_4 \qquad (16)$$

Attempts to detect tetrachloroethylene among the products of the benzoyl peroxide induced reaction of di-n-butylmercury and carbon tetrachloride were unsuccessful, despite the establishment of a 1% limit of detection. It is possible that tetrachloroethylene may have undergone further addition or telomerization under reaction conditions.

The cleavage of dialkylmercury can also be effected by vicinal dibromides in analogy with hexachloroethane. The pair of diasteriomeric 2,3-dibromobutanes reacted with di-n-propylmercury at 80° to afford cis and trans-butenes (Table V).

$$CH_3CH(Br)CH(Br)CH_3 + Pr_2Hg \longrightarrow CH_3CH{=}CHCH_3 + PrHgBr + PrBr \qquad (17)$$

The conversion of meso-2,3-dibromobutane mostly to trans-butene-2, and the d,l isomer to cis-butene-2, corresponds to a preferred but not exclusive trans-elimination of vicinal bromines during reduction. The stereochemistry of an analogous reaction with methylmagnesium bromide is also included in Table V for comparison.

Table V. Stereochemistry of the Reduction of 2,3-Dibromobutane by Organometals[a]

Organometal	$CH_3\underset{Br}{CH}\,\underset{Br}{CH}\,CH_3$	Butene - 2 cis	trans	Specificity (%)
$(n\text{-}Pr)_2Hg$	meso	18	82	82
$(n\text{-}Pr)_2Hg$	d,l	63	37	63
MeMgBr	meso	4	96	96
MeMgBr	d,l	89	11	89

Discussion

Dialkylmercury compounds RHgR' react in carbon tetrachloride in the presence of peroxide initiators by several simultaneous homolytic pathways, including reductive elimination and substitution. Reductive elimination has been shown to proceed via a chain process in which the abstraction of a β-hydrogen represents the rate-limiting step.[1] In a typical organomercurial such as di-n-butylmercury, reductive elimination to alkene and mercury(0) constitutes more that 50% of the mode of reaction, the remainder consisting of substitution processes leading to alkylmercury(II) derivatives RHgX. The substitution processes are of primary interest in this report, and they can be elucidated in part by examining an organomercurial such as di-neopentylmercury which has no β-hydrogens available for elimination.

Alkylmercuric Benzoates from Dialkylmercury. Homolytic Displacement by Benzoyloxy Radicals

Di-neopentylmercury does not react with carbon tetrachloride at any appreciable rate in the absence of an initiator. The effect of added peroxides depends on their structure. Thus an aromatic acyl peroxide such as dibenzoyl peroxide cleaves di-neopentylmercury, whereas an aliphatic analogue such as di-n-butyryl peroxide does not. Similarily, benzoyl peroxide initiates the reaction between tetraphenyllead and carbon tetrachloride, but acetyl peroxide is ineffective.[11]

The cleavage of di-neopentylmercury by benzoyl peroxide occurs at essentially the same rate as the initiator itself undergoes O–O homolysis. The benzoyloxy radicals so produced are found as neopentylmercuric benzoate, and the cleaved neopentyl group is accounted for as neopentyl chloride. Such a stoichiometric (i.e., nonchain) cleavage of di-neopentylmercury is consistent with the involvement of benzoyloxy radicals in a displacement reaction[12] such as,

$$PhCO_2\cdot + Np_2Hg \longrightarrow PhCO_2\text{-}HgNp + Np\cdot \qquad (18)$$

neopentyl radical in eq 18 is followed by chlorine transfer which is known to be rapid.[13]

$$\mathrm{Np}\cdot + \mathrm{CCl_4} \longrightarrow \mathrm{NpCl} + \mathrm{Cl_3\dot{C}} \qquad (19)$$

The rate of the substitution reaction in eq 18 must be sufficiently fast to allow efficient trapping of the benzoyloxy radical in competition with its ready decarboxylation ($k_c = 2.4 \times 10^4$ sec^{-1} at 80°C). Indeed, other S_H2 displacements of alkyl radicals from metal centers by oxygen-centered radicals, such as the reaction of tri-n-butylborane with t-butoxy radical, have second order rate constants in excess of 10^7 l mol^{-1} sec^{-1} at 30°C[14]. A similar S_H2 displacement between benzoyloxy radical and tetraethyllead has been recently reported.[15] [In the absence of direct evidence[16], we make no distinction here between synchronous and addition-elimination mechanisms in displacement reactions.]

The lack of any notable effect of di-n-butyryl peroxide on the decomposition of di-neopentylmercury in CCl_4 is in marked contrast to that observed with benzoyl peroxide. The quantitative yield of carbon dioxide and the resulting absence of neopentylmercuric butyrate indicate that a displacement reaction analogous to that in eq 18 does not occur. The half-life of the n-butyryloxy radical is about 10^6 times shorter than that of benzoyloxy radical, and decarboxylation must be too fast to allow trapping even by reactive mercurials. Furthermore, the n-propyl radicals derived from the peroxide are not directly involved in the cleavage of dineopentylmercury since it remains largely intact and only minor amounts of neopentyl chloride are obtained from cleavage of the neopentyl-mercury bond. Instead n-propyl radicals are quantitatively converted to n-propyl chloride by reaction with CCl_4.

