hexyl)-2-butanones. An 82:18 mixture of *trans*- and *cis*-4-(2′-methylcyclohexyl)-2-butanones was prepared in 73% yield (79% by glpc), bp 76–80° (1.6 mm). The two isomers were separated by glpc using a 10% Carbowax 20M column. The major component was the trans isomer: $n^{20}D$ 1.4568; pmr (CCl_4, TMS) δ 0.6–2.0 (complex multiplet with three major peaks at 0.93, 1.40, and 1.75 ppm, 15 H), 2.07 (s, 3 H), and 2.33 (t, J = 8 Hz, 2 H) ppm. The other product was identified as the cis isomer: $n^{20}D$ 1.4628; pmr (CCl_4, TMS) δ 0.87 (d, J = 7 Hz, 3 H), 1.0–2.0 (broad peak centered at 1.40, 12 H), and 2.33 (t, J = 7 Hz, 2 H) ppm. The ir spectra of both trans and cis isomers exhibited strong bands at 2950, 2880, 1720, 1455, 1360, and 1170 cm^{-1}.

Reaction of *B*-Cyclopentyl-9-borabicyclo[3.3.1]nonane with Methyl Vinyl Ketone. *B*-Cyclopentyl-9-BBN (40 mmol) was dissolved in 40 ml of THF. To this was added 60 mmol of MVK and the reaction was followed by glpc. The reaction turned out to be quite slow. Therefore, air was introduced at the rate of 4 ml/min. After 6 hr at 25° *B*-cyclopentyl-9-BBN disappeared. Glpc examination revealed the formation of 4-cyclopentyl-2-butanone in 24% yield.

Halomethyl–Metal Compounds. LXIII. Insertion of Phenyl(bromodichloromethyl)mercury-Derived Dichlorocarbene into Benzylic Carbon–Hydrogen Bonds. Stereochemistry and Mechanism[1,2]

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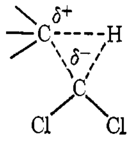
Abstract: The insertion of phenyl(bromodichloromethyl)mercury-derived dichlorocarbene into the benzylic C–H bond of (+)-2-phenylbutane occurs with predominant retention of configuration. The kinetic deuterium isotope effect for this process was determined to be 2.5. In a Hammett study, pairs of substituted cumenes, $ZC_6H_4CMe_2H$ (Z = p-CH_3, H, p-F, p-Cl, m-CF_3), were allowed to compete for a deficiency of $PhHgCCl_2Br$. These experiments demonstrated an equally good linear correlation of the log k_{rel} values with σ and σ^+ values, giving ρ values of −1.19 and −0.894, respectively. These results show that the insertion reaction in question is a concerted process in which a small partial positive charge is developed at the carbon atom into whose bond to hydrogen CCl_2 is being inserted.

In previous papers of this series we have described the insertion of dichlorocarbene derived by thermolysis of phenyl(bromodichloromethyl)mercury into C–H linkages, including those of aliphatic- and alkyl-substituted aromatic hydrocarbons,[3] of aliphatic ethers,[4] and of tetraalkyl derivatives of silicon, germanium, and tin.[5–7] The observed relative reactivities of tertiary, secondary, and primary C–H bonds to CCl_2 insertion and the nature of the groups which activated such insertion processes (α-aryl, α-alkoxy, α-vinyl, β-trialkylmetal) led us to propose transition state I for such insertion reactions. If such a simple three-center transition state



I

were indeed involved, then one might expect that such insertion into a C–H bond involving a chiral carbon center would proceed with retention of configuration at carbon. Also, one might expect to find a linear correlation between the relative rate constants for CCl_2 insertion into XC_6H_4C–H systems and the polar substituent constants of the X substituent groups, with electron-releasing groups accelerating the insertion reaction.

In view of these expectations which were based on extensive studies of C–H insertions by CCl_2, the results of a stereochemical study by Franzen and Edens[8] seemed rather surprising. These workers reported that insertion of CCl_2 derived from sodium trichloroacetate thermolysis into optically active 2-phenylbutane gave $PhC(CH_3)(C_2H_5)CHCl_2$ which was "practically inactive," while the insertion of $PhHgCCl_3$-derived dichlorocarbene into this hydrocarbon gave optically inactive product. These results, however, were obtained with starting material of low optical purity, and we decided that this question of stereochemistry was of sufficient importance to warrant reinvestigation. In this paper we report the results of our further work concerning stereochemistry and mechanism of dichlorocarbene insertion into the C–H bond.

Results and Discussion

A. Stereochemistry. In view of Franzen and Edens' report[8] and in view of the fact that $PhHgCCl_2Br$ reacts

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(1) Part LXII: D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, in press.

(2) Preliminary communication: D. Seyferth and Y. M. Cheng, *J. Amer. Chem. Soc.*, **93**, 4072 (1971).

(3) D. Seyferth, J. M. Burlitch, K. Yamamoto, S. S. Washburne, and C. J. Attridge, *J. Org. Chem.*, **35**, 1989 (1970).

(4) D. Seyferth, V. A. Mai, and M. E. Gordon, *ibid.*, **35**, 1993 (1970).

(5) D. Seyferth, S. S. Washburne, C. J. Attridge, and K. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 4405 (1970).

(6) D. Seyferth, H. Shih, P. Mazerolles, M. Lesbre, and M. Joanny, *J. Organometal. Chem.*, **29**, 371 (1971).

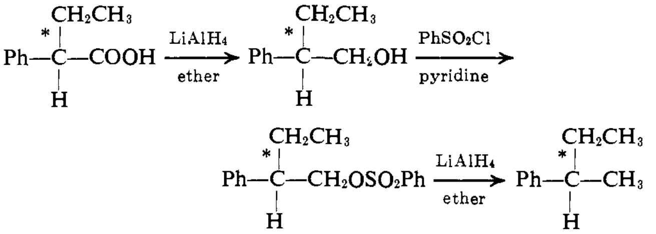
(7) D. Seyferth, Y. M. Cheng, and D. D. Traficante, *ibid.*, **46**, 9 (1972).

(8) V. Franzen and R. Edens, *Justus Liebigs Ann. Chem.*, **729**, 33 (1969).

with 2-phenylpropane to give $PhC(CH_3)_2CHCl_2$ in 58% yield as the sole insertion product, we chose to study the reaction of this mercury reagent with optically active 2-phenylbutane.

(+)-2-Phenylbutane was prepared by the reduction of (+)-2-phenylbutanoic acid following the procedure of Bonner and Greenlee[9] as shown in Scheme I. The optically active (+)-2-phenylbutanoic acid was obtained from its racemic acid by resolution of its cinchonidine salt.[10] The absolute configuration of (+)-2-phenylbutane was determined by Cram[11] to be of the *S* form.

