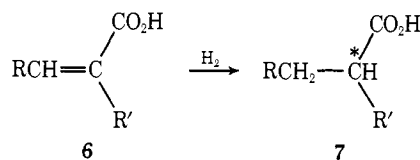


Table I. Asymmetric Hydrogenation of Olefins by Polymer-Supported Rh-DIOP Catalyst^a



	R	R'
a	H	NHCOCH ₃
b	Ph	NHCOCH ₃
c	H	Ph

Substrate	Time (h)	Conversion ^b (%)	Optical yield ^c (%)	Configuration
a	5	100	52–60 ^d (73) ^e	R
b	12	100	86 (81)	R
c	12	100	58–62 ^d (63)	S

^a Phosphinated polymer **4** = 1.6 g (0.51 mequiv of P); [RhCl(C₂H₄)₂]₂ = 25 mg (P/Rh = 4); substrate = 6.4 mmol (olefin/Rh = 50); solvent = benzene (5 ml) and ethanol (25 ml). Benzene was not used in recycle runs; reaction temperature = 25°C; P_{H₂} = 1–2.5 atm (abs). ^b Conversion was measured by ¹H NMR. ^c Optical yields are calculated with respect to the following values of the optically pure compounds: *N*-acetyl-(*R*)-alanine, [α]_D²⁵ +66.5° (C 2, H₂O) (S. M. Birbaum, L. Levintow, R. B. Kingsley, and J. P. Greenstein, *J. Biol. Chem.*, **194**, 455 (1952)); *L*-*N*-acetyl-(*S*)-phenylalanine, [α]_D²⁵ +46.0° (C 1, EtOH) (T. P. Dang, J. C. Poulin, and H. B. Kagan, *J. Organomet. Chem.*, **91**, 105 (1975)); (*S*)-hydratropic acid, [α]_D²⁵ +76.3° (C 1.6, CHCl₃) (S. P. Bakshi and E. E. Truner, *J. Chem. Soc.*, 171 (1961)). ^d Variations in optical yield were observed between batches; however, the optical yield varied <1%—upon repetitive use of the catalyst when oxygen was strictly excluded. ^e The results obtained using homogeneous Rh^I-DIOP catalyst are shown in parentheses.

selectivity is slowly lost.

Further work on the application of polymer-supported catalyst **5** and its analogues to hydrosilylation and hydroformylation is in progress.

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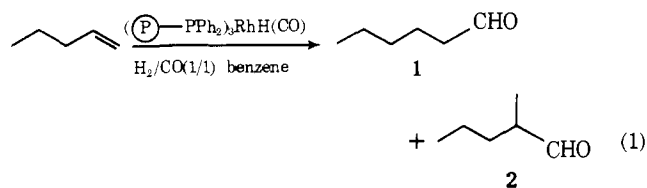
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Unusual Selectivities in Hydroformylations Catalyzed by Polymer-Attached (PPh₃)₃RhH(CO)

Sir:

Recent studies^{1–6} have shown that the use of homogeneous catalysts, attached to polymers, can exhibit several advantages when compared to normal homogeneous application. For example, increased substrate size selectivity,^{1,2} increased activity,^{3,4} easier catalyst recovery and recycle,^{1–6} and protection of catalyst sites from water^{6,7} have been demonstrated in various systems. We now present the results of a series of 1-pentene hydroformylations in benzene (eq 1), catalyzed by polymer-attached ((P—PPh₂)₃RhH(CO)),⁸ which demonstrate (a) an unusually high linear/branched product selectivity,⁹ (b) an unusual temperature dependence of this selectivity, and (c) an unusually high dependence of product selectivity upon pressure. The isomerization of 1-pentene to 2-pentene and production of pentane were not observed under the conditions studied.



