

ORGANOMERCURIALS. I.  
FREE RADICAL CHAIN MECHANISMS IN THE REDUCTIVE ELIMINATION  
OF DIALKYL MERCURY IN CARBON TETRACHLORIDE

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(Received August 16th, 1976; in revised form October 25th, 1976)

Abstract

Dialkylmercury compounds  $\text{RHgR}'$  undergo facile reductive elimination of olefins in carbon tetrachloride solutions. Quantitative material balance shows that isobutylene is lost from isobutylneopentylmercury together with metallic mercury, neopentyl chloride and chloroform. A similar reductive elimination is observed with mercuracycloheptane. The reactions can be induced photochemically or thermally with peroxides, and they can be inhibited by galvinoxyl or phenols. The free radical chain process is dissected into several discrete steps, involving (a)  $\beta$ -hydrogen atom abstraction from  $\text{RHgR}'$  by trichloromethyl radical, followed by (b and c) the elimination and fragmentation of alkylmercury radical and the subsequent (d) chain transfer with  $\text{CCl}_4$ . Specific deuterium labellings of di-*n*-heptylmercury with  $\beta, \beta\text{-d}_2$  and  $\beta, \beta'\text{-d}_2$  allow a measurement of the  $\beta$ -hydrogen involvement in the rate-limiting process. A substantial kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 4.9 \pm 0.1$ ) is observed. Competition studies provide the first evidence of the activation of  $\beta$ -hydrogens in metal alkyls to homolytic abstraction. The origin of  $\beta$ -hydrogen activation is discussed relative to the formation of reactive intermediates including  $\beta$ -mercuraalkyl radicals and alkylmercury(I) species

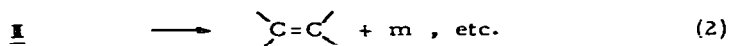
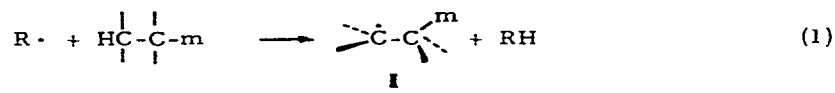
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Introduction

One of the major modes of decomposition of organo-

metallic intermediates is crucial to the elucidation of catalytic processes. Homolytic mechanisms once commonly held as the major pathway for the thermal decomposition of organometals have been mostly discredited.<sup>1, 2</sup> However, there has been a recent resurgence of interest in the role of free radicals in organometallic chemistry provoked by the observation of such diverse homolytic reactions as displacement, alkylation, reduction, and insertion as well as oxidative addition.<sup>3-8</sup> Moreover, the free radical chain nature of such useful processes as the demercuration reaction and trialkyltin hydride reduction suggests that this mode of reactivity deserves careful delineation.<sup>9, 10</sup>

Reductive elimination of alkenes represents one of the principal modes of decomposition of organometals. We speculated earlier that free radicals may be involved in a chain mechanism such as:<sup>11</sup>



Central to the efficacy of such a chain process is the enhanced reactivity of  $\beta$ -hydrogens in alkylmetals toward radical abstraction in eq 1. Whereas no direct evidence for such activation has been documented heretofore, a number of less direct observations are at least consistent with such a notion. Thus, electron spin resonance studies have shown that the  $\beta$ -metalloalkyl radicals I possess rather unique conformational and structural properties which reflect hyperconjugative and homoconjugative interactions between the metal substituent and the alkyl radical center.<sup>12</sup> Activation of hydrogen located in the  $\beta$ -position adjoining a variety of heteroatoms has been placed within the perspective of bridged radicals.<sup>13</sup> Indeed, hydrogen activation in an elimination sequence analogous to eqs 1-2 was proposed for thioethers ( $\text{m} = \text{SR}$ ), but subsequently rejected.<sup>14</sup>

There are earlier reports in which organomercury compounds are purported to undergo elimination by transfer of a  $\beta$ -hydrogen and loss of

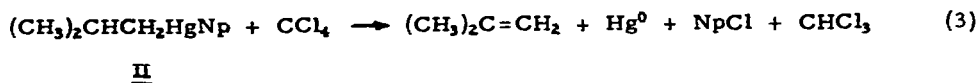
the metal.<sup>15, 16</sup> We wish to show that with the appropriate choice of substrates, the previous complications of incomplete material balance and mechanistic ambiguities resulting from the use of symmetrical dialkylmercury compounds are overcome.<sup>17</sup> This definition allows an unambiguous identification of radical chain processes in the reductive elimination, as well as the quantitative assessment of the enhanced homolytic reactivity of  $\beta$ -hydrogens in isobutyl, n-propyl and ethyl groups bonded to mercury. Moreover, these results provide insight into the nature of alkylmercuri radicals [i. e., mononuclear alkylmercury(I)] which have been the subject of some discussion.<sup>18</sup>

### Results

Reductive eliminations of alkene from dialkylmercury compounds were carried out thermally in carbon tetrachloride solution alone or in the presence of initiators. The use of unsymmetrical dialkylmercurials allowed the separate fates of the two alkyl groups to be distinguished. The neopentyl group was selected for the absence of an abstractable  $\beta$ -hydrogen.