Scheme I

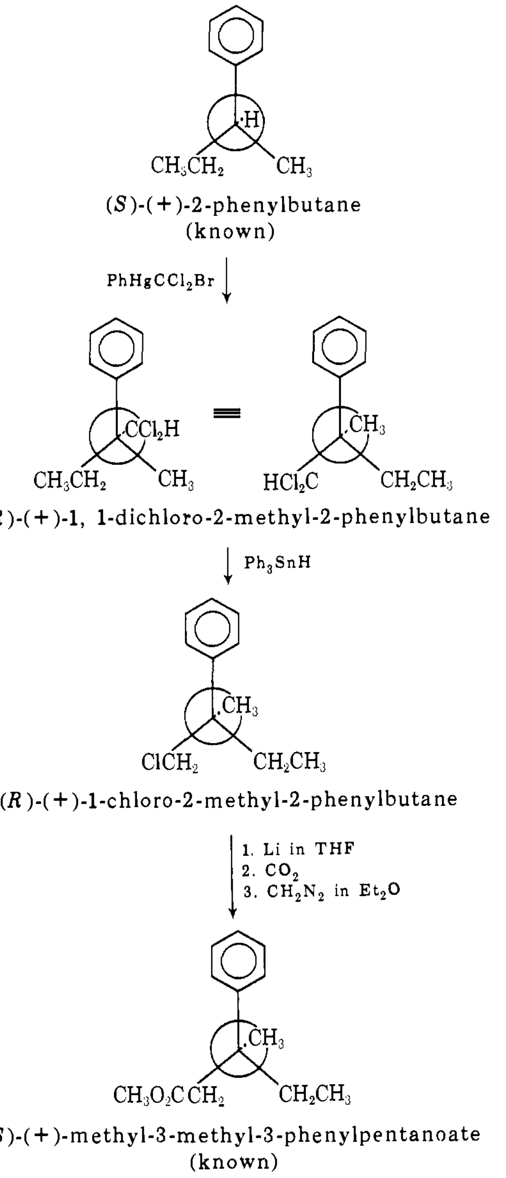


The reaction of phenyl(bromodichloromethyl)mercury with (+)-2-phenylbutane was carried out without diluent at 80° under nitrogen for 4 hr. The insertion product, (+)-1,1-dichloro-2-methyl-2-phenylbutane, obtained in moderate yield, was separated by fractional distillation, purified by preparative glc, and characterized by its ir and nmr spectra and its elemental analysis. Its optical activity was found to be $[\alpha]^{25}D$ +1.88° (neat). Unconverted (+)-2-phenylbutane was recovered from the reaction mixture and found to have essentially unchanged optical rotation.

In order to determine the steric course of this insertion reaction, the optically active 1,1-dichloro-2-methyl-2-phenylbutane was converted, *via* the sequence shown in Scheme II, to methyl 3-methyl-3-phenylpentanoate, a compound for whose optical isomers the absolute configuration had been determined by Cram, *et al.*[12]

The first step in Scheme II involves the reduction of one of the C–Cl bonds of the product by reaction with triphenyltin hydride, a reaction known[13] to proceed *via* a free radical chain process. Although there exists the possibility of phenyl group migration in the intermediate radical, it has been shown[14] that $PhCMe_2CH_2Cl$ is reduced to $PhCMe_3$ by tri-*n*-butyltin hydride without rearrangement. Thus such reduction of our insertion product should proceed without complication. The optically active $PhC(CH_3)(C_2H_5)CHCl_2$, $[\alpha]^{25}D$ +1.88°, was reduced to 1-chloro-2-methyl-2-phenylbutane with triphenyltin hydride at 80° for 12 hr under nitrogen. A single monochloride was formed, with $[\alpha]^{25}D$ +8.77° (neat).

Scheme II. Correlation of Configuration of Insertion Product



The next step in Scheme II also presented the possibility of complications involving rearrangement of the organolithium intermediate. However, Grovenstein and Cheng[15] had shown that neophyl chloride, $Ph(Me)_2CCH_2Cl$, can be converted to neophyllithium, $Ph(Me)_2CCH_2Li$, in high yield, with only minimal formation of the rearrangement product, $PhCH_2C(Me)_2Li$, providing the lithium reagent was formed and maintained at low temperature. Our optically active $Ph(CH_3)(C_2H_5)CH_2Cl$ was converted to the lithium reagent by reaction with lithium dispersion in THF at −40°, and the $PhC(CH_3)(C_2H_5)CH_2Li$ solution thus formed then was poured into a slurry of Dry Ice in diethyl ether. Acidification and further work-up gave 3-methyl-3-phenylpentanoic acid. A small portion of this crude acid was recrystallized from pentane to give a sample with $[\alpha]^{25}D$ +13.6° (*c* 3.8, $CHCl_3$). Cram[12] reported $[\alpha]^{25}D$ +14.6° (*c* 3.8, $CHCl_3$) for (*S*)-(+)-3-methyl-3-phenylpentanoic acid.

Methylation of the crude, unrecrystallized acid with ethereal diazomethane produced methyl (+)-3-methyl-3-phenylpentanoate, $[\alpha]^{25}D$ +12.27° (neat) (lit.[12] $[\alpha]^{25}D$ +12.7° (neat)). The reactions shown in Scheme II were repeated twice and in all cases the optical ac-

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[9] W. A. Bonner and T. W. Greenlee, *J. Amer. Chem. Soc.*, 81, 3336 (1959).

[10] P. A. Levene and R. E. Marker, *J. Biol. Chem.*, 100, 685 (1933).

[11] D. J. Cram, *J. Amer. Chem. Soc.*, 74, 2149 (1952).

[12] D. J. Cram, A. Langemann, J. Allinger, and K. R. Kopecky, *ibid.*, 81, 5746 (1959).

[13] H. G. Kuivila, *Advan. Organometal. Chem.*, 1, 47 (1964).

[14] H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, 28, 2165 (1963).

[15] E. Grovenstein, Jr., and Y. M. Cheng, *Chem. Commun.*, 101 (1970).

tivities of the compounds formed in each step differed by no more than 3% between the two runs.

