

ORGANOMERCURIALS. III. INITIATION PROCESSES IN THE HOMOLYTIC
CLEAVAGE OF DIALKYL MERCURY. SPONTANEOUS REACTION OF
DI-TERT-BUTYLMERCURY IN CARBON TETRACHLORIDE

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Abstract

Di-tert-butylmercury is spontaneously cleaved in carbon tetrachloride solution without the benefit of added initiator. Trichloromethyl-t-butylmercury is identified as an intermediate which undergoes further homolytic reactions leading to autocatalysis. The short kinetic chain length coupled with the high steady state concentrations of chain-carrying trichloromethyl radicals allude to a facile initiation process from the direct interaction of di-t-butylmercury with carbon tetrachloride. Vertical ionization potentials of a series of dialkylmercury compounds are consistent with a charge transfer interaction between carbon tetrachloride as the rate-limiting step leading to the spontaneous initiation of homolytic processes. Thus di-t-butylmercury is capable of inducing the cleavage of di-n-butylmercury, which otherwise requires peroxide initiation. Di-t-butylmercury is especially susceptible to homolytic displacement, being readily cleaved to trichloromethyl-t-butylmercury by trichloromethyl radicals.

Introduction

The mechanism of radical formation from organometals and electrophiles has not been clearly delineated. For example, the various cleavage reactions of dialkylmercury compounds in carbon tetrachloride reported earlier^{1, 2} required initiation by peroxides. In this study, we have observed that highly branched mercurials such as di-t-butylmercury react in carbon tetrachloride

without the benefit of added initiator. This striking observation provides us with an opportunity to examine routes by which radicals are generated spontaneously when organometals interact with electrophiles. The role of carbon tetrachloride and other poly-halogen compounds as free radical precursors relates to similar observations with other organometals.³

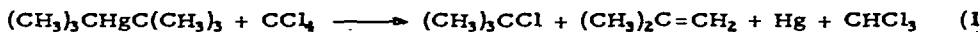
Results

Di-t-butylmercury is substitution-stable like other dialkylmercury compounds, but it is more readily autoxidized.⁴ Di-t-butylmercury also reacts with perhalomethanes such as carbon tetrachloride, carbon tetrabromide, and bromo-trichloromethane under relatively mild conditions.

Products and Stoichiometry

1. Di-t-butylmercury

The principal products derived from di-t-butylmercury and carbon tetrachloride are t-butyl chloride, isobutylene (as the CCl_4 adduct), chloroform and metallic mercury, which are all characteristic of reductive elimination examined earlier.¹



However, the amounts of each product listed in Table I are not in accord with those expected from eq 1. Closer examination reveals the presence of trichloromethyl-t-butylmercury in the initial stage of the reaction. However, as the reaction progresses, t-BuHgCCl₃ passes through a maximum concentration and ultimately disappears as shown in Figure 1. Similarly, t-butylmercuric chloride is formed but subsequently consumed when the reaction is carried out to higher conversions. The further decomposition of each of these intermediates is described later, but suffice it to indicate here that it is unlikely that they are formed simultaneously.

The dimerization of trichloromethyl radicals to hexachloroethane represents a termination step in a radical chain process. Thus, the large amount of

Table I. Reaction of *t*-Butylmercury Compounds with Perhalomethanes.^a

REACTANTS		Temp.	Time	PRODUCTS (mmol/mmol starting mercurial)				
Mercurial	CXY ₃	(°C)	(hr)	<i>t</i> -BuX	CY ₃ CH ₂ CX(CH ₃) ₂ ^c	<i>t</i> -BuHgX	CY ₃ H	C ₂ Y ₆
<i>t</i> -Bu ₂ Hg	CCl ₄	100	12	1.33	0.48	<0.01	0.54	0.58
	CBrCl ₃	45	25	0.89	0.40	0.63	0.42	n.d.
	CBr ₄ ^b	45	25	1.28	0.51	0.15	n.d.	n.d.
<i>t</i> -BuHgBr	CBr ₄ ^b	56	42	0.64	0.35	0.03	n.d.	n.d.

^aReaction of 0.2 M solution of mercurial *in vacuo* under stated conditions. ^bAs 50% w/w solution in benzene. ^cAddition product of perhalomethane to isobutylene.