#### Products and Stoichiometry

When a solution of isobutylneopentylmercury II in carbon tetrachloride is heated, metallic mercury is formed as a shiny globule along with equimolar amounts of chloroform and neopentyl chloride (NpCl). In addition isobutylene is observed, but as the heating is continued the amounts reach a maximum then decrease with the concomitant formation of 1, 1, 1, 3-tetrachloro-3-methylbutane, as anticipated from the well-known addition of  $\text{CCl}_4$  to olefins under free radical conditions.<sup>19</sup> Significantly, only traces of isobutyl chloride obtain, and neither isobutyl nor neopentylmercuric chloride is found. The results in Table I establish the overall stoichiometry for the reductive elimination of II according to eq 3.



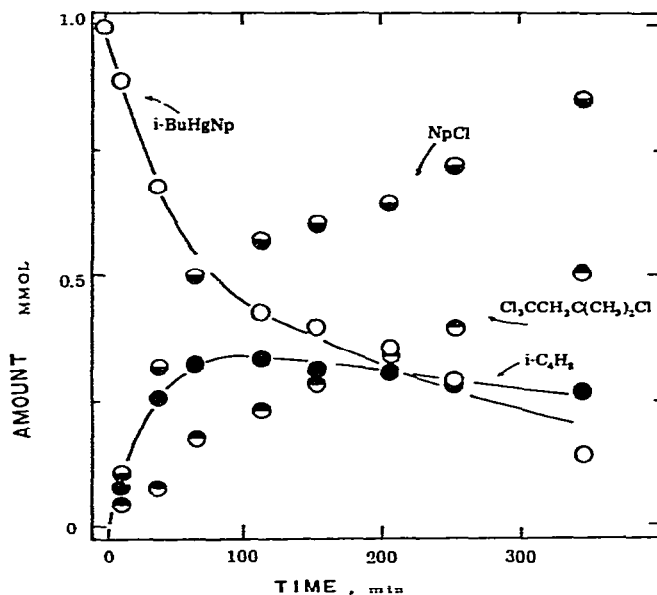


Figure 1. Reductive elimination of isobutylneopentylmercury (0.12M) in carbon tetrachloride at 100°C. Formation of isobutylene [●] and its conversion to the  $\text{CCl}_4$  adduct  $\text{Cl}_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{Cl}$  [●]. All quantities expressed as mmol per mmol  $i\text{-BuHgNp}$  [O] consumed, calculated from the yield of neopentyl chloride [●]. See text.

Table I. Reductive Elimination of Dialkylmercury in Carbon Tetrachloride Solutions.<sup>a</sup>

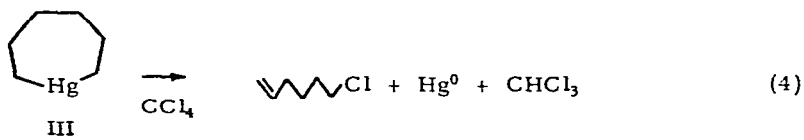
Mercurial <sup>b</sup> R-Hg-R'	Conversion <sup>c</sup> (%)	Products (mmol) <sup>d</sup>			
		R(-H) <sup>e</sup>	R'-Cl	$\text{CHCl}_3$	$\text{Hg}^0$
$i\text{-BuHgMe}$	51	1.01	0.93	0.93	1.02
$i\text{-BuHgNp}$	88	0.96	0.87	0.91	0.97
$\text{Hg}(\text{CH}_2)_6^f$	g	0.84	0.86	1.07	0.80

<sup>a</sup>At 100°C, no initiator added. <sup>b</sup>2.25 mmol in 5 ml  $\text{CCl}_4$ . <sup>c</sup>Based on recovered  $\text{RHgR}'$  after 300 hrs. <sup>d</sup>Per mmol of unrecovered  $\text{RHgR}'$ . <sup>e</sup>Alkene plus  $\text{CCl}_4$  adduct. <sup>f</sup>Contains 0.28 mmol di-*n*-butyryl peroxide, yields based after 7 hrs on reactant charged. <sup>g</sup>Not determined.

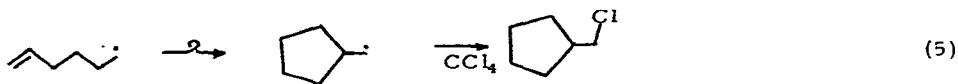
Reaction 3 is markedly accelerated by the addition of catalytic amounts of butyryl peroxide and to a lesser extent by azo-bis-isobutyronitrile. Moreover, it is inhibited by either galvinoxyl or *o*, *o'*-di-*tert*-butyl-*p*-cresol.