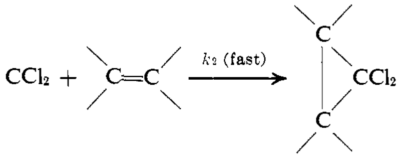
Since in the sequence shown in Scheme II no bonds directly attached to the chiral center are involved in the bond cleavage and formation processes, the relative configurations of (+)-$PhC(CH_3)(C_2H_5)CHCl_2$ and (+)-$PhC(CH_3)(C_2H_5)CH_2CO_2CH_3$ should be the same. The ester obtained in the final step had an optical purity of 97%. Thus we can conclude that the reaction of phenyl(bromodichloromethyl)mercury-derived CCl_2 with (+)-2-phenylbutane proceeds essentially stereospecifically with retention of configuration.

The difference between these results and those of Franzen and Edens finds an explanation when one considers the details of their experiments. In their reaction with sodium trichloroacetate they used (+)-2-phenylbutane with $[\alpha]^{25}D$ +3.400° (12.8% optical purity), and in the experiment with $PhHgCCl_3$ this value was 3.496° (13.2% optical purity). As indicated above, for (+)-$PhC(CH_3)(C_2H_5)CHCl_2$ of *ca.* 90% optical purity the $[\alpha]^{25}D$ is only ~+1.9° and so in the experiments of Franzen and Edens a maximum $[\alpha]^{25}D$ of ~+0.25° would be expected. It is not surprising, therefore, that they reported obtaining optically inactive insertion products.

It is interesting to note that the formally similar insertion of mercurial-derived dichlorocarbene into the Si–H bond of optically active α-$C_{10}H_7(C_6H_5)(CH_3)SiH$ also occurred with predominant retention of configuration.[16]

B. A Hammett Study. The reactions of phenyl(bromodichloromethyl)mercury with olefins to give *gem*-dichlorocyclopropanes[17] and with triethylsilane to give triethyl(dichloromethyl)silane[18] proceed by way of a free dichlorocarbene intermediate (eq 1,2 and 1,3).

$$PhHgCCl_2Br \underset{k_{-1}\text{ (fast)}}{\overset{k_1\text{ (slow)}}{\rightleftharpoons}} PhHgBr + CCl_2 \qquad (1)$$



(2)

$$CCl_2 + Et_3SiH \xrightarrow{k_3\text{ (fast)}} Et_3SiCCl_2H \qquad (3)$$

For both types of substrates, olefins[19,20] and triorganosilicon hydrides,[18] relative rate studies have been carried out in order to obtain information concerning mechanism and, in particular, concerning electronic effects on the carbene addition or insertion steps (k_2 or k_3). Of interest to the present study was the finding that the presence of electron-releasing substituents, Z, in $ZC_6H_4SiMe_2H$ compounds accelerated CCl_2 insertion into the Si–H bond and electron-withdrawing substituents retarded it, relative to Z = H. A good linear correlation was found between log k_{rel} for this insertion process and the σ constants for the Z substituents, giving $\rho = -0.632 \pm 0.032$.[18]

We have carried out a similar Hammett study of the insertion of CCl_2 into the benzylic C–H bond of substituted cumenes, $ZC_6H_4C(CH_3)_2H$, Z = H, *p*-CH_3, *p*-Cl, *p*-F, and *m*-CF_3. In preparative reactions, each of these was shown to react with phenyl(bromodichloromethyl)mercury to give the expected $ZC_6H_4C(CH_3)_2CCl_2H$ in fair yield (Table I). Competition reactions then were carried out using pairs of cumenes, allowing them to compete for a deficiency of $PhHgCCl_2Br$ under standard conditions (80.45 ± 0.03° for 4 hr, no diluent, under nitrogen). The yields of the two products were determined using quantitative gas chromatography. These yield data, together with the initial cumene concentrations, permitted the calculation of the relative rate constants (*vs.* $C_6H_5C(CH_3)_2H$ = 1) by the method of Doering and Henderson.[21] The results are summarized in Table II. The correlation of the log k_{rel} thus determined with σ,[22] σ^0,[22] and σ^+[23] was examined (Table III). Equally good linear correlations were obtained for σ ($\rho = -1.191$) and σ^+ values ($\rho = -0.894$).

Table I. Reaction of $ZC_6H_4C(CH_3)_2H$ with $C_6H_5HgCCl_2Br$ to Give $ZC_6H_4C(CH_3)_2CHCl_2$

Z	% yield	Z	% yield
H	51.4	*p*-F	58.3
p-CH_3	32.8	*m*-CF_3	33.8
p-Cl	57.0		

Table II. Relative Rate Constants for Insertion of $C_6H_5HgCCl_2Br$-Derived CCl_2 into C–H Bonds of $ZC_6H_4C(CH_3)_2H$

Z	$k_{ZC_6H_4C(CH_3)_2H}/k_{C_6H_5C(CH_3)_2H}$
p-CH_3	1.73
H	1.00
p-F	0.87
p-Cl	0.67
m-CF_3	0.31

Table III. Correlation[a] of Log k_{rel} for Substituted Cumenes with σ, σ^0, σ^+

Constants used	ρ	SD[b]	C[c]	SEE[d]	NSE[e]
σ	−1.191	0.0248	0.0290	0.0362	0.1357
σ^0	−1.109	0.0251	0.0688	0.0522	0.1959
σ^+	−0.894	0.0262	−0.0571	0.0392	0.1485

[a] Values of ρ, C, standard deviations, and NSE for log $k_Z/k_H = \sigma\rho + C$. [b] SD = standard deviation. [c] C = constant. [d] SEE = standard error of estimate. [e] NSE = normalized standard error (SEE/root mean square value of the independent variable); the smaller the NSE, the better the fit: *cf.* G. R. Howe and R. R. Hiatt, *J. Org. Chem.*, **35**, 4007 (1970).

C. Kinetic Deuterium Isotope Effect. 2-Phenylbutane-α-d_1 was prepared as shown in eq 4. Analysis

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(16) L. H. Sommer, A. Ulland, and G. A. Parker, *J. Amer. Chem. Soc.*, **94**, 3469 (1972).

(17) D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *ibid.*, **89**, 4953 (1967).

(18) D. Seyferth, R. Damrauer, J. Y.-P. Mui, and T. F. Jula, *ibid.*, **90**, 2944 (1968).

(19) D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964).

(20) D. Seyferth, J. Y.-P. Mui, and R. Damrauer, *ibid.*, **90**, 6182 (1968).

(21) W. von E. Doering and W. A. Henderson, Jr., *ibid.*, 80, 5274 (1958).

(22) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, p 356.

(23) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.