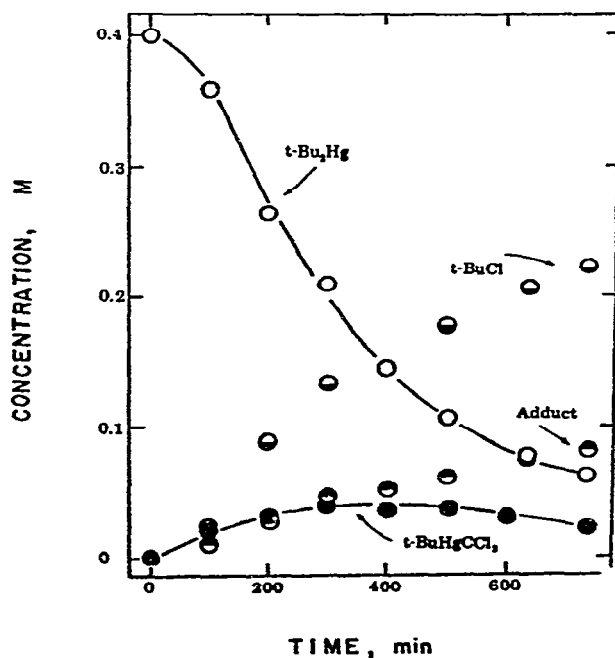
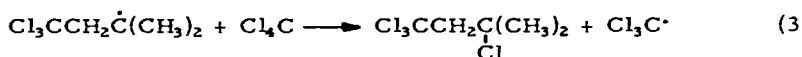
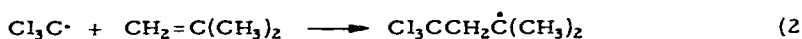


Figure 1. Formation of trichloromethyl-*t*-butylmercury [●] during the spontaneous decomposition of 0.4 M di-*t*-butylmercury [O] in carbon tetrachloride at 78°C. *t*-Butyl chloride [⊙] and CCl₄ adduct to isobutylene [⊙] also noted. *t*-Butylmercuric chloride obser-

hexachloroethane obtained in Table I indicates that a relatively high steady state concentration of chain-carrying trichloromethyl radicals is extant during the reaction. The latter is also supported by the rapid and complete conversion of isobutylene (formed on reductive elimination) to the CCl_4 adduct by the known radical chain process,⁵



Indeed, isobutylene itself is never observed in any significant quantities during the reaction. The high yield of termination product also indicates an efficient production of radicals and an inefficient chain process (i.e., low kinetic chain length)⁶ during the reaction of di-*t*-butylmercury with carbon tetrachloride. In comparison, the reductive elimination of isobutylneopentylmercury was shown earlier to be an efficient chain process which proceeds only slowly in the absence of (peroxide) initiation. In the absence of an added initiator, isobutylene actually builds up, and little or no hexachloroethane is formed.

The reactions of di-*t*-butylmercury with carbon tetrabromide and bromotrichloromethane are also described in Table I. In each case, products similar to those obtained with carbon tetrachloride are observed. The reactivity of these perchloromethanes in the order: $\text{CBr}_4 > \text{BrCCl}_3 > \text{CCl}_4$, was determined by following the disappearance of di-*t*-butylmercury under similar reaction conditions. The sequence reported in Table II is necessarily qualitative since the multiple pathways precluded a rigorous determination of the kinetics for the disappearance of the mercurial (*vide infra*). Thus, the results in Table II represent the time required for 50% decomposition and not first order half-lives.

2. Trichloromethyl-*t*-butylmercury

Trichloromethyl-*t*-butylmercury is obtained from an independent synthesis as a colorless solid by the reaction of trichloromethylmercuric bromide and *t*-butyl Grignard reagent at -78°C . A solution of trichloromethyl-*t*-butylmercury

Table II. Decomposition of Di-*t*-butylmercury in the Presence of Various Perhalomethanes^a

<u>Perhalomethane</u>	<u>Temp (°C)</u>	<u>Time (min)^b</u>
CCl ₄	100	30
	80	250
	70	1200
	60	>6000
CBrCl ₃	100	<<5
	60	23
	45	420
CBr ₄ ^c	45	165

^aIn 0.2 M solution in sealed tube in vacuo. ^btime for disappearance of 50% of the di-*t*-butylmercury (see text). ^cas 50% w solution in benzene.

accord with the decompositions of other trichloromethylmercury analogs previously established by Seyferth and coworkers.⁷