Reductive elimination also occurs with isobutylmethylmercury and

mercuracycloheptane III. In the latter case, the observation of discrete



amounts of rearranged cyclopentylmethyl chloride is consistent with the intermediacy of the  $\omega$ -hexenyl radical.<sup>20</sup>



$\omega$ -Hexenyl chloride in eq 4 was recovered largely as 1, 1, 1, 3, 7-pentachloroheptane, known to be the  $\text{CCl}_4$  adduct under free radical conditions.

When these reactions were carried out in the absence of initiators, the use of relatively low concentrations of mercurials was necessitated by the incursion of side reactions involving (kinetically second order) redistribution processes at the higher temperatures required. Even at these concentrations (Table I), attempts to carry the reaction of *i*-BuHgMe beyond 50% conversion led to increasing amounts (> 5%) of  $\text{Me}_2\text{Hg}$ .

The nature of the initiation process in the absence of promoters will be presented separately.<sup>21</sup> Suffice it to indicate at this point that isobutyl chloride and neopentyl chloride should be formed rather indiscriminately from isobutylneopentylmercury in the initiation step since both are derived primary alkyl groups. From the low yields of isobutyl chloride observed, we conclude that the kinetic chain length for reductive elimination is greater than 50.

#### Activation of $\beta$ -Hydrogen

Reactions of the dialkylmercury such as mercuracycloheptane III with  $\text{CCl}_4$  in excellent stoichiometry (eq 4), suggest the high specificity for  $\beta$ -elimination under conditions in which a number of otherwise equivalent hydrogens are also available for abstraction. In order to obtain a quantitative assessment of such an activation, we carried out competition studies

for hydrogen transfer. The reactivity of *i*-BuHgNp **II** toward hydrogen abstraction by trichloromethyl radical was determined in CCl<sub>4</sub> solutions relative to isooctane and to cyclohexane. Reactions described in Table II were carried out to less than 10% conversion in order to maintain an essentially constant ratio of reactants. Based on the relative yields of neopentyl chloride and 2-chloro-2,4,4-trimethylpentane in the absence of initiator, we find the  $\beta$ -hydrogen in **II** to be 580 times more reactive than those in isooctane.<sup>22</sup> Similarly, the  $\beta$ -hydrogen in **II** is 600 times more reactive than a given hydrogen in cyclohexane. As a cross-check, the relative hydrogen reactivities of cyclohexane were determined directly using di-*n*-butyryl peroxide as an initiator. The average (per hydrogen) value of  $k_{C_6H_{12}}/k_{C_8H_{18}} = 0.94$  is in good agreement with the indirect value of 0.97 obtained from competition with the mercurial. In all cases studied, chloroform was always

Table II. Relative Rates of Hydrogen Abstraction from Hydrocarbons and from *i*-BuHgNp by Trichloromethyl Radicals.<sup>a</sup>

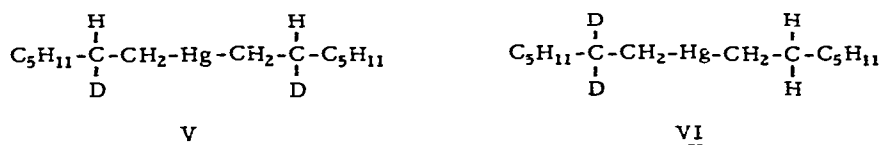
Substrate A	Substrate B	Average Substrate Ratio [B]/[A]	Product Ratio [P <sub>A</sub> ]/[P <sub>B</sub> ]	Relative Reactivity	Reactivity per Hydrogen <sup>c</sup>
<i>i</i> -Bu-HgNp	Isooctane	10.3	58.3	600	600
		15.9	36.4	580	580
		21.2	25.8	550	550
<i>i</i> -Bu-HgNp	Cyclohexane	15.8	3.12	49	590
		21.1	2.45	52	620
Et-HgNp	Cyclohexane	12.5	0.086	1.08	4.3
		26.6	0.041	1.09	4.4
<i>n</i> -Pr-HgNp	Cyclohexane	17.9	0.81	14.5	87
		36.9	0.47	17.4	104
Cyclohexane	Isooctane <sup>b</sup>	1.30	8.03	10.4	0.87
		2.39	5.12	12.2	1.02
		5.37	2.02	10.8	0.90
		4.97	2.28	11.3	0.94

<sup>a</sup>All reactions carried out in 5 ml degassed CCl<sub>4</sub> solution containing 0.235 mmol

formed in equimolar amounts relative to alkyl chlorides. Side products arising from the bimolecular reactions of radicals were negligible.

In order to determine quantitatively the effect of the degree of alkyl substitution on the reactivity of the  $\beta$ -hydrogen, ethylneopentylmercury and n-propyl-neopentylmercury were also examined in competition with cyclohexane. A hydrogen reactivity profile of primary : secondary : tertiary = 1 : 22 : 139 was thereby obtained. Significantly, the per hydrogen reactivity of even a primary  $\beta$ -hydrogen in the ethylmercurial is 4.4 times greater than that of a secondary hydrogen in the hydrocarbon substrate.

