concentrations, Wilkinson[14] postulated (because the equilibrium would favor formation of $(PPh_3)_2RhH(CO)_2$) that the associate pathway was increasingly favored, thus accounting for the increased selectivity at high phosphine concentrations.

(16) For recent ESR studies of spin-labeled polymers which provide information about resin mobilities see (a) S. L. Regen, *J. Am. Chem. Soc.*, **96**, 5275 (1974); (b) *ibid.*, **97**, 3108 (1975); (c) *Macromolecules*, **8**, 689 (1975); (d) Z. Veksli and W. Miller, *ibid.*, **8**, 248 (1975); (e) T. C. Ward and J. T. Books, *ibid.*, 7, 207 (1974); and (f) P. Tormala, J. Martinmaa, K. Silvennoinen, and K. Vaahtera, *Acta Chem. Scand.*, **24**, 3066 (1970).

(17) The rate of hydroformylation was slower using the resin attached catalysts. Over the range conditions reported here, the ratio of reaction half times (time to 50% yield, anchored/homogeneous) ranged from 2.5 to 85. However, this is a complex function of many factors and detailed studies will be reported later.

(18) Electron microprobe studies on larger resin beads, which were even more heavily cross-linked, prepared in the same fashion show that phosphorus and rhodium are evenly distributed throughout the bead. Thus, even distribution of the catalyst sites on an internal macroscale is assumed in the beads employed here.

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Reductive Elimination of Organometals by Free Radical Chain Mechanisms. Enhanced Activation of β-Hydrogens in Dialkylmercury

Sir:

Free radical reactions of organometals have been studied less extensively than electrophilic processes,[1] yet the homolytic nature of such useful procedures as the demercuration reaction[2] and trialkyltin hydride reduction[3] suggests that this mode of reactivity deserves careful delineation. Noteworthy in this regard are reports[4,5] in which organomercurials are purported to undergo elimination via abstraction of a β-hydrogen atom and loss of the metal. We now 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, thus allowing an unambiguous identification of radical chain processes in the reductive elimination and the quantitative assessment of the homolytic reactivity of β-hydrogens in dialkylmercurials.

Table I. Reductive Elimination of Dialkylmercury in Carbon Tetrachloride Solutions[a]

Mercurial[b] R-Hg-R′	Conversion (%)[c]	Products (mmol)[d]			
		R(-H)[e]	R′-Cl	$CHCl_3$	Hg^0
i-BuHgMe	51	1.01	0.93	0.93	1.02
i-BuHgNp	88	0.96	0.87	0.91	0.97
$Hg(CH_2)_6$[f]	*g*	0.84	0.86	1.07	0.80

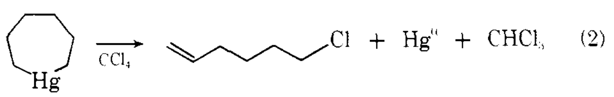
[a] At 100 °C, no initiator added. [b] 2.25 mmol in 5 ml of CCl_4. [c] Based on recovered RHgR′ after 300 h. [d] Per millimole of unrecovered RHgR′. [e] Alkene plus CCl_4 adduct. [f] Contains 0.28 mmol of di-*n*-butyryl peroxide, yields based after 7 h on reactant charged. [g] Not determined.

When a solution of isobutylneopentylmercury[6] (I) 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 CCl_4 to olefins under free radical conditions.[7] Significantly, only traces of isobutyl chloride[8] obtain, and neither isobutyl nor neopentylmercuric chloride is found.[9] The results in Table I establish the overall stoichiometry for the reductive elimination of I according to eq 1.

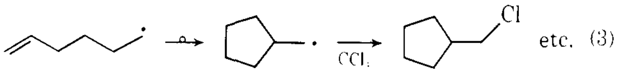
$$\underset{\text{I}}{(CH_3)_2CHCH_2HgNp} \xrightarrow[CCl_4]{} (CH_3)_2C{=}CH_2 + Hg^0 + NpCl + CHCl_3 \quad (1)$$

Reaction 1 is markedly accelerated by the addition of catalytic amounts of butyryl peroxide and to a lesser extent by azobisisobutyronitrile. Moreover it is inhibited by either galvinoxyl or *o,o′*-di-*tert*-butyl-*p*-cresol.