3. *t*-Butyl-phenylmercury

The effect of the second organic ligand on the thermolysis of *t*-butylmercury compounds was examined with *t*-butyl-phenylmercury, which shows negligible tendency to undergo symmetrization in nonpolar solvents. Heating a solution of 0.2 M *t*-butyl-phenylmercury in carbon tetrachloride at 80°C produced no perceptible change within a 24 hr period. The low reactivity under these conditions reflects a slow rate of initiation (relative to that of di-*t*-butylmercury), since *t*-butyl-phenylmercury is completely cleaved to *t*-butyl chloride in the presence of 0.2 equivalents of di-*n*-butyl peroxide as initiator.* This low rate of initiation is consistent with the tendency of electron-withdrawing groups such as phenyl, to lower the energy of the highest occupied molecular orbital of mercurials (vide infra).

Rates of Decomposition of Di-*t*-butylmercury

The disappearance of di-*t*-butylmercury in solution was conveniently

* Under all conditions no more than 10% isobutylene (or its CCl₄ adduct) was

monitored in evacuated sealed tubes by following its characteristic singlet resonance at δ 1.20 in the proton nmr spectrum. Either methylene chloride or cyclohexane was employed as an internal standard.

The autocatalytic nature of the decomposition of di-*t*-butylmercury in CCl_4 at 80°C is illustrated in Figure 2. The "induction" period becomes more marked at lower temperature, increasing to more than 200 minutes at 70°C .

The rate of thermal decomposition of di-*t*-butylmercury was also examined in benzene- d_6 for comparison. The disappearance of the mercurial in this solvent could be carried out reproducibly, and also followed apparent first order kinetics (half-life of 588 minutes at 100°C and 10,300 minutes at 80°C). The formation of a bead of metallic mercury was observed at both temperatures. The presence of isobutane and isobutylene was also confirmed by gas liquid chromatography but not determined quantitatively.

The autocatalytic behavior of the decomposition suggested that one or more of the products was involved as accelerators. The presence of mercurous chloride, *t*-butyl chloride or mercury metal in as much as equimolar amounts had little or no effect on the reaction of di-*t*-butylmercury in carbon tetrachloride. However, the addition of 0.3 equivalents of trichloromethyl-*t*-butylmercury removed the induction period in Figure 2, and itself disappeared with the concomitant formation of equimolar quantities of *t*-butylmercuric chloride. The rate of disappearance of trichloromethyl-*t*-butylmercury under these conditions was about the same as that carried out alone in benzene- d_6 .

The effects of hexachloroethane were also examined since it is a major product of the reaction of di-*t*-butylmercury in CCl_4 (see Table I). Treatment of 0.16 M di-*t*-butylmercury with 1.0 M hexachloroethane in chlorobenzene at 80°C resulted in a quantitative conversion to *t*-butyl chloride and *t*-butylmercuric chloride after 20 minutes. Moreover, *t*-butylmercuric chloride was susceptible to further cleavage since continued heating at 80°C for 105 minutes led to complete conversion to *t*-butyl chloride and mercuric chloride.

Alkyltrichloromethylmercury compounds RHgCCl_3 are known from Seyferth's studies to be sources of dichlorocarbene via the facile α -elimination reaction in eq

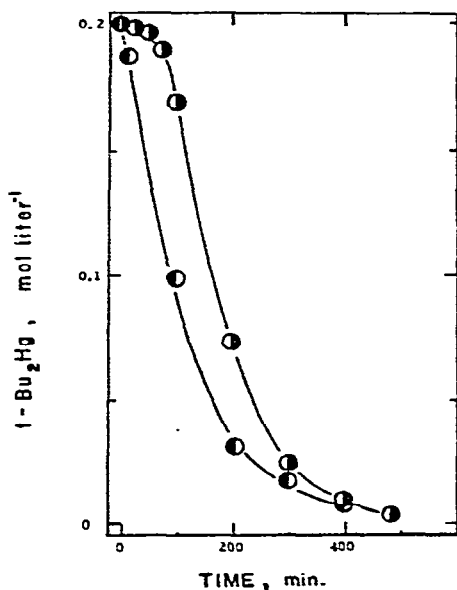
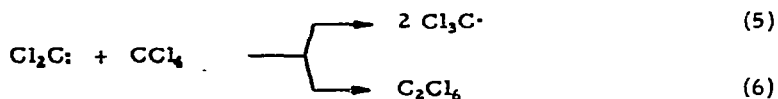
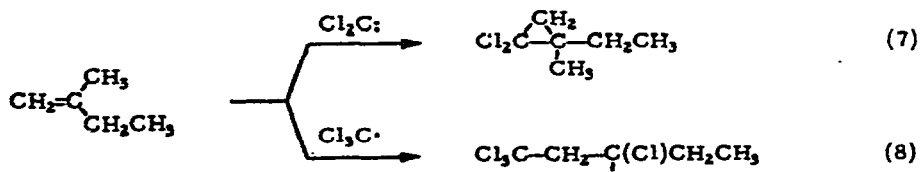