Deuterium Isotope Effects. As a mechanistic probe, we examined the kinetic isotope effects resulting from replacement of a  $\beta$ -hydrogen with deuterium in the symmetrical and unsymmetrical di-n-heptylmercury compounds, V and VI, respectively.



The isotope effects for hydrogen atom abstraction were calculated from the proton NMR spectrum (220 MHz) of the product 1, 1, 1, 3-tetrachlorooctane, by integrating the resonances at  $\delta$  3.06 and 3.24 for the protons on carbon-2 relative to that on carbon-3 at  $\delta$  4.17. The two substrates afforded the same results within the experimental uncertainty, viz.,  $k_{\text{H}}/k_{\text{D}} = 4.9 \pm 0.1$ .

#### Other Alkylmetals

Based on some limited attempts to extend these reactions to other organometals, we conclude that the radical chain process for reductive elimination is dependent on the metal. Thus, an equimolar mixture of isobutyltrimethylsilane and isobutylneopentylmercury in  $\text{CCl}_4$  solution was heated at  $100^\circ \text{C}$  until approximately 50% of the mercurial was consumed. Quantitative recovery (> 99%) of the isobutyltrimethylsilane indicates it to be at

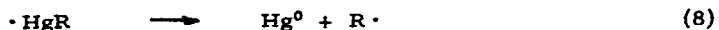
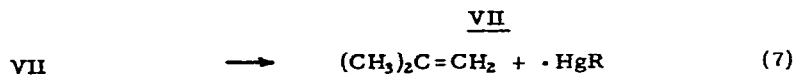
The ethyltungsten derivative  $Cp(Et)W(CO)_3$  was treated with *t*-butyl peroxalate in carbon tetrachloride solutions. The *t*-butoxy radicals (derived by the ready thermolysis of the peroxide) were apparently trapped by the ethyltungsten compound as evidenced by a four-fold reduction in products of  $\beta$ -scission.<sup>23</sup> In no case was more than a 6% yield of ethylene observed.

A facile decomposition of isobutyl(pyridine)cobaloxime in a solution of bromotrichloromethane was induced either thermally or photochemically. Elimination of isobutylene was not an important process, since chloroform could be observed in only 7-10% yields. Instead, the formation of isobutyl bromide as the major organic product (81-85%) suggests the participation of an alternative pathway for decomposition involving homolytic substitution. Further studies with these and other organometals are in progress.

#### Discussion

Reductive elimination from dialkylmercury in carbon tetrachloride solutions shows all the earmarks of an efficient radical chain process. Thus, it is initiated photochemically or thermally with peroxides and it is inhibited by galvinoxyl or hindered phenols. Moreover, the formation of cyclopentylmethyl chloride from mercuracyclohexane indicates the intermediacy of  $\omega$ -hexenyl radical according to eq 5. The efficient conversion of the olefinic products to  $CCl_4$  adducts under reaction conditions also suggests the presence of a high steady state concentration of trichloromethyl radicals during the reductive elimination of organomercurials.

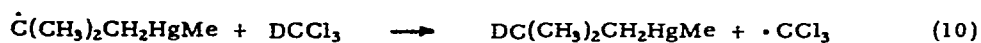
The relatively large kinetic isotope effect for reductive elimination is consistent with hydrogen atom transfer as the rate-limiting step in the propagation sequence presented in Scheme I:





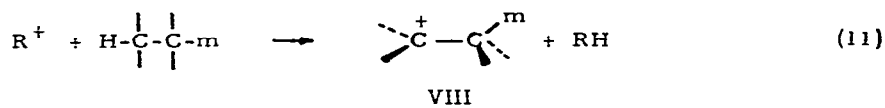
There are several mechanistic features in Scheme I which merit emphasis. Fragmentation as the exclusive fate of the alkylmercuric radical in eq 8 is consistent with the low bond energy calculated for such species (vide infra) and also with their apparent behavior in other processes, notably demercuration. <sup>9</sup> Chlorine atom transfer from carbon tetrachloride by alkyl radicals in eq 9 is known to be facile.<sup>24</sup> Of particular interest, however, is the selective removal of a hydrogen located  $\beta$  to mercury with such facility in eqs 6 and 7 as to afford high yields of elimination products in competition with other processes.