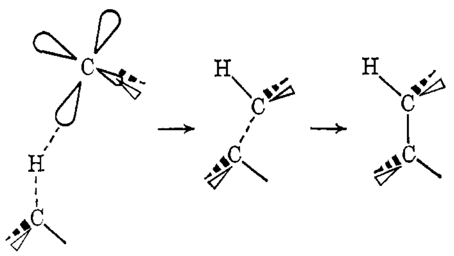
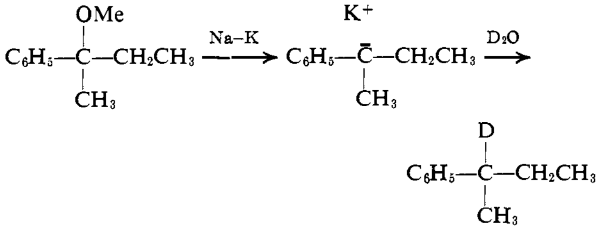


Figure 1.



$$C_6H_5\text{—}\overset{\displaystyle OMe}{\underset{\displaystyle CH_3}{C}}\text{—}CH_2CH_3 \xrightarrow{\text{Na–K}} C_6H_5\text{—}\overset{\displaystyle K^+}{\underset{\displaystyle CH_3}{\bar{C}}}\text{—}CH_2CH_3 \xrightarrow{D_2O} C_6H_5\text{—}\overset{\displaystyle D}{\underset{\displaystyle CH_3}{C}}\text{—}CH_2CH_3 \quad (4)$$

of the product by the falling drop method showed it to contain 6.92 atom % excess of deuterium, which corresponds to 96.7% deuteration. The nmr spectrum of the deuterated product showed no benzylic hydrogen signal in the δ 2.0–3.0-ppm region, confirming the structure indicated. The reaction of PhCD(Me)Et with phenyl(bromodichloromethyl)mercury gave a product whose deuterium content corresponded to 87.6% $C_{11}H_{13}Cl_2D$ and 12.4% $C_{11}H_{14}Cl_2$, and whose nmr spectrum confirmed the structure $C_6H_5C(Me)(Et)CCl_2D$. Retention of deuterium in the product also was observed in the reaction of $PhHgCCl_2Br$ with a mixture of $C_6H_5C(Me)(Et)D$ and $C_6H_5C(Me)_2H$. The insertion product from the former was 86.4% deuterated.

The kinetic isotope effect in the insertion reaction of CCl_2 into the benzylic C–H bond, k_H/k_D, was determined in two ways.

In one approach, 2-phenylbutane and 2-phenylbutane-α-d_1 were allowed to compete with cumene individually. The relative rate constant for each competition reaction then was calculated. If one makes the reasonable assumption that in both competition reactions the internal standard, cumene, reacted at the same rate, irrespective of the difference in competing substrate, the relative rate of the insertion of CCl_2 into the benzylic C–H(D) bonds of 2-phenylbutane and 2-phenylbutane-α-d_1 may be calculated. The relative rate

$$k_H/k_D = (k_{PhCMeEtH}/k_{PhCMe_2H})(k_{PhCMe_2H}/k_{PhCMeEtD}) = k_{PhCMeEtH}/k_{PhCMeEtD}$$

of reaction for cumene and 2-phenylbutane-α-d_1 was adjusted to 100% deuterated 2-phenylbutane-α-d_1.

In a second approach, a direct competition method was used. A mixture of 2-phenylbutane and 2-phenylbutane-α-d_1 was allowed to react with phenyl(bromodichloromethyl)mercury. The isolated insertion product then was analyzed for deuterium by the falling drop procedure and from this result the relative rate constant was calculated and adjusted to 100% deuterated 2-phenylbutane-α-d_1. The experimental results are shown in Table IV. To minimize experimental error, the reaction conditions and work-up procedures used were those used in the Hammett study discussed above.

The observed k_H/k_D value makes understandable why the insertion product obtained from 96.7% PhC(Me)(Et)D was only 87.6% deuterated. A calculation leads to the prediction that the insertion product should have been 88.3% deuterated, in close agreement to the observed value.

$$(\%\ \text{D in sample})k_D/k_D - (\%\ \text{H in sample})k_H/k_D = (96.7)(1) - (3.3)(2.5) = 88.3\%\ \text{D in product}$$

We may compare this value of 2.5 for the kinetic deuterium isotope effect with the k_H/k_D values for insertion reactions of CH_2 (1.55 – 1.96).[24]

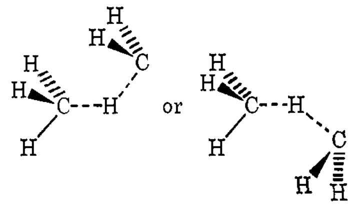


Figure 2.

Table IV. Relative Rate in Deuterium Isotope Effects Study

Substrate A	Substrate B	k_A/k_B	$k_{PhC(Et)(Me)H}/k_{PhC(Et)(Me)D}$
PhC(Et)(Me)H	$PhC(Me)_2H$	0.429[a]	2.51
$PhC(Me)_2H$	PhC(Et)(Me)D	5.84[a]	
PhC(Et)(Me)H	PhC(Et)(Me)D	2.50[b]	2.50

[a] By quantitative glc analysis. [b] By deuterium falling drop method of analysis.

Discussion

There has been much interest in the mechanism of insertion of CH_2 and other carbenes into C–H bonds.[25–30] The latest views[27–30] suggest a concerted process in which the new C–C bond has begun to form before the hydrogen atom involved in the insertion process has begun to move. As Hoffmann, *et al.*,[29] point out, in such a process, "the hydrogen transfer in the transition state region is characterized by considerable negative charge accumulating on the methylene carbon, balanced by positive charge on the methane carbon (*i.e.*, the carbon into whose bond to H the insertion is occurring), with relatively minor charge imbalance at H_t" (the H atom involved in the transfer process). Figures 1 and 2 show the Hoffmann[29] and Dewar[30] pictures of the insertion process at the *intermediate* stages (both agree that *initial* approach of the CH_2 is along the axis of the C–H bond but differ with regard to the carbon–carbon distance at which the hydrogen transfer occurs).

Such a picture accommodates nicely the previously obtained experimental results concerning insertion of $PhHgCCl_2Br$-derived dichlorocarbene into C–H bonds mentioned in the introduction, as well as the additional

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(24) J. W. Simons and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **85**, 1023 (1963).

(25) W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1956).

(26) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).

(27) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).

(28) W. B. DeMore and S. W. Benson, *ibid.*, **2**, 219 (1964).

(29) R. C. Dobson, D. M. Hayes, and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6188 (1971).

(30) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *ibid.*, **94**, 9095 (1972).

information relating specifically to CCl_2 insertion into benzylic C–H bonds obtained in this study.

(1) The insertion occurs with predominant retention of configuration at the carbon atom into whose bond to hydrogen the CCl_2 insertion is taking place. This speaks in favor of a concerted process rather than one involving free radical or ionic intermediates.