S_H2 displacement on di-neopentylmercury by n-propyl radical as represented in eq 20,

$$n\text{-}\mathrm{Pr}\cdot + \mathrm{Np_2Hg} \longrightarrow n\text{-}\mathrm{PrHgNp} + \mathrm{Np} \qquad (20)$$

is essentially a thermoneutral reaction. The absence of a significant driving force could provide the distinction between alkyl radicals such as propyl and oxygen-centered radicals such as benzoyloxy and t-butoxy in their behavior toward dialkylmercury.

The facility with which alkyl groups are displaced from dialkylmercury appears to be highly dependent on the nature of the alkyl ligand. The results in Table II afford a measure of the efficiency with which benzoyloxy radicals are trapped by dialkylmercury in the order: Me < n-Bu < i-Pr. Indeed, the reaction between di-t-butylmercury and CCl_4 in the absence of initiators provides evidence that t-butyl radicals are displaced even by the poorly nucleophilic trichloromethyl radical.[10] The reactivity sequence, Me < prim. < sec. < tert., reflects a trend in both the decreasing strength of the alkyl-Hg bond as well as the increasing stability of the displaced alkyl radical.*

Previous studies have commonly employed benzoyl peroxide as initiator in concentrations sufficient to yield as much as 0.25 equivalents or more of benzoyloxy radicals for each equivalent of organometal, on the assumption that it plays a rather innocent role described in eqs 3-5.[3,11,17] We wish to emphasize the caveat that the choice of initiator can be critical in minimizing side reactions, especially if high concentrations of initiator are required owing to the poor kinetic chain length of the desired process.

Alkylmercuric Chloride from Dialkylmercury in Carbon Tetrachloride Solutions

The formation of alkylmercuric chloride as the other substitution product derived from the decomposition of dialkylmercury in CCl_4 has been attributed to alkylmercuri radicals $RHg\cdot$ in eq 2. Such a formulation, however, cannot be reconciled with the absence of a kinetic isotope effect in the cleavage of di-n-heptylmercury-β,β-d_2. There is other evidence that also indicates that alkylmercuric radicals are extremely unstable and too short-lived to participate effectively in bimolecular processes. [Electrochemical reductions are not included in this context owing to ambiguities inherent in the elucidation of processes occuring at the electrode surface.[18,19]]

Hexachloroethane is found in varying yields in all reactions of dialkylmercury in CCl_4, since it is derived from the dimerization of the chain-carrying trichloromethyl radicals. The amounts generally parallel the yields of alkylmercuric chloride and increase with temperature due to faster initiation rates. [As

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* Homolytic displacements on mercury are discussed further in reference 10.

the product of the termination process, the yields of hexachloroethane are also higher in inefficient chain processes.] The facile chlorinolysis of dialkylmercury by hexachloroethane can be represented by a chain process,[*]

$$\mathrm{Cl\cdot + RHgR \longrightarrow RHgCl + R\cdot} \qquad (20)$$

$$\mathrm{R\cdot + C_2Cl_6 \longrightarrow RCl + C_2Cl_4 + Cl\cdot} \qquad (21)$$

which is analogous to that shown for hydrocarbons.[20] Such a mechanism is consistent with the stereochemical results presented in Table V for the analogous meso and d,l 2,3-dibromobutanes, and not a direct cyclic process.[21,22]

Chlorinolysis as represented in eq 20 is another example of S_H2 displacement on dialkylmercury (similar to oxygen-centered radicals), the driving force being derived by the formation of a strong Cl-Hg bond. Displacement by the ubiquitous trichloromethyl radical followed by α-elimination[23] is less likely,

$$\mathrm{Cl_3C\cdot + R_2Hg \longrightarrow R\cdot + RHgCCl_3 \longrightarrow RHgCl + Cl_2C} \text{ etc.} \qquad (22)$$

since there are dialkylmercury compounds which can react in CCl_4 without the formation of alkylmercuric chloride.[1] Finally, a molecule-assisted cleavage of dialkylmercury by CCl_4 is conceivable,[24] but the mechanism of such processes is unknown at this juncture.

Conclusion

We have identified at least three concurrent processes when dialkylmercury(II) compounds react in carbon tetrachloride under free radical conditions First, alkylmercuric carboxylates are formed via S_H2 displacement by oxygen-centered radicals derived from benzoyl peroxide but not butyryl peroxide. Second, the formation of metallic mercury by reductive elimination is a chain process propagated by trichloromethyl radicals. Third, alkylmercuric chloride is produced by chlorinolysis of dialkylmercury with hexachloroethane, and it is not formed via alkylmercuri radicals under reaction conditions.