Scheme I is the simplest stepwise representation of a radical chain process for reductive elimination of dialkylmercury. [An alternative pathway involving oxidative addition to form an Hg(III) species  $R_2HgCCl_3$  followed by the simultaneous reductive elimination of  $CHCl_3$  and olefin is disfavored.] As such, alternative formulations involving synchronous processes should also be considered. For example, hydrogen transfer and elimination may occur stepwise as represented in eqs 6 and 7, or the overall process may be concerted. Driving force for the two-step process could be derived from a stabilized  $\beta$ -metalloalkyl radical intermediate VII, which is expected to have unusual properties in view of what is known about somewhat related species I (vide supra). Attempts to obtain direct chemical evidence for its formation during reductive elimination unfortunately remain inconclusive as yet. Thus, the butyryl peroxide-induced decomposition of isobutylmethylmercury was carried out to 50% completion in chloroform- $d_1$ . Conversion of the recovered mercurial to isobutyl bromide with bromine followed by mass spectral examination failed to show significant (< 1%) deuterium incorporation in the recovered mercurial. If VII were an intermediate, hydrogen transfer in eq 10



(which is the reverse of the abstraction step 6) must be at least a hundred times slower than fragmentation in eq 7. With such a limitation, the steady state concentration of VII will be too low for direct observation by the

Since there is no prior example of hydrogen atom activation in organometals via free radical intermediates, we draw attention to the observations of hydride activation via  $\beta$ -metallocarbonium ions VIII from both main group as well as transition metal alkyls.<sup>25, 26</sup> Hydride transfer in eq 11 is the cation counterpart to hydrogen atom transfer by radicals in eq 6 (or 1).



The unique properties of VIII ( $m = Hg^{+2}$ ) including the importance of  $\sigma - \pi$  hyperconjugative stabilization have been stressed.<sup>27, 28</sup> The  $\beta$ -metalloalkyl radical VII (or I) is formally related to the cation VIII by the presence of an additional electron in an antibonding orbital, and factors involved in its stabilization should also partly reflect that of the ion insofar as the properties of alkyl radicals parallel those of alkyl cations.<sup>29</sup> Further discussions regarding any unusual properties of intermediate VII including bridged structures<sup>30</sup> must await its direct observation, e. g., by electron spin resonance spectroscopy.

The energetics of an alternative pathway involving a concerted hydrogen transfer and elimination in eq 12



is roughly thermoneutral since the cleavage of a C-Hg bond is more or less compensated by the formation of the double bond. A large driving force is clearly not provided in such a synchronous process. Noteworthy with regard to the possibility of a concerted elimination is the suggestion by Kampmeier<sup>14b</sup> that the reactivity profile for such processes should deviate markedly from that observed in hydrogen abstraction from alkanes. In the present study, the relative reactivities for primary, secondary and tertiary hydrogens which increase in the order: 1, 22 and 139 show substantially higher sensitivity than 1, 9 and 43, respectively, observed in hydrogen abstraction from alkanes by phenyl radical.<sup>31</sup> Unfortunately, the requisite values for tri-

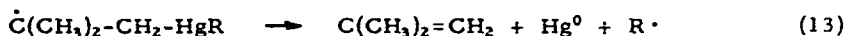
selectivity of trichloromethyl radical compared to phenyl radical<sup>23</sup> the interpretation of these results is not clear.

### Nature of Alkylmercury(I)

According to the stepwise reactions 7 and 8 in Scheme I, olefin is formed by the ejection of alkylmercury(I), the presence of which is not observed due to its instability. The existence of these alkylmercuri radicals was first inferred from gas kinetic data, e. g., as unstable intermediates in the thermolysis of dialkylmercury.<sup>18</sup> Subsequently, they have also been implicated as intermediates in the electrochemical reduction of alkylmercuric salts, reductive symmetrization reactions and demercuration.<sup>32, 33, 9</sup> Calculations indicate the bond energy of RHg· to be low (~6 kcal mol<sup>-1</sup>) or nil.<sup>18</sup>

Some of the lines in the ESR spectrum of <sup>60</sup>Co γ-irradiated ethylmercuric chloride at -200° C have been attributed to EtHg· and ClHg· species.<sup>34</sup> However, these assignments must be accepted with reservations since neither proton nor chlorine hyperfine splittings could be resolved (observed).

Our attempts to obtain the ESR spectra of alkylmercuri radicals and other mercury(I) species in solution have been unsuccessful.<sup>35-36</sup> If such species exist as discrete intermediates, the available evidence suggests that their lifetimes are exceedingly short.<sup>37</sup> Indeed, it is possible that alkyl radicals are produced directly by a concerted fragmentation,



in which the formation of RHg· is circumvented.

### Conclusion

An efficient radical chain process is established for the reductive elimination of olefin from dialkylmercury, and it is shown to arise from activation of the β-hydrogen to abstraction by ·CCl<sub>3</sub>. The stepwise mechanism presented in Scheme I invokes β-mercuroalkyl radicals VII and alkylmercury

radicals  $\text{RHg}\cdot$  as highly unstable intermediates for which there are ample analogies. In the absence of direct evidence for their existence as reactive intermediates, however, synchronous processes for hydrogen abstraction, elimination and fragmentation represented in the stepwise reactions 6, 7, and 8 must also be considered. Additional investigations involving the stereochemical dependence on the  $\beta$ -hydrogen and the effect of metals (particularly alkyl-lead derivatives<sup>25</sup> and transition metal analogues<sup>26</sup>) would doubtlessly aid in further delineating the mechanisms of free radical chain processes and their relevance to reductive eliminations generally.