The normal/branched (i.e., **1/2**) selectivity was 12.1 at 100° (16.1 at 120°) and 100 psi using highly phosphinated resin-A (40% of the phenyl rings contain -PPh₂ groups, % P = 7.01, P/Rh = 19), while the corresponding homogeneous application of the catalyst¹⁰ (at 100°, 100 psi, P/Rh = 19) only produced a **1/2** ratio of 3.3. Similarly, at 140° and 400 psi, the selectivity was 6.1 for resin-A vs. 2.4 for homogeneous runs.¹⁰ Resin-B (32% of the phenyl rings contain -PPh₂, % P = 6.16, P/Rh = 15.5) exhibited a selectivity of 4.9 at 800 psi and 70 °C vs. a value of 2.9 for corresponding homogeneous runs.¹⁰ In general, polymer-attached catalysts were notably more selective than their homogeneous counterparts at high phosphine loadings and high P/Rh ratios. At low phosphine loadings and lower P/Rh ratios, the polymer-attached catalysts' selectivity resembled that of the corresponding homogeneous runs (see Figure 1, resin-C, and Table I). The selectivity decreased slightly in homogeneous runs as the temperature was increased (Figure 1). Wilkinson¹¹ previously observed this phenomena. In sharp contrast to homogeneous systems, selectivity increased slightly between 50 and 100 °C and then remained almost constant to 150 °C when resin-A was employed (400 psi). At 100 psi, resin-A exhibited a maximum selectivity of 16.1 at 120 °C. The selectivity, using resin-B at 800 psi, increases sharply

Table I. Representative Hydroformylations of 1-Pentene Catalyzed by $(\text{P-PH}_2)_3\text{RhH}(\text{CO})$ vs. Homogeneous Application of $(\text{PPh}_3)_3\text{RhH}(\text{CO})^a$

Catalyst	Temp, °C	Pressure, psig	Yield, %	Selectivity 1/2	Catalyst	Temp, °C	Pressure, psig	Yield, %	Selectivity 1/2	
Resin-A ^b	50	400	35	5.1	Resin-A ^b	100	800	98.6	4.3	
	60	400	60.5	5.3		100	600	98.3	4.6	
	80	400	96.2	5.5		100	400	97.6	6.2	
	100	400	97.6	6.1		100	200	95.9	8.8	
	120	400	98.1	6.0		100	100	96	12.1	
	140	400	95.9	6.1		$(\text{PPh}_3)_3\text{RhH}(\text{CO})^b$	100	800	99.7	2.8
$(\text{PPh}_3)_3\text{RhH}(\text{CO})^b$	160	400	90.8	5.7	100		600	99.6	2.8	
	60	400	99.7	3.1	100		400	100	2.9	
	80	400	99.8	2.9	100		200	98.3	3.2	
	100	400	100	2.9	100		100	93.7	3.3	
	120	400	99.8	2.7	Resin-A ^b		60	100	62.7	9.6
	140	400	96.2	2.4		80	100	96.1	12.6	
Resin-B ^c	40	800	13	2.5		100	100	92.4	12.1	
	50	800	53	3.6		120	100	94.2	16.1	
	60	800	60	4.0		140	100	57	10.2	
	70	800	94	4.9		160	100			
	80	800	96.3	3.1	140	100	57	10.2		
	100	800	99	2.5	140	200	87	8.74		
$(\text{PPh}_3)_3\text{RhH}(\text{CO})^c$	40	800	26.8	3.2	140	400	95.9	6.1		
	60	800	98.7	3.1	140	600	97.5	4.35		
	80	800	100	3.0	140	800	98.2	4.25		
	Resin-C ^d	40	800	10.8	3.0	$(\text{PPh}_3)_3\text{RhH}(\text{CO})^b$	60	100	99	3.6
50		800	37.6	2.6	80		100	98.7	3.8	
60		800	66.3	2.3	100		100	93.7	3.3	
70		800	98.5	2.5	120		100	90.5	2.2	
80		800	80	2.5	140		100	48.6	2.3	
$(\text{PPh}_3)_3\text{RhH}(\text{CO})^d$		40	800	42	2.9		$(\text{PPh}_3)_3\text{RhH}(\text{CO})^b$	80	400	99.8
	50	800	83.4	2.9	$(\text{PPh}_3)_3\text{RhH}(\text{CO})^e$	80		400	99.6	3.2
	60	800	99	3.0	$(\text{PPh}_3)_3\text{RhH}(\text{CO})^f$	80		400	99.5	3.5
	70	800	100	2.9	$(\text{PPh}_3)_3\text{RhH}(\text{CO})^g$	80		400	99.3	3.6
	80	800	100	2.6						

^a The 1/2 ratio does not vary appreciably with the percent conversion. Isomerization of 1-pentene to 2-pentene was not found in these reactions.