(2) Electron-releasing substituents, Z, in $ZC_6H_4C(Me)_2H$ accelerate the rate of CCl_2 insertion into the benzylic C–H bond; electron-attracting substituents retard the rate, relative to Z = H. Equally good linear correlations were found for log k_{rel} *vs.* σ and σ^+ (a not uncommon observation when ρ values are low), giving ρ values of -1.19 and -0.894, respectively. Such relatively small and negative values are in good agreement with a transition state of a concerted insertion process in which a small partial positive charge is developed at the carbon atom to which the aryl group is attached.

(3) Deuterium in the benzylic position of PhCMeEtD is retained in the product, giving $PhC(Me)(Et)CCl_2D$. The kinetic isotope effect, k_H/k_D, for insertion of CCl_2 into the benzylic C–H bond is 2.5. These observations also speak in favor of a concerted process of the type discussed above.

We thus may consider the CCl_2 insertion reaction to involve the carbene acting as an electrophilic reagent, but the numerically small value of ρ indicates that the degree of charge separation developed in the transition state is not large. The log k_{rel} values of the corresponding insertion of CCl_2 into the Si–H bond of analogous silanes, $ZC_6H_4Si(Me)_2H$, gave the best linear correlation with σ values, giving $\rho = -0.632 \pm 0.032$.[13] This difference is understandable. Mesomeric delocalization of the partial positive charge, which develops in the transition state, into the benzene ring of $ZC_6H_4Y(Me)_2H$ is an important factor for the carbon case (Y = C), but such delocalization does not play an important role in arylsilicon compounds (Y = Si).[31,32]

Another way of picturing the concerted insertion of CCl_2 into the C–H bond which accommodates all of our experimental observations and which we feel is useful because of its simplicity is by means of the transition state shown in Figure 3. Implied in this picture is a transitory three-center, two-electron bonding situation of the type long recognized in metal hydride and organometallic chemistry and similar to that suggested recently by Olah, *et al.*, in the case of the protonation of alkanes[33] and the reaction of carbonium ions with alkanes.[34]

Experimental Section

General Comments. All reactions were carried out in flame dried glassware under an atmosphere of dry nitrogen. All solvents used were dried using standard procedures. Infrared spectra were recorded using Perkin-Elmer 257 or 457A grating infrared spectrophotometers, nmr spectra using a Varian Associates T60 spectrophotometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Unless otherwise specified, the solvent used was carbon tetrachloride. Optical rotations were measured using a Perkin-Elmer 141 polarimeter at 589 mμ and an open slit. A 10-cm microcell was used at all times. The constant-temperature bath used was regulated to 80.45 ± 0.03°. Gas–liquid chromatography (glc) was used extensively in the analysis of reaction mixtures, determination of product yields (by the internal standard procedure), and the isolation of products. F&M Model 700, 720, or 5754 gas chromatographs were used, in addition to the MIT isothermal unit.

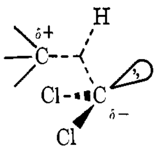

Figure 3.

Preparation of Starting Materials. (a) 2-Phenylbutane. Commercial 2-phenylbutane (Aldrich), 100 ml, was treated with 15 ml of concentrated H_2SO_4 and subsequently with another two portions of 25 ml of the acid. The organic layer was washed with two 20-ml portions of distilled water, twice with 20-ml portions of 20% K_2CO_3 solution, and finally twice with 25-ml portions of distilled water. After it had been dried over $MgSO_4$, the 2-phenylbutane was distilled at 171.5–172°.

(b) (+)-2-Phenylbutane. 2-Phenylbutanoic acid (200 g) was resolved by repeated crystallization of its cinchonidine salt from 95% ethanol following the procedure of Levene and Marker.[10] After four recrystallizations, 250 g of white needles, mp 117–131° dec, were obtained. The salt was decomposed by suspension in 1400 ml of 4 *N* HCl, and the resolved acid was extracted with three 300-ml portions of diethyl ether. The combined ether extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Vacuum distillation gave 87.7 g of (+)-2-phenylbutanoic acid, bp 108–110° (0.8 mm), $n^{25}D$ 1.5142, $d^{25}{}_4$ 1.059, $[\alpha]^{25}D$ +80.0° (neat). Bonner and Greenlee[9] reported bp 115–130° (1–2 mm), $[\alpha]^{25}D$ +84.4° (neat); Levene and Marker[10] reported $[\alpha]^{25}D$ +87.3° (neat) for the resolved acid.

A 1-l. round-bottomed flask equipped with a mechanical stirrer, a pressure equalizing dropping funnel, and a reflux condenser topped with a nitrogen inlet tube was charged with 26.0 g (0.685 mol) of $LiAlH_4$ and 400 ml of dry ether. To this mixture was added dropwise with stirring 84.4 g (0.515 mol) of (+)-2-phenylbutanoic acid in 100 ml of ether. The reaction mixture was heated at reflux for 2 hr, cooled to 0°, and treated cautiously with water to decompose unconverted hydride. Subsequently, enough potassium sodium tartrate solution to dissolve the aluminum hydroxide was added. Extraction with three 200-ml portions of ether was followed by evaporation of the dried extracts and distillation of the residue to afford 70.0 g (91%) of (+)-2-phenylbutanol, bp 101–101.5° (5 mm), $n^{25}D$ 1.5182, $d^{25}{}_4$ 0.985, $[\alpha]^{25}D$ +17.05° (neat). Reported have been $[\alpha]^{25}D$ +19.45° (neat)[9] and +18.9° (neat)[10] for (+)-2-phenylbutanol.

A solution of 67.0 g (0.446 mol) of this alcohol in 140 ml of dry pyridine was chilled to 0° and then treated slowly with 80 g (0.455 mol) of benzenesulfonyl chloride with stirring and cooling under nitrogen. The reaction mixture was kept at room temperature overnight and then poured onto 1400 ml of ice–water. Extraction with four 300-ml portions of ether was followed by removal of the ether at reduced pressure. The residue was heated at 50° under high vacuum overnight to leave a light yellow oil.

The benzenesulfonate of (+)-2-phenylbutanol thus prepared was dissolved in 300 ml of dry ether and added dropwise with stirring under nitrogen over 1 hr to 16.0 g of $LiAlH_4$ in 200 ml of ether. The reaction mixture was heated at reflux for 2 hr, cooled to 0°, and treated successively with water and potassium sodium tartrate solution. Extraction with three 150-ml portions of ether was followed by evaporation of the solvent and distillation to give 45.2 g (75%) of (+)-2-phenylbutane, bp 95–97° (62 mm), $n^{25}D$ 1.4876, $d^{25}{}_4$ 0.858, $[\alpha]^{25}D$ +28.00 (neat). Glc (4-ft 10% UC-W98 at 120°) indicated the presence of one component. Reported

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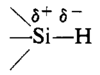
(31) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, Chapter 1, Section 7.