### Experimental Section

Materials. Carbon tetrachloride was Fisher spectranalyzed grade purified by fractional distillation prior to use. Di-n-butyryl peroxide, prepared as previously reported,<sup>38</sup> titrated by the method of Silbert and Swern<sup>39</sup> as 96% active oxygen. Neopentyl bromide was prepared by both the method of Sommer<sup>40</sup> and that of Mosher.<sup>41</sup> The latter method afforded superior results in both yields and purity. Isobutyl bromide was purified by stirring it for two 1-hour periods with an equal volume of 2N nitric acid to hydrolyze any t-butyl bromide impurity, followed by drying over  $\text{CaCl}_2$  and distillation from  $\text{CaH}_2$ .

Alkylmercuric halides were prepared in the usual manner<sup>33</sup> by treating the Grignard reagent with a slight excess of the appropriate mercuric halide, or by the reaction of the symmetrical dialkyls (Eastman reagent) with an equimolar amount of the appropriate mercuric halide. The alkylmercuric halides were purified by sublimation under high vacuo and/or recrystallization from ethanol. Unsymmetrical dialkyls were prepared by the method of Singh and Reddy.<sup>42</sup> Methylisobutylmercury, b. p.  $50^\circ\text{C}$  at 15 torr. Anal. calc. for  $\text{C}_5\text{H}_{12}\text{Hg}$ : C, 22.04%, H, 4.44%. Found: C, 22.24%, H, 4.62%. Neopentylisobutylmercury, b. p.  $40^\circ\text{C}$  at 0.75 torr. Anal. calc. for  $\text{C}_9\text{H}_{20}\text{Hg}$ : C, 32.87%, H, 6.13%. Found: C, 33.18%, H, 6.37%. All dialkylmercury compounds gave appropriate proton NMR spectra.<sup>43</sup>

They contained < 1 % impurities by gas liquid chromatography (glc) analysis on a 6 foot column consisting of 10% polyethylene glycol 600 and 1% Quadrol on 80/100 Chromosorb W. Mercuracycloheptane was prepared from 1,6-dibromohexane and sodium amalgam by the procedure of Wright.<sup>44</sup>

Authentic 1,1,1,3-tetrachloro-3-methylbutane and 1,1,1,3,7-pentachloroheptane were prepared by the benzoyl peroxide-initiated addition of carbon tetrachloride<sup>49</sup> to isobutylene and  $\omega$ -hexenyl chloride, respectively. In both cases the compounds were contaminated with several impurities not removed by distillation. Pure samples were therefore obtained by preparative gas liquid chromatography using a 4 foot column of FFAP on Chromosorb W at low injection port and oven temperatures to minimize thermal decomposition. NMR spectra for the latter compound,  $\delta$  4.17 (1H, deceptively simple sextet, C-3, CHCl), 3.48 (2H, t,  $J_{H-H} = 6$  Hz, C-7, CH<sub>2</sub>Cl), 3.06, 3.24 (2H, two doublets of doublets, C-2, AB portion of ABX spectrum), 1.79 (6H, broad s, CH<sub>2</sub>). Mass spectral M-Cl<sub>2</sub> peak at m/e 200, 202, 204 (obsvd. 22.7 : 21.5 : 5.9, calc. 21.9 : 21.3 : 6.9). 2-Chloro-2,4,4-trimethylpentane was precipitated as a solid by treating technical diisobutylene with gaseous hydrogen chloride for one hour at -46° C<sup>45</sup> (dry ice-cyclohexanone bath). It was purified by distillation, b. p. 57° C at 41 torr. The compound was found to be > 99% pure by gas chromatography at low (< 100° C) injection port temperatures. It showed some decomposition at higher temperatures. Cyclopentylmethyl chloride was prepared by refluxing cyclopentylmagnesium bromide with paraformaldehyde and treatment of the crude mixture of the alcohol (and its formal) directly with thionyl chloride.<sup>46</sup>

Isobutyltrimethylsilane was prepared by refluxing trimethylsilyl chloride with isobutylmagnesium bromide in tetrahydrofuran for 12 hours. However, the fraction boiling at 109° C showed impurities (two minor peaks at short and two at long retention times). The material used in this study was repurified by preparative gas chromatography to afford material which had an NMR spectrum identical to that reported in the literature.<sup>47</sup> Ethyltricarbylcyclopentadienyl tungsten was prepared from tungsten hexacar-

48.  $\delta$  1.15 (3H, s, 0.22), 0.22, 5° C (sealed capil-

lary). Isobutyl(pyridine)cobaloxime<sup>49</sup> was prepared following the procedure of Schrauzer<sup>50</sup> for the methyl compound by substituting isobutyl iodide. Since its low solubility limited the resolution of the NMR spectrum, the purity of the compound was further assessed by cleaving a weighed sample with bromine in ether. It afforded 97% of the theoretical amount of isobutyl bromide.