Figure 2. Autocatalysis in the decomposition of 0.20 M di-*t*-butylmercury in carbon tetrachloride at 80 °C [●]. Effect of 30 mol% trichloromethyl-*t*-butylmercury in removing the induction period [●].

It was of interest thus to determine whether the observed acceleration was due to the conversion of *t*-BuHgCCl₃ to hexachloroethane, which in turn would be responsible for autocatalysis. Such a transformation could arise from dichlorocarbene via synproportionation in eq 5 or direct insertion in eq 6.



In order to test for the former, the relative yields of the dichlorocarbene adduct and the free radical adduct to 2-methyl-1-butene in eqs 7 and 8 respectively, were investigated in the presence of carbon tetrachloride.



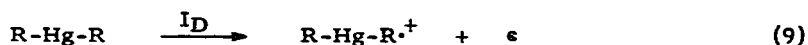
When a solution of phenyl-trichloromethylmercury (a known dichlorocarbene precursor) was heated with excess 2-methyl-1-butene in bromobenzene as solvent, only the dichlorocarbene adduct was formed in nearly quantitative yields. Essentially the same results were obtained when the reaction was carried out in a solvent consisting of 67 vol % carbon tetrachloride/bromobenzene. The small amount (~1%) of free radical adduct can be attributed to some process other than synproportionation as described in eq 5. The same experiment carried out with trichloromethyl-*t*-butylmercury afforded a preponderance of dichlorocarbene adduct and only a 5% yield of the free radical adduct.

A sample of phenyltrichloromethylmercury was also heated in a 50% volume solution of carbon tetrachloride and bromobenzene in the absence of olefin. No hexachloroethane was observed by gas chromatography, designed to detect less than 0.1%, even after heating the solution for 50 hours at 80°C. [The rate of decomposition of phenyltrichloromethylmercury is much slower in the absence of olefin as indicated by the sharply reduced rate of formation of phenylmercuric chloride also noted previously.⁷]

The disappearance of di-*t*-butylmercury in CCl₄ is not affected by the presence of conventional free radical inhibitors such as galvinoxyl or *c,o'*-di-*t*-butyl-*p*-cresol in small amounts of less than 5%, although they are rapidly consumed. Some retardation was observed only when as much as stoichiometric amounts of galvinoxyl were used.

Ionization Potentials of Dialkylmercury Compounds

The first vertical ionization potential I_D of di-*t*-butylmercury was compared to that of other analogs to determine whether the energetics of electron detachment as described in eq 9 was a determining factor in its reactivity.



The ionization potentials in Table III were determined by helium(I) photoelectron spectroscopy.⁸ The homologous series of dialkylmercury compounds

Table III. Effect of α and β -Branching on the Ionization Potentials of Dialkylmercury.^a

α -Branching		β -Branching	
R in R ₂ Hg	I.P. (eV)	R in R ₂ Hg	I.P. (eV)
Methyl	9.33	Ethyl	8.45
Ethyl	8.45	n-Propyl	8.29
i-Propyl	8.03	i-Butyl	8.30
t-Butyl	7.57	neo-Pentyl	8.30

^aFirst vertical ionization potentials by He(I) photoelectron spectroscopy.

The results show that increased α -branching markedly lowers the ionization potential, whereas β -branching has little effect. The high reactivity of di-*t*-butylmercury among dialkylmercury compounds does parallel its uniquely low ionization potential.