(32) Nevertheless, Si–H bonds are much more reactive toward CCl_2 insertion than are analogous C–H bonds. This is no doubt related to the higher polarity of the silicon–hydrogen bond



in the ground state, which facilitates electrophilic attack by dichlorocarbene. The effect of substituents (a transition state effect for the most part), however, is smaller in the case of the silanes since mainly inductive effects are involved.

(33) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 1251 (1971).

(34) G. A. Olah and J. A. Olah, *ibid.*, **93**, 1256 (1971).

for (+)-2-phenylbutane has been $[\alpha]^{25}\mathrm{D}$ +26.6° (neat)[10] and for (−)-2-phentylbutane, $[\alpha]^{25}\mathrm{D}$ −27.3° (neat).[35]

(c) **2-Phenylbutane-α-d_1.** To a solution of 0.97 mol of methyllithium in 600 ml of diethyl ether (Foote Mineral Co.) was added dropwise with stirring under nitrogen over 2 hr 90.0 g (0.67 mol) of propiophenone. The reaction mixture was stirred and heated at reflux for 30 min, cooled to 0°, and treated (dropwise) with 84.5 g (0.67 mol) of dimethyl sulfate. The resulting mixture was stirred overnight at room temperature. The separated organic layer was washed with 5 *N* NaOH several times and finally dried over $MgSO_4$. The solvent was removed at reduced pressure, and the residue was distilled from 2 g of $LiAlH_4$ to give 102.7 g (93% crude yield) of liquid, bp 105–110° (24 mm). Na-K alloy (1:10; 5 g) was added to the distillate. Redistillation gave 77.0 g (70%) of liquid: bp 108–110° (28 mm), $n^{25}\mathrm{D}$ 1.4856, PhC(Me)(Et)OMe; nmr δ 0.73 (t, *J* = 7.2 Hz, 3 H), 1.47 (s, 3 H), 1.72 (q, *J* = 7.0 Hz), 3.03 (s, 3 H), and 7.25 ppm (s, 5 H).

A 1-l. Morton (creased) three-necked flask equipped with a high speed stirrer (Labline Catalog No. 1280), a pressure-equalizing dropping funnel, and a reflux condenser topped with a nitrogen inlet tube was charged with Na-K alloy (from 40 g of potassium and 4 g of sodium) in 500 ml of dry diethyl ether. To the alloy was added dropwise with stirring under nitrogen 40.0 g (0.244 mol) of PhC(Me)(Et)OMe. An exothermic reaction resulted in a dark red solution which then was stirred at room temperature for 24 hr. Deuterium oxide (excess) was added *cautiously* at 0°. The organic layer was separated; the white precipitate was washed with ether, dissolved in 1 l. of water, and extracted with ether again. The combined ether solutions were dried, concentrated at reduced pressure, and distilled to give 25.5 g (77.5%) of 2-phenylbutane-α-d_1, bp 95–97° (65 mm), $n^{25}\mathrm{D}$ 1.4873. *Anal.* Calcd for $C_{10}H_{13}D$: atom % excess D, 7.14. Found: 6.92 (equivalent to 96.7% deuteration). Nmr: δ 0.79 (t, *J* = 7.2 Hz, 3 H), 1.18 (s, 3 H), 1.38 (q, *J* = 7.2 Hz, 2 H), and 7.14 ppm (s, 5 H). No benzylic C–H signals in the region δ 2.0–3.0 ppm were observed.

(d) ***p*-Chlorocumene.** *p*-Chloroacetophenone, 100 g (0.65 mol), in an equal volume of dry ether was added dropwise with stirring under nitrogen to 0.72 mol of methyllithium in 450 ml of ether. The reaction mixture was stirred and heated at reflux for 1 hr and then was hydrolyzed with 20 ml of water. Enough 6 *N* H_2SO_4 was added to dissolve all salts. The ether layer was evaporated at reduced pressure. The residue, together with 100 ml of 20% H_2SO_4, was stirred and heated at 130° overnight. The organic layer was separated and distilled to give 62.0 g (70%) of *p*-chloro-α-methylstyrene, bp 85–87° (7 mm), $n^{25}\mathrm{D}$ 1.5538 (lit.[36] bp 80–83° (10 mm), $n^{25}\mathrm{D}$ 1.5529).

p-Chloro-α-methylstyrene, 51.8 g (0.34 mol), in 120 ml of absolute ethanol was hydrogenated at room temperature in the presence of 0.5 g of platinum oxide (initial hydrogen pressure 45 psi) in a Parr hydrogenator. Distillation after filtration gave 45.9 g (87.5 %) of *p*-chlorocumene, bp 73.5–74.5° (12 mm), $n^{25}\mathrm{D}$ 1.5093 (lit.[37] bp 81° (15 mm), $n^{25}\mathrm{D}$ 1.5094).

(e) ***p*-Fluorocumene.** The Grignard reagent prepared from 88.0 g (0.5 mol) of *p*-bromofluorobenzene and 0.5 g-atom of magnesium turnings in 150 ml of diethyl ether was treated with 0.55 mol of anhydrous acetone. The mixture was heated at reflux, with stirring under nitrogen, for 1 hr and hydrolyzed with 6 *N* H_2SO_4, and the dried ether layer was evaporated at reduced pressure. The residue was heated with 20% H_2SO_4 at 135° as in (d). Distillation gave 36.0 g (58%) of *p*-fluoro-α-methylstyrene, bp 125–127° (220 mm), $n^{25}\mathrm{D}$ 1.5084 (lit.[38] bp 97.5–101.5° (95 mm), $n^{20}\mathrm{D}$ 1.5120). *Anal.* Calcd for C_9H_9F: C, 79.43; H, 6.66. Found: C, 79.12; H, 6.79.

p-Fluoro-α-methylstyrene was hydrogenated as in (d) to give *p*-fluorocumene, bp 97–99° (133 mm), $n^{24.5}\mathrm{D}$ 1.4683, in 92% yield. *Anal.* Calcd for $C_9H_{11}F$: C, 78.22; H, 8.02. Found: C, 78.35; H, 8.11. Nmr: δ 1.21 (d, *J* = 7.6 Hz, 6 H), 2.87 (m, 1 H), and 7.01 ppm (m, 4 H).