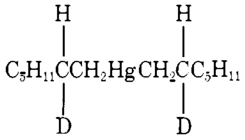
Reductive elimination also occurs with isobutylmethylmercury and mercuracycloheptane (II). In the latter case, the observation of discrete amounts of rearranged cyclopentylmethyl chloride is consistent with the intermediacy of the ω-hexenyl radical.[11]



II

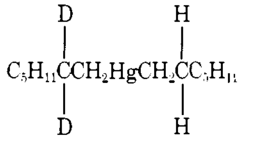


As a mechanistic probe, we have examined the kinetic isotope effects resulting from the replacement of a β-hydrogen with deuterium in the reactions of both deuterated di-*n*-heptylmercury compounds III and IV. The isotope effects for hydrogen atom abstraction were conveniently calculated from the proton NMR spectrum (220 MHz) of the product 1,1,1,3-tetrachlorooctane, by integrating the resonances at δ 3.06 and 3.24 ppm for the protons on carbon-2 relative to that



$$C_5H_{11}C(H)(D)CH_2HgCH_2C(H)(D)C_5H_{11}$$

III



$$C_5H_{11}C(D)(D)CH_2HgCH_2C(H)(H)C_5H_{11}$$

IV

Table II. Relative Rates of Hydrogen Abstraction from Hydrocarbons and from *i*-BuHgNp by Trichloromethyl Radicals[a]

Substrate A	Substrate B	Av substrate ratio [B]/[A]	Product ratio $[P_A]/[P_B]$	Relative reactivity	Reactivity per hydrogen
i-BuHgNp	Isooctane	10.3	58.3	600	600
		15.9	36.4	580	580
		21.2	25.8	550	550
i-BuHgNp	Cyclohexane	15.8	3.12	49	590
		21.1	2.45	52	620
Cyclohexane	Isooctane[b]	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

[a] All reactions carried out in 5 ml of degassed CCl_4 solution containing 0.235 mmol of substrate A at 95 °C. [b] Contains 0.03 mmol of di-*n*-butyryl peroxide.

on carbon-3 at δ 4.17. The two substrates afforded the same results within experimental error, viz., $k_H/k_D = 4.9 \pm 0.1$.

All of these results are consistent with a free radical chain mechanism for reaction 1 in which the propagation sequence is represented in Scheme I.

Scheme I

$$HC(CH_3)_2CH_2HgR + CCl_3 \rightarrow \cdot C(CH_3)_2CH_2HgR + HCCl_3 \quad (4)$$

$$\cdot C(CH_3)_2CH_2HgR \rightarrow (CH_3)_2C{=}CH_2 + \cdot HgR \quad (5)$$

$$\cdot HgR \rightarrow Hg^0 + R\cdot \quad (6)$$

$$R\cdot + CCl_4 \rightarrow R\text{-}Cl + Cl_3C\cdot \quad (7)$$

There are several mechanistic features in Scheme I which merit emphasis. Fragmentation as the exclusive fate of the alkylmercuric radical in eq 6 is consistent with the low bond energy ($\sim$6 kcal mol^{-1}) calculated for such species[12] and also with their apparent behavior in other processes, notably demercuration.[2] Chlorine atom transfer from carbon tetrachloride by alkyl radicals in eq 7 is known to be facile.[13] Of particular interest, however, is the selective removal of a hydrogen located β to mercury with such facility as to afford high yields of elimination products in competition with other processes. In order to obtain a quantitative assessment of this activation we carried out competition studies for hydrogen transfer.

The reactivity of I toward hydrogen abstraction by trichloromethyl radical was determined in CCl_4 solutions relative to isooctane and to cyclohexane. Reactions described in Table II were carried out to less than 10% conversions in order to maintain an essentially constant ratio of substrates. Based on the relative yields of neopentyl chloride and 2-chloro-2,4,4-trimethylpentane in the absence of initiator, we find the hydrogen in I to be 580 times more reactive than that in isooctane. Similarly, the β-hydrogen in I is 600 times more reactive than a given hydrogen in cyclohexane. As a cross-check, the relative hydrogen reactivities of cyclohexane and isooctane were determined directly using di-*n*-butyryl peroxide as 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.[14] In all cases studied the chloroform was always formed in equimolar amounts relative to alkyl chlorides, and side products arising from the bimolecular reactions of radicals were negligible.

To our knowledge these data represent the first evidence for substantial activation of a β-hydrogen in a metal alkyl to homolytic abstraction.[15] As such they bear an interesting relationship to hyperconjugative effects observed in β-metallocarbonium ions formed by hydride transfers,[17] and it is reasonable that similar effects are applicable to radicals in measure. We hope to extend these studies to the reductive elimination of other organometallic species, particularly those derived from transition metals.[18,19]

References and Notes

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(2) (a) H. C. Brown and D. Geoghegan, *J. Am. Chem. Soc.*, **89**, 1522 (1967); (b) G. M. Whitesides and J. San Filippo, Jr., *ibid.*, **92**, 6611 (1970), and references contained therein.