Discussion

The results indicate that a variety of homolytic processes occur simultaneously when di-*t*-butylmercury reacts in carbon tetrachloride solution. Fortunately, the prior identification in the foregoing studies of radical chain processes in reductive elimination¹ as well as homolytic mechanisms in substitution reactions² of dialkylmercury facilitate the unscrambling of the added complexities present with di-*t*-butylmercury. In the following discussion, we wish to focus our attention on several unique features present in the Initiation and Propagation processes during the decomposition of di-*t*-butylmercury in carbon tetrachloride.

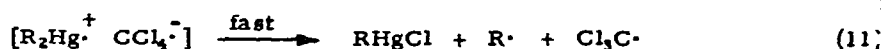
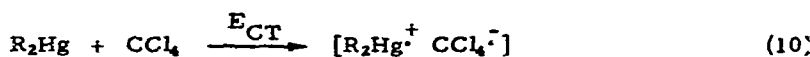
Initiation of Radical Chain Processes

The initiation of known chain processes, such as the addition of CCl₄ to isobutylene described in eqs 2-3, provides evidence for the intermediacy of free radicals during the reactions of di-*t*-butylmercury. The addition of 0.2 M di-*t*-

mercury in CCl_4 described earlier,^{1,9} without the benefit of added peroxide initiators. Di-n-butylmercury alone in CCl_4 shows no reaction under these conditions. The observation of autocatalysis indicates that at least two mechanisms are involved in radical initiation, including a "slow" process in the early stages of the reaction, followed by a "fast" process coming into effect as the reaction progresses.

Initiation Processes

The "slow" initiation of homolytic processes of dialkylmercury compounds by di-t-butylmercury may proceed by either a stepwise fragmentation of a C-Hg bond or concerted scission of both bonds, in analogy with the methyl, ethyl and isopropyl analogs.^{10,11} It is reasonable that the relatively facile thermolysis of di-t-butylmercury observed in benzene will also occur in carbon tetrachloride. However, there are two observations which suggest that homolysis may not be the exclusive process in the primary "slow" initiation of homolytic processes. First, the rate of reaction in the presence of radical traps still exceeds that of the thermolysis in benzene at the same temperature. Secondly, homolysis, either stepwise or concerted cannot account for the formation of t-butylmercuric chloride in substantial amounts even in the presence of radical inhibitors. We suggest that there is a direct reaction between the mercurial and CCl_4 leading to charge transfer and radical production in eqs 10 and 11, respectively.



Charge transfer interactions of dialkylmercury donors have been recently observed with tetracyanoethylene acceptors,¹² and we expect similar interactions with carbon tetrachloride as acceptors. In general, the energy of a contact charge transfer interaction is given by eq 12,

$$E_{\text{CT}} = I_{\text{D}} - E_{\text{A}} - G_1 \quad (12)$$

the electron affinity of the acceptor A, respectively; G_1 represents the coulombic interaction of D^+ and A^- . We suspect that the range of E_{CT} for the dialkylmercury compounds with carbon tetrachloride is comparable to that with tetracyanoethylene in view of their similar electron affinities.¹³ Furthermore, the process should become more facile along the series: $Cl_4C < BrCCl_3 < Br_4C$, since the interaction is directly related to the energy of the lowest unoccupied orbital of the perhalomethane acceptor. Finally, the rate-limiting charge transfer mechanism for initiation also predicts that di-t-butylmercury, due to its exceptionally low ionization potential, should be uniquely disposed toward radical production. The latter derives from the rapid decomposition of the ion-pair in eq 11. Thus dialkylmercury cation readily fragments to alkyl radicals $[R_2Hg^{\ddagger} \rightarrow RHg^+ + R^{\cdot}]^{14}$ and alkyl halide anions are highly metastable $[CCl_4^- \rightarrow CCl_3\cdot + Cl^-]^{15,16}$

The "fast" initiation process during the reaction of di-t-butylmercury results from the homolytic reaction of one or more intermediates. Trichloromethyl-t-butylmercury is known to be an intermediate which can accelerate the decomposition of di-t-butylmercury. However, our experiments have failed to establish the mechanism by which it is involved in the "fast" initiation. Progress on this problem must await a closer examination as to how dichlorocarbene formed in eq 4 enters the homolytic cycle.