^b 4.58×10^{-3} M Rh; 400:1, pentene:Rh; P:Rh = 19:1. ^c 1.87×10^{-4} M Rh; 100:1, pentene:Rh; P:Rh = 15.6:1. ^d 1.87×10^{-4} M Rh; 100:1, pentene:Rh; P:Rh = 3.6. ^e 9.16×10^{-3} M Rh; 400:1, pentene:Rh; P:Rh = 19:1. ^f 1.31×10^{-2} M Rh; 400:1, pentene:Rh; P:Rh = 19:1. ^g 2.74×10^{-2} M Rh; 400:1, pentene:Rh; P:Rh = 19:1.

going from 40 to 70 °C (2.4 to 4.9) and then rapidly *decreases* (to 2.5) as the temperature is raised to 100 °C. Resins with lower phosphine loadings and P/Rh ratios exhibited selectivity-temperature dependences similar to that of their corresponding homogeneous runs (i.e., see the temperature dependence of resin-C with 8.5% of its phenyl rings phosphinated, % P = 2.22, and P/Rh ratio of 3.5 in Figure 1). The shape of the selectivity-temperature plots depended upon (a) the resin's phosphorus loading, (b) the P/Rh ratio, (c) the resin's crosslink density, and (d) the pressure.

A remarkable difference in the pressure dependence of the selectivity was observed upon comparing polymer-attached vs. homogeneous systems (see Figure 2). In the homogeneous case, selectivity increased from 2.8 to 3.3 as the pressure was reduced from 800 to 100 psi (1:1, CO:H₂) at 100 °C.¹² At the same conditions¹⁰ using resin-A, the increase in selectivity was far more pronounced, going from 4.3 to 12.1 over the same pressure range. This phenomenon appears general in resins with high phosphine loadings. For example, resin-A exhibits a similar sharp pressure dependence at 140 °C (Figure 2). Since the selectivity was remarkably higher at 100 psi, using resin-A, the temperature dependence was also examined at this pressure. The highest ratio of 1/2 was 16.1 at ~120 °C. At both higher and lower temperatures the selectivity was lower (see Figure 1).

The high selectivities given by the polymer bound catalysts could be due, in part, to an artificially high catalyst-ligand concentration effect within the volume of the swollen resin beads. Wilkinson¹³ showed the selectivity to linear product increased slightly as soluble catalyst's concentration increased

from 1×10^{-3} to 5×10^{-2} mol l⁻¹. We confirmed this effect with $(\text{PPh}_3)_3\text{RhH}(\text{CO})$ (Table I). At constant P/Rh, the number of phosphine-rhodium collisions increases as catalyst concentration is raised. An abnormally high phosphine-rhodium collision rate might occur within polymers having high phosphine loadings and high P/Rh ratios, due to close proximity of such groups. Alternatively, if rhodium sites are well separated from excess phosphine groups on the polymer (low phosphine loadings and lower P/Rh ratios) the selectivity ratio should be low.

At high effective P/Rh ratios and at the artificially high phosphine loadings encountered in some resins, $(\text{PPh}_3)_2\text{RhH}(\text{CO})_2$ might be the predominant active catalyst due to a shift in the equilibrium $(\text{PPh}_3)_2\text{RhH}(\text{CO})_2 \rightleftharpoons (\text{PPh}_3)\text{RhH}(\text{CO})_2 + \text{PPh}_3$.^{13,14} In terms of Wilkinson's hydroformylation mechanism,^{14,15} a shift to $(\text{PPh}_3)_2\text{RhH}(\text{CO})_2$ would favor the associative pathway which gives a higher selectivity.¹⁵ Conversely, at the lower phosphine concentrations present within resins having low phosphine loadings, the inherently less selective dissociative pathway would be favored.¹⁵