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(5) See also J. C. Pommier and D. Chevolleau, *J. Organomet. Chem.*, **74**, 405 (1974).

(6) A mixed mercurial RHgR' allows the separate fates of the two alkyl groups to be differentiated. The choice of an isobutyl group reflects the increasing ease of hydrogen atom abstraction in the series: primary < secondary < tertiary; the neopentyl group was selected for its lack of β-hydrogens.

(7) M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1100 (1947).

(8) Initiation in the absence of promoters may proceed by slow thermolysis of the mercurial or electron transfer with CCl_4. In either case, *i*-BuCl and NpCl should be found rather indiscriminately; the low yields of isobutyl chloride suggest a kinetic chain length of greater than 50.

(9) Alkylmercuric chloride reported in earlier studies[4a] actually consists of a mixture of benzoate derived from benzoyl peroxide as initiator, with the chloride arising from a competing chlorinolysis.[10]

(10) W. A. Nugent and J. K. Kochi, to be submitted for publication.

(11) D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).

(12) D. G. Gowenlock, J. C. Polyani, and E. Warhurst, *Proc. R. Soc. London, Part A*, **219**, 270 (1963).

(13) M. L. Poutsma in "Free Radicals", J. K. Kochi, Ed., Vol. I, Wiley, New York, N.Y., 1973, p 333ff; K. U. Ingold, *ibid.*, p 37, Vol. II.

(14) The reactivity of the tertiary hydrogen of isooctane has been noted: F. F. Rust and D. O. Collamer, *J. Am. Chem. Soc.*, **76**, 1055 (1954).

(15) Hydrogen transfer and elimination in Scheme I may occur stepwise as in eq 4 and 5 or they may be concerted. An alternative pathway involving oxidative addition of $\cdot CCl_3$ to form a Hg(III) species followed by reductive elimination of $CHCl_3$ and alkene is disfavored but cannot be rigorously disproved at present. For other examples of β-hydrogen activation in free radical reactions see ref 16.

(16) P. S. Skell and K. J. Shea, p 809 in ref 13.

(17) J. M. Jerkunica and T. G. Traylor, *J. Am. Chem. Soc.*, **93**, 6278 (1971).

(18) J. K. Kochi, *Acc. Chem. Res.*, 7, 351 (1974).

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

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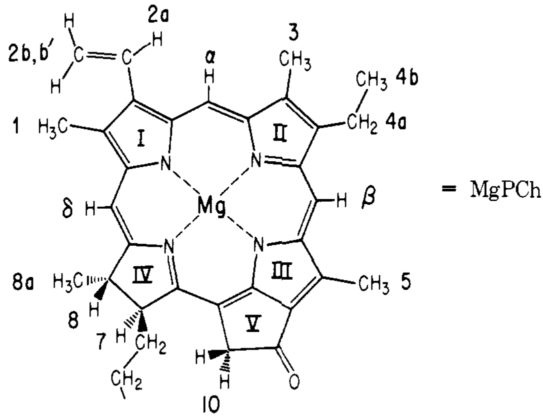
A Covalently Bound Dimeric Derivative of Pyrochlorophyllide *a*. A Possible Model for Reaction Center Chlorophyll[1]

Sir:

Molecular aggregation of chlorophyll has been the subject of intense study in several laboratories.[2-6] While there is good evidence for keto carbonyl-Mg interactions in nonbasic solvents, there is much less structural information on a different form of association postulated to contain a Mg-H_2O-carbonyl link. Reaction center chlorophyll (P-700) has been associated with such a "special pair"[3] structure where exciton interactions presumably give rise to the observed red shift in the absorption maximum. Attempts to produce a well-defined molecular assembly in vitro which mimic these properties have only been marginally successful.[4]

It occurred to us that it might be possible to construct a model for P-700 by linking two chlorophyll chromophores covalently, thus reducing the entropy of dissociation. We



1, $H_2PChl\cdot CO_2CH_3$
2, $H_2PChl\text{-}CO_2CH_2CH_2OH$
3, $(H_2PChl\text{-}CO_2CH_2\text{-})_2$
4, $(MgPChl\text{-}CO_2CH_2\text{-})_2$
5, $MgPChl\text{-}CO_2CH_3$