(f) ***m*-Trifluoromethylcumene.** The Grignard procedure was to prepare *m*-trifluoromethyl-α-methylstyrene from *m*-bromo(trifluoromethyl)benzene and acetone in 46% yield. The product had bp 112–114° (100 mm), $n^{25}\mathrm{D}$ 1.4624 (lit.[36] bp 83–84° (40 mm), $n^{25}\mathrm{D}$ 1.4625). The dehydration of the intermediate alcohol was carried out as described in (d).

Hydrogenation of *m*-trifluoromethyl-α-methylstyrene was carried out as described in (d) to give *m*-trifluoromethylcumene in 91% yield, bp 59.5–60.5° (20 mm), $n^{25}\mathrm{D}$ 1.4332. *Anal.* Calcd for $C_{10}H_{11}F_3$: C, 63.81; H, 5.89. Found: C, 63.74; H, 6.04. Nmr: δ 1.29 (d, *J* = 7.4 Hz, 6 H), 2.74 (m, 1 H), and 7.39 ppm (s, 4 H).

(g) **Phenyl(bromodichloromethyl)mercury.** This reagent was prepared by the reaction of phenylmercuric chloride, potassium *tert*-butoxide, and bromodichloromethane in THF.[39]

Reaction of Phenyl(bromodichloromethyl)mercury with Benzylic Hydrocarbons. The reaction of this mercurial with 2-phenylbutane is described to illustrate the procedure used.

A 150-ml round-bottomed flask equipped with a magnetic stirring assembly and a reflux condenser topped with a nitrogen inlet tube was charged, under nitrogen, with 44.2 g (0.1 mol) of $PhHgCCl_2Br$ and 75 ml of purified 2-phenylbutane. The mixture was stirred and heated at 80° under nitrogen for 3 hr, cooled to room temperature, and filtered to remove 33.3 g (93%) of PhHgBr, mp 272–275°. Most of the unconverted 2-phenylbutane was removed at aspirator pressure. The residue was trap-to-trap distilled at 0.3 mm (pot temperature to 100°). Fractional distillation of the distillate gave 8.45 g (39%) of the insertion product, 1,1-dichloro-2-methyl-2-phenylbutane, bp 88.0–96.0° (1 mm). Further purification by glc (6-ft UC-W98 column at 118°) gave product with $n^{25}\mathrm{D}$ 1.5383, $d^{25}{}_4$ 1.173. *Anal.* Calcd for $C_{11}H_{14}Cl_2$: C, 60.84; H, 6.49; Cl, 32.66. Found: C, 60.78; H, 6.44; Cl, 32.55. Nmr: δ 0.68 (t, *J* = 7.4 Hz, 3 H), 1.54 (s, 3 H), 1.82 (q, *J* = 7.4 Hz, 2 H), 5.91 (s, 1 H), and 7.32 (s, 5 H); ir (neat, cm^{-1}) 3069 w, 3038 w, 2999 s, 2955 m, 2892 m, 1500 m, 1451 m, 1385 m, 1226 m, 1080 w, 927 w, 902 w, 877 w, 796 m, 759 s, 730 s, 702 s, and 609 m.

With (+)-2-Phenylbutane. A similar reaction of 79.4 mmol of the mercury reagent with 35 ml of (+)-2-phenylbutane ($[\alpha]^{25}\mathrm{D}$ +28.00°, neat) gave PhHgBr (92%) and (+)-$PhC(Me)EtCCl_2H$ (26%), bp 100–101° (2.0 mm) after fractional distillation, collection by glc, and redistillation, $n^{25}\mathrm{D}$ 1.5383, $[\alpha]^{25}\mathrm{D}$ +1.88° (neat). *Anal.* Calcd for $C_{11}H_{14}Cl_2$: C, 60.84; H, 6.49; Cl, 32.65. Found: C, 60.99; H, 6.43; Cl, 32.23. The nmr and ir spectra of the insertion product were essentially identical with those of the racemic product.

The unconverted 2-phenylbutane was distilled at reduced pressure to give a 70% recovery of material with bp 89–91° (65 mm), $[\alpha]^{25}\mathrm{D}$ +27.89° (neat), which was pure by glc analysis. This material was used in another reaction with $PhHgCCl_2Br$ to give insertion product with $[\alpha]^{25}\mathrm{D}$ +1.95° (neat). The 2-phenylbutane recovered from this reaction had $[\alpha]^{25}\mathrm{D}$ +27.85° (neat).

With 2-Phenylbutane-α-d_1. The same procedure was used in the reaction of 7.7 mmol of the mercurial with 6.2 ml of 2-phenylbutane-α-d_1 (96.7% deuterated by the falling drop method). Trap-to-trap distillation was followed by glc collection of the insertion product from the distillate (18-in. 20% SE-30 at 150°) to give material with $n^{25}\mathrm{D}$ 1.5384. *Anal.* Calcd for $C_{11}H_{13}DCl_2$: atom % excess D, 7.14. Found (falling drop method): 6.24 (equivalent to 87.6%, deuteration). Nmr: δ 0.67 (t, *J* = 7.2 Hz, 3 H), 1.55 (s, 3 H), 1.88 (q, *J* = 7.2 Hz, 2 H), and 7.26 ppm (s, 5 H). A small singlet at 5.87 ppm indicated the presence of a small amount of $PhC(Me)(Et)CCl_2H$.

With Cumene. Thermolysis of 50.0 g (0.113 mol) of $PhHgCCl_2Br$ in 100 ml of purified cumene at 78° for 1 hr and at 85° for 3 hr and subsequent work-up followed the procedure described above. Phenylmercuric bromide was obtained in 94% yield. Fractional distillation gave $PhC(Me)_2CCl_2H$, bp 87–89° (1 mm), $n^{25}\mathrm{D}$ 1.5408 (lit.[3] $n^{25}\mathrm{D}$ 1.5400), 11.79 g (51.4% yield). Its ir and nmr spectra agreed with those reported.[3]

With *p*-Methylcumene (*p*-Cymene). Fifteen grams (0.034 mol) of the mercurial and 25 ml of *p*-cymene were stirred and heated under nitrogen at 80–81° for 4 hr. Work-up as above gave *p*-methyl-β,β-dichloro-*tert*-butylbenzene, bp 92–94° (0.55 mm), $n^{25}\mathrm{D}$ 1.5357, in 33% yield. An analytical sample was collected by glc (20% SE-30 at 150°). *Anal.* Calcd for $C_{11}H_{14}Cl_2$: C, 60.84; H, 6.49; Cl, 32.65. Found: C, 60.73; H, 5.97; Cl, 32.43. Nmr: δ 1.52 (s, 6 H), 2.31 (s, 3 H), 5.86 (s, 1 H), and 7.13 ppm (m, 4 H).