The increases in selectivity with rising temperature exhibited by resins-A and -B can be explained in terms of the resins' internal mobility.¹⁶ At higher temperatures the rate and amplitude of a given chain segment's mobility will be higher. For example, as temperature increases from 40 to 70 °C using resin-B, the attendant mobility increase could permit a substantially greater number of phosphines to encounter a given rhodium site within the time frame of the important mechanistic events. This would lead to a higher selectivity. For res-

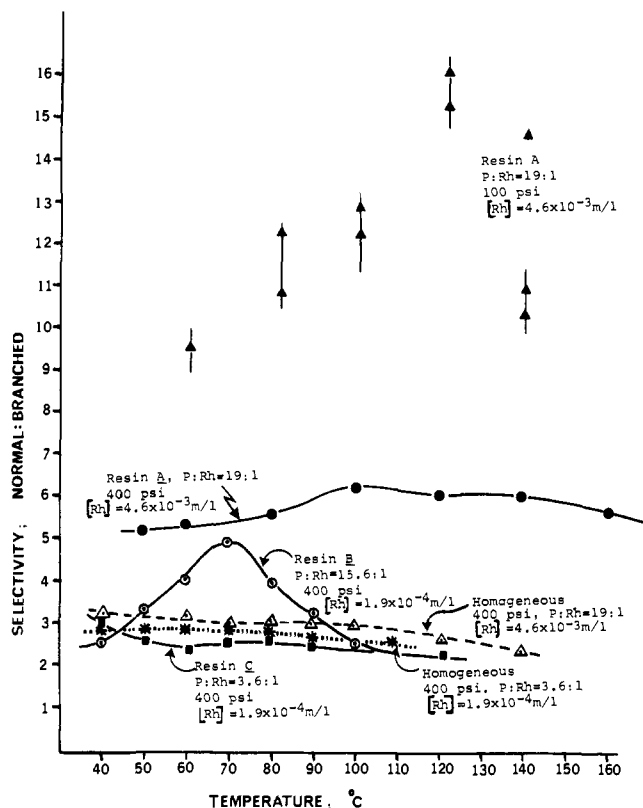


Figure 1. Dependence of selectivity on temperature. Comparison of resin-attached vs. homogeneous catalysts. Key: (■) resin C, 400 psi, P:Rh = 3.6:1, $[Rh] = 1.87 \times 10^{-4}$ M, pentene:Rh = 100:1; (*) homogeneous, 400 psi, P:Rh = 3.6:1, $[Rh] = 1.87 \times 10^{-4}$ M, pentene:Rh = 100:1; (○) resin-B, 400 psi, P:Rh = 15.6:1, $[Rh] = 1.87 \times 10^{-4}$ M, pentene:Rh = 100:1; (●) resin-A, 400 psi, P:Rh = 19:1, $[Rh] = 4.58 \times 10^{-3}$ M, pentene:Rh = 400:1 (Δ) homogeneous, 400 psi, P:Rh = 19:1, $[Rh] = 4.58 \times 10^{-3}$ M, pentene:Rh = 400:1; (\blacktriangle) resin-A, 100 psi, P:Rh = 19:1, $[Rh] = 4.58 \times 10^{-3}$ M, pentene:Rh = 400:1.