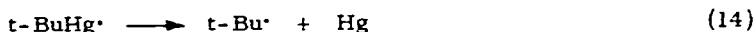
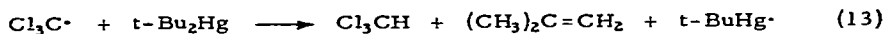
Hexachloroethane is the other intermediate which is known to accelerate the homolytic reactions of di-t-butylmercury. The facile reactions even in the absence of carbon tetrachloride suggest that these species also interact to produce free radicals, most simply accounted for as a charge transfer interaction analogous to CCl_4 . The tetrachloroethylene generated in these reactions² is involved further in the formation of telomers, and their participation in radical-generating processes must also be considered.

Propagation of Chain-Carrying Steps in Reductive Elimination

The formation of isobutylene (as the CCl_4 adduct), chloroform, t-butyl chloride and mercury(0) arises by a radical chain process outlined in eqs 13-15.¹

The reaction of di-t-butylmercury described in this manner

has a short kinetic chain length attendant with high steady-state concentrations of chain-carrying trichloromethyl radicals.

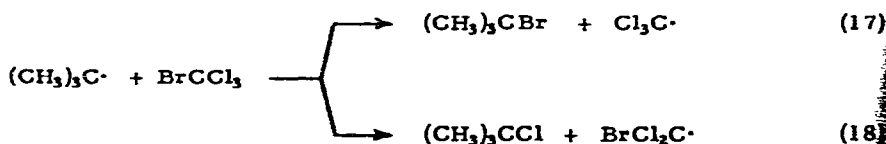


Since hydrogen transfer in eq 13 is rate-limiting, it is not surprising that reductive elimination of di-t-butylmercury which involves loss of a primary hydrogen occurs less readily than that of isobutylneopentylmercury in which a more reactive tertiary hydrogen is transferred.^{1,17} The lower reactivity of primary hydrogens on the t-butyl group is only poorly compensated by a statistical factor of 18.

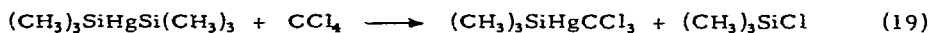
We attribute the formation of t-butyltrichloromethylmercury as a discrete, albeit transient, intermediate to homolytic displacement in eq 16.



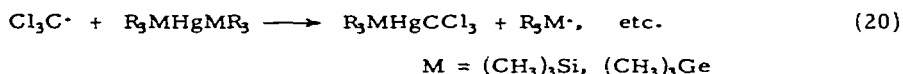
Such an $S_{\text{H}}2$ process is a reasonable extension of the trend established for the displacement of alkyl groups by benzoyloxy radicals,² in which the weaker $\text{Bu}^{\text{t}}\text{-Hg}$ bond and the higher stability of t-butyl radicals favors the reaction in eq 16 rather than the microscopic reverse process. The additional t-butyl radicals formed in this manner would then contribute to the "extra" t-butyl chloride found in Table I relative to that expected from reductive elimination alone (eq 1). Halogen transfer to t-butyl radicals in eq 15 as the source of t-butyl halide is also supported by the exclusive formation of t-butyl bromide when the reaction of di-t-butylmercury is carried out in bromotrichloromethane at 45°C. The selective transfer of bromine from BrCCl_3 in eq 17,



The formation of $\text{Cl}_3\text{C-Hg}^{\text{II}}$ derivatives from di-*t*-butylmercury and CCl_4 is quite comparable to that in a recent report¹⁹ with the silicon analogue,



A radical chain process involving an $\text{S}_{\text{H}}2$ displacement analogous to eq 16 was proposed.



A "clean" stoichiometric process, uncomplicated from myriad side reactions, results from the silicon-mercurial we think because it is optimally constituted (1) to discourage reductive elimination owing to the unfavorable formation of an unstable $\text{C}=\text{Si}$ double bond and (2) to facilitate homolytic displacement at the weak Si-Hg bond. Displacement of trimethylsilyl radicals in eq 20 by alkyl radicals other than trichloromethyl¹⁹, shows similar selectivity to that described with dialkylmercury compounds.² The analogy between trimethylsilyl and *t*-butyl derivatives of mercury cannot be carried too far since $(\text{CH}_3)_3\text{SiHgCCl}_3$ reductively eliminates to $(\text{CH}_3)_3\text{SiCCl}_3$ and mercury metal at -20°C , in contrast to the slow conversion of $(\text{CH}_3)_3\text{CHgCCl}_3$ to $(\text{CH}_3)_3\text{CHgCl}$ described above.