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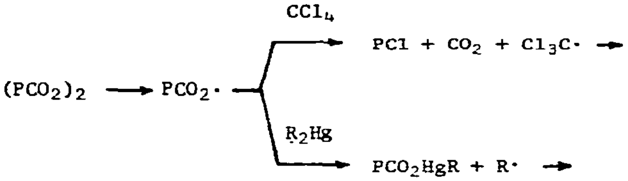
[*] The pentachloroethyl radical rather than chlorine atom may be the actual chain-

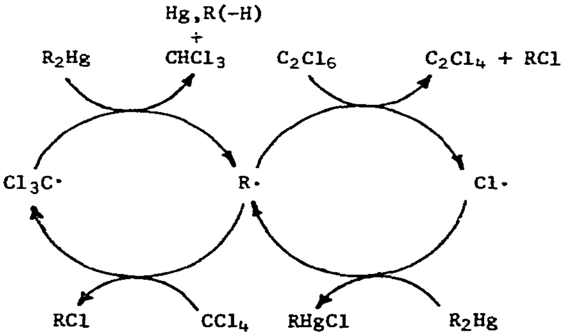
These diverse observations can be accommodated within a single mechanisti framework. Economy is emphasized in Scheme I, and only those steps which can be verified independently are included.

Scheme I.

Initiation:



Propagation:



Termination:

$$2Cl_3C\cdot \rightarrow C_2Cl_6$$

According to Scheme I, several radical intermediates are shared in common during reductive elimination to metallic mercury and substitution to alkylmercuric derivatives. Attack on dialkylmercury occurs primarily by β-hydrogen abstraction and S_H2 displacement. The role of alkylmercuri radicals is unimportant in substitution processes. No doubt other processes will be uncovered owing to the presence of a realtively large variety of reactive intermediates during the decomposition of dialkylmercury in carbon tetrachloride, and they must await further studies.

Relative Yield of Isobutyl and Neopentyl Chlorides.

The reactions summarized in Table III were all run in sealed tubes *in vacuo* as described in detail previously.[1]

Alkylmercuric Salts from Benzoyl Peroxide-Initiated Reactions

A sealed tube containing a degassed solution at 1.12 g di-n-butylmercury, 0.083 g benzoyl peroxide, and 6.0 ml carbon tetrachloride *in vacuo* was heated for 7 hours at 100°C. A portion of the product solution was cooled to -20°C. It produced white crystals which after several pentane washes at -20°C were recrystallized from ethanol, mp 129°-130°C (lit[29] mp 129°C). A second portion was placed in a flask on a vacuum line whereupon the volatile components were removed by vacuum transfer. The nmr spectrum of the non-volatile components was examined by comparing the integration of the benzoate protons against the butyl protons. The n-butylmercuric derivatives were found to consist of a mixture containing 42% of the benzoate and 58% of the chloride salts. A sample of the non-volatiles was placed on a tlc plate coated with Corasil I and eluted with benzene. The presence of n-butylmercuric chloride (R_f 0.76) and n-butylmercuric benzoate (R_f 0.05) could be confirmed. Unfortunately, column chromatography could not be applied on a larger scale separation of these products, since alkylmercuric salts are known to undergo symmetrization on both alumina and silica gel supports under such conditions.[30]

Stereochemical Studies.

A 25 ml flask containing a stirring bar was sealed with a rubber septum and flushed thoroughly with argon. To the flask was added 2 ml of a 1.0 M solution of the appropriate organometal dissolved in THF and 5 ml butane internal standard. An aliquot of the appropriate 2,3-dibromobutane corresponding to 1.0 mmol was injected. Reactions with methylmagnesium bromide were stirred for one half hour at room temperature. Those with di-n-propylmercury were heated in an oil bath at 80°C for 2 hours. Yields of *cis*- and *trans*-butene-2 were determined by gas chromatography.

Isotope Effects on Reactions Leading to Alkylmercuric Chloride.

The reaction of di-n-heptylmercury-β,β-d_2 was carried out as previously described[1], after which the products were cooled to -20°C. At this temperature n-heptylmercuric chloride precipitated as white crystals which were isolated and cleaved with a solution of bromine in ether. The ethereal solution was washed with sodium thiosulfate solution, and dried. Distillation of the ether afforded a mixture of deuterated and non-deuterated bromides which was subjected to mass spectral analysis. The molecular ion was observed at m/e 178 and 180 for the protio compound and at m/e 180 and 182 for the deuterium compound. The ratio of the intensities of the peak at m/e 182 to that at m/e 178 was 0.9 averaged for four spectra. Due to the low intensity of the molecula ion, the M-43 peaks corresponding to loss of C_3H_7 (m/e = 135, 137, 139) were also examined. The average intensity ratio of the peak m/e = 139 to the peak m/e = 135 was 1.3.

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