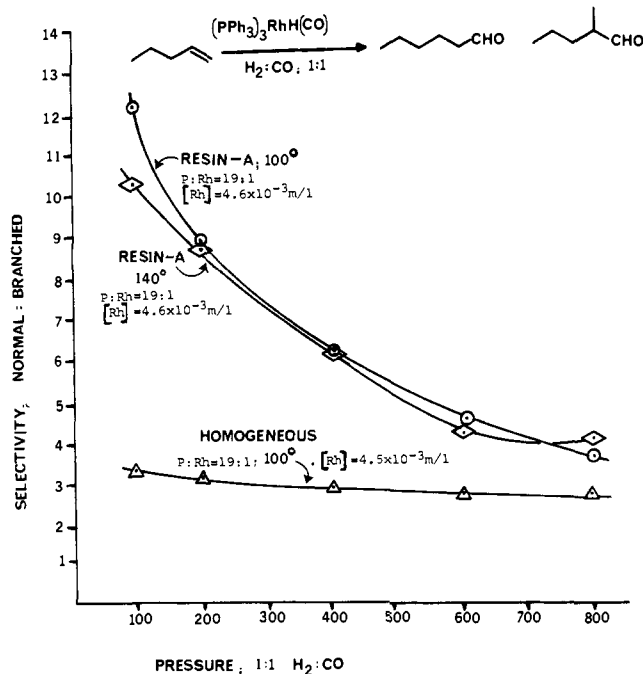


Figure 2. Pressure dependence of selectivity. Comparison of hydroformylations catalyzed by resin-attached vs. homogeneous $(PPh_3)_3RhH(CO)$. Key: (○) resin-A, 100 °C, P:Rh = 19:1, $[Rh] = 4.58 \times 10^{-3}$ M, pentene:Rh = 400:1; (◇) resin-A, 140 °C, P:Rh = 19:1, $[Rh] = 4.58 \times 10^{-3}$ M, pentene:Rh = 400:1; (Δ) homogeneous, 100 °C, P:Rh = 19:1, $[Rh] = 4.45 \times 10^{-3}$ M, pentene:Rh = 400:1.

in-B, raising the temperature still further does not continually raise the available phosphine concentration because of restrictions imposed by cross-linking, and other factors, such as the normal response of selectivity to temperature, take over. According to this model, the temperature of maximum selectivity should increase as the overall rate decreases. This was observed (compare maximum selectivity temperatures for resin-B, 70 °C, with resin-A at 100 psi, i.e., 120 °C).

The local concentration of phosphine and rhodium within the resin was, of course, higher than it is in "equivalent" homogeneous reactions because the resin beads occupy only a portion of the total solution volume. Therefore, selectivity was compared for reactions where resin-A occupied about 0.12 of the volume of the reaction mixture to reactions where the homogeneous concentration had been increased by a factor of six to 2.74×10^{-2} M Rh. In these comparisons, the local concentrations of phosphine and rhodium in the resin were only about 1.4 times greater than in the homogeneous reactions (all other factors were equal). At 80 °C, the resin-A-catalyzed reactions were still substantially more selective (i.e., 1/2 = 5.5–5.6 vs. 3.6–3.7).

These findings suggest that improved "oxo" processes might be forthcoming by using the polymer anchoring technique.^{17,18}

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- (8) Styrene-divinylbenzene resins (1% DVB, BioRad SX-1, 200–400 mesh, 14 000 mol wt exclusion limit) were brominated (Br_2 , $FeBr_3$) and then phosphinated ($LiPPh_2$, THF) as described before.⁵ A series of resins with different total phosphine loadings was prepared. $(PPh_3)_3RhH(CO)$ was attached by thermal phosphine exchange followed by extensive extraction (Soxhlet).⁵ The hydroformylations were carried out in stainless steel autoclaves which were rapidly shaken at constant temperature after careful deoxygenation. All reactions were held at constant pressure using pressure regulator valves, and the consumption of hydrogen and carbon monoxide was followed by monitoring the pressure drop (by a pressure transducer) in a constant volume reservoir which fed directly through a pressure regulator valve to the reactor.
- (9) The ratio of hexanal, **1**, to 2-methylpentanal, **2**, was determined by analytical GLC on 6 ft \times $\frac{1}{8}$ in. OV-17/Chromosorb W columns using electronic integration and normalization techniques.
- (10) The polymer-attached and homogeneously catalyzed reactions were always compared using an equal volume of solution for equivalent amounts of rhodium, at the same 1-pentene to Rh ratios (400:1 for resin-A and 100:1 for resins B and C), and at the same 1-pentene:benzene ratios.
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- (15) Wilkinson¹³ demonstrated that $(PPh_3)_3RhH(CO)$ was converted to an equilibrium mixture of $(PPh_3)_2RhH(CO)_2$, $(PPh_3)RhH(CO)_2$, and $[Rh(CO)_2(PPh_3)_2]_2$ in solution in the presence of CO. He then postulated that hydroformylation proceeded through one of two paths, depending on the conditions.¹⁴ In the associative pathway, olefin first coordinates to $(PPh_3)_2RhH(CO)_2$ followed by rapid metal hydride addition across $C=C$. In the dissociative pathway, PPh_3 is lost from $(PPh_3)_2RhH(CO)_2$ giving $(PPh_3)RhH(CO)_2$ which coordinates with olefin followed by fast metal hydride addition. The selectivity is determined in the metal hydride addition step. For both electronic and steric reasons,¹⁴ the dissociative pathway, where $(PPh_3)RhH(CO)_2$ adds across the olefin, is less selective than the associative path where $(PPh_3)_2RhH(CO)_2$ adds across the olefin. At higher phosphine