Experimental Section

Materials

Di-*t*-butylmercury was prepared by the procedure of Blaukat and Neumann.²⁰ However, the initial reaction was carried out in tetrahydrofuran (THF) which was replaced with ether prior to work-up. The product was further purified by vacuum sublimation. Anal. calc. for $\text{C}_8\text{H}_{18}\text{Hg}$: C, 30.52; H, 5.76. Found: C, 30.77; H, 5.87. The nmr chemical shifts and ^{199}Hg -H coupling constants of *t*-butylmercury derivatives are markedly dependent on the electron withdrawing characteristics of the substituents. The values in Table IV thus are useful for identifying these species in solution. The preparation and all subsequent transfers

Table IV. Proton nmr Spectra of t-Butylmercury Derivatives.^a

X in t-BuHgX	δ (ppm) ^b	$J_{199}^{\text{Hg-H}}$ (Hz)
Br	1.56	250
Phenyl	1.39	117
Trichloromethyl	1.37	170
Methyl	1.30	112
Ethyl	1.27	107
i-Propyl	1.24	104
t-Butyl	1.20	103

^aIn 10% CCl₄ solution ^bTMS internal standard.

of t-butylmercury derivatives were carried out in an inert atmosphere to prevent autoxidation of the organomercury compounds which is known to be particularly facile for the t-butyl derivatives.^{4,21}

t-Butylmercuric bromide was prepared by treating t-butylmagnesium bromide with an excess of mercuric bromide in THF.²² The product was contaminated with a small amount of di-t-butylmercury which was readily removed by soxhlet extraction with pentane. mp. 107-108° (decomp). Lit. 106° d.²²

Phenyl-t-butylmercury was prepared as follows. t-Butyl magnesium chloride was prepared by addition of t-butyl chloride (17.5 g, 0.16 mol) in 150 ml THF to 4.5 g of triply sublimed magnesium. The solution was filtered through a plug of glass wool whereupon a slurry of 12.5 gram (0.04 mol) phenylmercuric chloride was added gradually at -5°C. The mixture was stirred for several hours at room temperature. The THF was stripped and water-saturated ether was added which was subsequently extracted with saturated aqueous Rochelle salt solution. Drying the ether phase over MgSO₄, followed by filtration and stripping, afforded 7 grams of crude white solid which contained 20% di-t-butylmercury by nmr analysis. Two recrystallizations from ethanol afforded the desired compound, mp. 60°C.

For the synthesis of t-butyltrichloromethylmercury, the starting material

(trichloromethylmercuric bromide) was prepared by the method of Logan²³ with one improvement. In order to avoid the tedious freeze-drying step, sodium trichloroacetate was prepared in methanol solvent. A Grignard solution was prepared from 20 ml. ether, 2.0 ml t-BuBr, and 0.5 gram magnesium. On a vacuum line, two grams of trichloromethylmercuric bromide was placed in a two neck flask equipped with a rubber septum and a stirring bar. The flask was cooled to -78° with a dry ice/acetone slurry. Fifteen ml of the Grignard solution was added. After 10 minutes the dry ice bath was replaced with an ice bath and stirring was continued for one half hour. The solution was then allowed to warm to room temperature. The mixture was quenched with 1% aqueous HCl then washed several times with water while maintaining the nitrogen atmosphere. After drying with MgSO₄ and filtration, the ether was removed to afford the white crystalline solid, mp. 95-97°C (sealed capillary).

Carbon tetrabromide (Matheson, Coleman and Bell) was refluxed with dilute aqueous Na₂CO₃ then recrystallized from ethanol, mp. 92.5°C. Bromotrichloromethane was washed with dilute aqueous Na₂CO₃, then with water, dried over CaCl₂, and distilled with exclusion of light (bp. 104°C).

1,1,1,3-Tetrachloro-3-methylpentane was prepared by the benzoyl peroxide initiated addition of CCl₄ to 2-methyl-1-butene using the procedure of Kharasch, Jensen and Urry.¹⁴ 1,1-Dichloro-2-methyl-2-ethylcyclopropane was prepared via dichlorocarbene generated from chloroform following the procedure of Robinson.²⁴ (bp. 67-68°C at 45 torr.) 1,1-Dichloro-2,2,3,3-tetramethylcyclopropane was prepared from tetramethylethylene using phenyltrichloromethylmercury as a dichlorocarbene source⁷ and was purified by sublimation in vacuo. (mp. 50°C, nmr singlet at 1.21 δ). Phenyltrichloromethylmercury was prepared according to Logan²⁵ and was dissolved in hexane and filtered to remove phenylmercuric chloride prior to several recrystallization. (mp. 110°C). Other materials were prepared and purified as described previously.^{1,2}