The preparation of the deuterium-labelled compounds is discussed in the following paper.<sup>21</sup> Other compounds were reagent grade materials used as such.

Analysis by Gas Liquid Chromatography. Methane, methyl chloride, and isobutylene were determined by glc using a 6 foot column of Porapak Q at 120° C. Neopentyl chloride, n-propyl chloride and isobutyl chloride were determined on a 15 foot 25% FFAP column on 60/80 Chromosorb P at 100° C. Cyclohexyl chloride, cyclopentylmethyl chloride, chloroform, 2-chloro-2,4,4-trimethylpentane, isobutyltrimethylsilane, 1,1,1,3-tetrachloro-3-methylbutane, and 1,1,1,3,7-pentachloroheptane were determined on a 6 foot column of 20% FFAP on 60/80 non-acid washed Chromosorb W.

Thermal Reactions of Dialkylmercury with Carbon Tetrachloride. In a constricted tube equipped with a 14/40 ground glass joint was placed 0.739 g (2.25 mmol) of I and 5.0 ml of a stock solution of 0.056 M di-n-butyryl peroxide in CCl<sub>4</sub>. The mixture was immediately degassed on a vacuum line by three freeze-pump-thaw cycles. The evacuated tube was sealed with a torch and heated for 24 hours in an 80° C oil bath. The neck of the tube was then scored and a rubber tubing was slipped over the neck. The tube was opened and restored to one atmosphere by means of a hypodermic syringe filled with argon. Five ml of internal standard gas (usually ethane) was injected into the tube and gaseous products were analyzed by comparison with a set of standards calibrated under the same conditions. One ml of NMR internal standard consisting of methylene chloride in CCl<sub>4</sub> was added and a sample of the solution was examined by NMR spectroscopy. The NMR

ternal standard containing chlorobenzene and cyclohexane in carbon tetrachloride was added. The solution was analyzed by glc. The bead of metallic mercury was washed in pentane, dried, and weighed. The solution was then concentrated to approximately 0.5 ml on the rotary evaporator and re-examined for any traces of alkylmercuric chloride. Other reactions of dialkylmercury compounds with  $\text{CCl}_4$  were carried out in an analogous manner.

A similar procedure was employed in those reactions carried out with no initiators. The mercurial (2.25 mmol) was dissolved in 5 ml of pure carbon tetrachloride, and the solution after thorough degas was heated at  $100^\circ\text{C}$  for 300 hrs.

#### Photochemical Decomposition of *i*-Butylneopentylmercury in $\text{CCl}_4$

Irradiation of a 0.45 M solution of isobutylneopentylmercury in  $\text{CCl}_4$  was carried out for 10 hrs in a Rayonet photochemical reactor equipped with 350 nm bulbs at an ambient temperature of  $30^\circ\text{C}$ . In addition to the substantial yields of neopentyl chloride formed in the thermal reactions described above, significant amounts of *i*-butyl chloride were also found. The yields of *i*-BuCl increased with increasing light intensity which could be effected by changing the numbers of bulbs in the reactor. For example, the ratio of *i*-BuCl to NpCl increased from 0.089 (heavy pyrex tube, 1 bulb) to 0.109 (heavy wall pyrex tube, 14 bulbs) to 0.140 (thin wall pyrex tube, 14 bulbs). In all cases the yields of chloroform, 3-methyl-1,1,1,3-tetrachlorobutane and mercury metal were formed in more or less equimolar amounts. We tentatively attribute the formation of substantial amounts of *i*-BuCl in the photochemically induced process to the indiscriminate photolysis of I in the initiation process, e. g.,  $i\text{-BuHgNp} \rightarrow i\text{-Bu}\cdot + \text{Np}\cdot + \text{Hg}$  etc.

Competition Studies on Hydrogen Transfer (Typical Procedure). Into a 5 ml volumetric was placed 0.0772 g (0.235 mmol) of I and 0.296 g (3.52 mmol) of cyclohexane. The solution was sealed in a tube as above and heated at  $95^\circ\text{C}$  for 20 hours. One ml of a solution of internal standard consisting of pentane and chlorobenzene in  $\text{CCl}_4$  was added. The mixture was

mmol), and chloroform (0.031 mmol). To simplify calculations the average substrate ratio was taken as the mean of the initial and calculated final substrate ratios, i. e.,  $(14.98 + 16.60)/2 = 15.8$ . The (per hydrogen) reactivity of substrate A relative to substrate B could then be calculated according to

$$R = \frac{[B]}{[A]_{\text{avg.}}} \times \frac{P_A}{P_B} \times \frac{n_B}{n_A} = 15.8 \times \frac{.0232}{.00744} \times \frac{12}{1} = 590$$

where P is the product derived from a given substrate and n is the number of equivalent hydrogens available for abstraction.