concentrations, Wilkinson¹⁴ 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 reaction² and trialkyltin hydride reduction³ 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 com-

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>i</i> -BuHgMe	51	1.01	0.93	0.93	1.02
<i>i</i> -BuHgNp	88	0.96	0.87	0.91	0.97
Hg(CH ₂) ₆ ^f	<i>g</i>	0.84	0.86	1.07	0.80

^a At 100 °C, no initiator added. ^b 2.25 mmol in 5 ml of CCl₄.

^c Based on recovered RHgR' after 300 h. ^d Per millimole of unrecovered RHgR'. ^e Alkene plus CCl₄ adduct. ^f Contains 0.28 mmol of di-*n*-butyryl peroxide, yields based after 7 h on reactant charged. ^g Not determined.

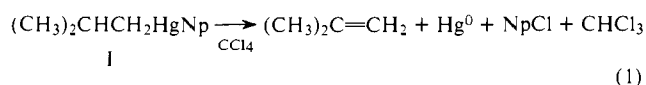
Table II. Relative Rates of Hydrogen Abstraction from Hydrocarbons and from *i*-BuHgNp by Trichloromethyl Radicals^a

Substrate A	Substrate B	Av substrate ratio [B]/[A]	Product ratio [P _A]/[P _B]	Relative reactivity	Reactivity per hydrogen
<i>i</i> -BuHgNp	Isooctane	10.3	58.3	600	600
		15.9	36.4	580	580
		21.2	25.8	550	550
<i>i</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 CCl₄ solution containing 0.235 mmol of substrate A at 95 °C. ^b Contains 0.03 mmol of di-*n*-butyryl peroxide.

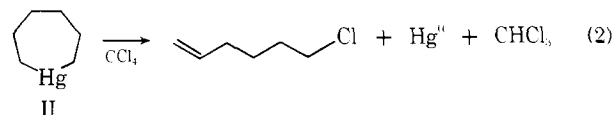
pounds are overcome, thus allowing an unambiguous identification of radical chain processes in the reductive elimination and the quantitative assessment of the homolytic reactivity of β -hydrogens in dialkylmercurials.

When a solution of isobutylneopentylmercury⁶ (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 CCl₄ to olefins under free radical conditions.⁷ Significantly, only traces of isobutyl chloride⁸ 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.

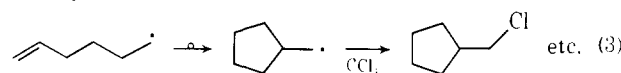


Reaction 1 is markedly accelerated by the addition of catalytic amounts of butyryl peroxide and to a lesser extent by azobisisobutyronitrile. Moreover it is inhibited by either galvinoxyl or *o,o'*-di-*tert*-butyl-*p*-cresol.

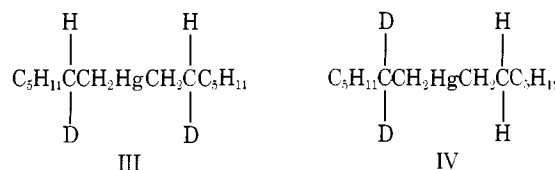
Reductive elimination also occurs with isobutylmethylmercury and mercuracycloheptane (II). In the latter case, the



observation of discrete amounts of rearranged cyclopentylmethyl chloride is consistent with the intermediacy of the ω -hexenyl radical.¹¹



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