General Procedures

In a glove bag 0.063 ga (0.2 mmol) of di-t-butylmercury was placed into

stopcock which was attached to one arm of a Y-tube on a vacuum line. The other arm was attached to a small flask containing the perhalomethane and the internal standard which had previously been degassed by three freeze-pump-thaw cycles. The internal standard was generally methylene chloride or cyclohexane (occasionally benzene). The nmr tube was evacuated and the solvent transferred in vacuo. The tube was then sealed with a torch. Non-volatile additives were generally loaded in the nmr tube along with the mercurial, whereas volatile additives were transferred with the solvent perhalomethane by bulb to bulb distillation in vacuo. The tubes were heated in an oil bath and the course of the reaction was followed by periodic examination of the nmr spectrum. The exceptions to the above procedure were the reactions of carbon tetrabromide. This reactant was added directly to the nmr tube in the glove bag as a degassed 50 vol % solution in benzene (1 ml). Larger scale reactions were carried out in analogous manner using 20 ml tubes equipped with ground glass joints. No internal standard was added initially with 5 ml of perhalomethane and 0.32 gm (1.0 mmol) of di-t-butylmercury. These tubes were also sealed with a torch and heated in a thermostated oil bath. Upon cooling, the tubes were opened and 1.00 ml of a solution containing internal standard was added. Products were determined by flame ionization gas chromatography under the conditions described earlier^{1,2} with the following exceptions. t-Butylmercuric halides and t-butyltrichloromethylmercury were determined by quantitative nmr. The mercury-containing precipitate was collected by filtration, washed with pentane, and weighed. The mercury is recovered as a grey precipitate in 60%w of the di-t-butylmercury consumed in carbon tetrachloride as described in Table I. The semi-solid consisted primarily of finely divided mercury metal as shown by its tendency to collect in metallic beads on standing. The remainder is mercurous chloride which turns black on the addition of concentrated ammonium hydroxide.

Reactions with hexachloroethane were carried out as described previously.²

Products of Synproportionation

Into each of two tubes was placed 0.35 gm phenyltrichloromethylmercury

3.0 ml bromobenzene. The second tube contained 2.0 ml CCl_4 and 1.0 ml bromobenzene. The tubes were thoroughly degassed and sealed in vacuo. They were then heated at 80°C for 48 hours. Both tubes showed a quantitative (> 98%) yield of 1,1-dichloro-2-methyl-2-ethylcyclopropane. In the tube containing CCl_4 , there was additionally found some 1% (based on mercurial) of 1,1,1,3-tetrachloro-3-methylpentane. Another tube was prepared containing 0.17 gm t-butyltrichloromethylmercury in 1.0 ml bromobenzene, 1.0 ml 2-methyl-1-butene, and 2 ml CCl_4 . The yield of 1,1,1,3-tetrachloro-3-methylpentane was now 5% based on mercurial. A tube containing 2.0 ml benzene and 2.0 ml CCl_4 together with 0.40 gm phenyltrichloromethylmercury was heated at 80°C for 48 hours. No hexachloroethane was observed among the products under conditions where as little 0.1% based on mercurial could be detected. The rate of precipitation of phenylmercuric chloride was markedly slower in the tube containing no olefin.

2. t-Butylmercuric Bromide.

Alkylmercuric halides are generally stable in carbon tetrachloride solution in the absence of initiators. t-Butylmercuric bromide, however, is one of the more reactive derivatives, and reacts with a concentrated solution of carbon tetrabromide in benzene to afford t-butyl bromide and isobutylene (as the CBr_4 adduct). However, no metallic mercury is formed under these conditions. The only mercury-containing product consisted of mercurous bromide appearing as a white, water-insoluble product. This result is consistent with an earlier report that mercurous chloride is the exclusive mercury-containing product of the peroxide-induced reaction of alkylmercuric chlorides with carbon tetrachloride.²⁶

NMR Spectra were determined on a Varian EM360 NMR spectrometer in 10% CCl_4 solution vs. a TMS internal standard. First vertical ionization potentials were determined by He(I) photoelectron spectroscopy by Drs. J. Ulman and T. P. Fehlner.

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