Reactions of Isobutyltrimethylsilane. A solution was prepared containing 0.300 mmol each of I and isobutyltrimethylsilane in 25 ml  $\text{CCl}_4$  solution. Five ml of this solution was placed in each of four identical tubes which were degassed and sealed. Two tubes were placed in a freezer at  $-20^\circ\text{C}$  and two were heated at  $100^\circ\text{C}$  for 100 hours. Addition of internal standards and glc analysis of the four tubes showed that while reaction of I had proceeded as usual, no (<1%) decomposition of isobutyltrimethylsilane had occurred.

Studies with Isobutyl(pyridine)cobaloxime. A solution of 0.0389 g (0.0915 mmol) of the cobaloxime in a mixture of 4 ml chlorobenzene and 2 ml bromotrichloromethane was heated at  $100^\circ\text{C}$  in the absence of light. The solution turned dark green after one half hour. Continued heating for an additional 12 hours resulted in a black precipitate. Glc analysis indicated the presence of 0.0064 mmol (7%) chloroform and 0.078 mmol (85%) isobutyl bromide. Photolysis of a similar solution (350 nm, room temperature) yielded 10% of chloroform based on cobaloxime added, together with a green precipitate. In neither case were the cobalt-containing products characterized.

Preliminary Studies with Ethylcyclopentadienyltricarbonyltungsten. A solution of 0.310 g of the subject complex in 2 ml benzene remained clear and unchanged (judging by its NMR spectrum) after heating for 100 hrs at  $45^\circ\text{C}$  under  $\text{N}_2$ . On the other hand, an identical solution in  $\text{CCl}_4$  turned dark green within minutes and black within a few hours. NMR studies indi-



cated that in  $\text{CCl}_4$  the complex was 50% decomposed after 1700 min and glc analysis indicated that only traces of ethylene but up to a 13% yield of carbon dioxide were formed. Induced decomposition of peroxides in the presence of the complex was evidenced by the decrease in the half-life for decomposition of *t*-butyl peroxyoxalate (0.0162 M  $\text{CCl}_4$  solution, 45° C) from 34 min to 19 min (21 min in *t*-butylbenzene) in the presence of 0.0615 M tungsten complex. Similarly,  $t_{1/2}$  for di-*n*-butyryl peroxide dropped from 78 min (0.0548 M *t*-butylbenzene solution, 80° C) in the absence of additive to 48 min in the presence of 0.0330 M tungsten complex. Trapping of *t*-butoxy radicals derived from *t*-butylperoxyoxalate by the tungsten complex is inferred from a decrease in the yield of products of  $\beta$ -scission (i. e., acetone, methyl chloride, methane) in the presence of the complex. This effect is shown for  $\text{CCl}_4$  solution in Table III. In addition, 1-Cl-2-Me-2-propanol was observed by

Table III. Effect of Ethylcyclopentadienyltricarbonyltungsten on the Products of Decomposition of *t*-Butyl Peroxyoxalate in  $\text{CCl}_4$ .<sup>a</sup>

Product	Yield (mmol)	
	No Additive	$\text{EtWCp}(\text{CO})_3$ <sup>b</sup>
methane	.022	.006
ethylene	-	.002
$\text{CO}_2$	.323	.194
$\text{CH}_3\text{Cl}$	.030	.006
acetone	.042	.006
$\text{BuOOBu}^c$	.005	.004

<sup>a</sup>0.16 mmol *t*-butylperoxyoxalate in 3.0 ml  $\text{CCl}_4$  at 45° C. <sup>b</sup>Contains 0.14 mmol ethylcyclopentadienyltricarbonyltungsten. <sup>c</sup>Di-*t*-butyl peroxide.

glc but not determined quantitatively. The absence of any effect on the yield of di-*t*-butyl peroxide is expected since this product derives exclusively from cage recombination of *t*-butoxy radical pairs.

#### Deuterium Isotope Effects

A 0.45 M solution of di-*n*-heptylmercury (V or VI) in carbon tetrachloride

containing 0.056 M benzoyl peroxide was degassed and heated in sealed tubes at 80 °C. The solvent together with heptyl chloride and other volatiles were removed in vacuo, and the residue redissolved in fresh carbon tetrachloride to allow separation from the heptylmercuric salts. The isotope effects for hydrogen abstraction were determined by integrating the resonances at  $\delta$ 3.06 and 3.24 for the protons on carbon-2 of 1,1,1,3-tetrachlorooctane to that on carbon-3 at  $\delta$ 4.17. The isotope effect for compound V was calculated according to,  $k_H/k_D = (0.50 - R)/R$  and that for compound VI as  $k_H/k_D = R/(0.50 - R)$ . In each equation R is the ratio of the intensities of the proton resonances on carbon-3 to those on carbon-2 in the 220 MHz spectra.

Acknowledgment: We wish to thank the donors of the Petroleum Research Fund administered by the American Chemical Society, the National Science Foundation for financial support and the Lubrizol Corporation for a fellowship to W. A. Nugent.

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