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[35] P. W. B. Harrison, J. Kenyon, and J. R. Shepard, *J. Chem. Soc.*, 658 (1926).

[36] G. B. Bachman and H. M. Hellman, *J. Amer. Chem. Soc.*, 70, 1773 (1948).

[37] R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, 41, 2875 (1949).

[38] D. Seymour and K. B. Wolfstirn, *J. Amer. Chem. Soc.*, 70, 1178 (1948).

[39] D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **16**, 21 (1969).

Table V. Experimental Data for Hammett Study for the Reactions

$$\underset{(I_1)}{Z^1\text{-}C_6H_4CMe_2H} + \underset{(I_2)}{Z^2\text{-}C_6H_4CMe_2H} \xrightarrow{PhHgCCl_2Br} \underset{(P_1)}{Z^1\text{-}C_6H_4CMe_2CCl_2H} + \underset{(P_2)}{Z^2\text{-}C_6H_4CMe_2CCl_2H}$$

					P₁			P₂					
Z^1	Z^2	I_1 Wt, g (mmol)	I_2 Wt, g (mmol)	PhHg-CCl_2Br Wt, g (mmol)	Wt, mg	mmol	Yield, %	Wt, mg	mmol	Yield, %	k_{Z^1}/k_{Z^2}	k_{Z^1}/k_H	Log (k_{Z^1}/k_H)
p-F	*p*-Cl	2.7374 (19.80)	3.1284 (20.23)	1.0993 (2.50)	151.6	0.686	27.4	128.5	0.541	21.7	1.2953	0.8683	−0.0596
p-F	*p*-CH_3	2.6238 (18.98)	2.6954 (20.08)	1.1104 (2.52)	64.6	0.292	11.6	132.8	0.612	24.3	0.5047	0.8753	
p-CH_3	H	2.6880 (20.04)	2.4045 (20.00)	1.0256 (2.33)	127.5	0.587	25.2	67.1	0.330	14.2	1.7751	1.7343	0.2391
p-CH_3	H	2.7073 (20.17)	2.4127 (20.07)	1.0333 (2.35)	127.8	0.589	25.2	70.2	0.346	14.76	1.6936		
p-Cl	H	2.0062 (12.97)	1.5738 (13.09)	0.8710 (1.98)	96.6	0.407	20.6	126.5	0.623	31.6	0.6592	0.6704	−0.1737
p-Cl	H	2.0031 (12.95)	1.5234 (12.67)	0.8590 (1.95)	101.0	0.425	21.3	123.8	0.610	31.3	0.6816		
m-CF_3	*p*-Cl	2.2838 (12.13)	2.0070 (12.97)	0.7107 (1.61)	51.1	0.188	11.7	103.0	0.434	26.9	0.463	0.305	−0.5157
m-CF_3	*p*-Cl	1.2597 (6.69)	1.0047 (6.49)	0.3675 (0.834)	26.0	0.0959	12.0	49.4	0.208	25.0	0.447		

Table VI. Experimental Data for Study of Kinetic Deuterium Isotope Effects

Substrate		Amount of A		Amount of B		$PhHgCCl_2Br$		Product[b] from A			Product[b] from B				
A	B	Wt, g	mmol	Wt, g	mmol	Wt, g	mmol	Wt, mg	mmol	Yield, %	Wt, mg	mmol	Yield, %	k_A/k_B	k_H/k_B
PhC(Me)(Et)H	$PhC(Me)_2H$	1.3213	9.84	0.6081	5.05	0.6920	1.57	72.5	0.334	21.3[c]	81.2	0.403	25.5[c]	0.429	2.51
$PhC(Me)_2H$	PhC(Me)(Et)D	0.5830	4.85	1.3539	10.01[a]	0.7022	1.59	92.9	0.457	28.8[c]	40.7	0.186	11.7[c]	5.84[d]	
PhC(Me)(Et)H	PhC(Me)(Et)D	3.9908	29.73	4.0083	29.64[a]	4.5520	10.32								2.50[d]

[a] 96.7% D uncorrected. [b] Quantitative glc analysis. [c] Based on $PhHgCCl_2Br$ used. [d] Corrected to 100% deuterated starting material.

With *p*-Chlorocumene. The same procedure was used in the reaction of 0.034 mol of $PhHgCCl_2Br$ with 25 ml of *p*-chlorocumene. *p*-Chloro-β,β-dichloro-*tert*-butylbenzene, bp 89–90° (0.35 mm), $n^{25}D$ 1.5526, was obtained in 58% yield. *Anal.* Calcd for $C_{10}H_{11}Cl_3$: C, 50.55; H, 4.67; Cl, 44.78. Found: C, 50.64; H, 4.65; Cl, 44.67. Nmr: δ 1.55 (s, 6 H), 5.83 (s, 1 H), and 7.31 (s, 4 H).

With *p*-Fluorocumene. A similar reaction of 23.3 mmol of the mercurial with 20 ml of *p*-fluorocumene gave PhHgBr (95%) and *p*-fluoro-β,β-dichloro-*tert*-butylbenzene, bp 94.5–95.0° (4.5 mm), $n^{25}D$ 1.5209, in 57% yield. An analytical sample was collected by glc. *Anal.* Calcd for $C_{10}H_{11}Cl_2F$: C, 54.32; H, 5.01; Cl, 32.07. Found: C, 54.00; H, 5.12; Cl, 32.08. Nmr: δ 1.58 (s, 6 H), 5.86 (s, 1 H), and 6.85–7.50 (m, 4 H).

With *m*-Trifluoromethylcumene. A similar reaction of 10.2 g (23 mmol) of the mercury reagent and 11.0 g of *m*-trifluoromethylcumene gave PhHgBr (93%) and *m*-trifluoromethyl-β,β-dichloro-*tert*-butylbenzene, bp 83.5–85.5° (0.37 mm), in 34% yield. Glc was used to obtain an analytical sample, $n^{25}D$ 1.4840. *Anal.* Calcd for $C_{11}H_{11}Cl_2F_3$: C, 48.72; H, 4.08; Cl, 26.15. Found: C, 48.72; H, 4.21; Cl, 25.74. Nmr: δ 1.64 (s, 6 H), 5.93 (s, 1 H), and 7.56 ppm (m, 4 H).

Competition Reactions. One such reaction is described in detail. The remainder are summarized in Table V.

A 15-ml round-bottomed flask fitted with a reflux condenser topped with a nitrogen inlet tube was charged with 2.7374 g (19.80 mmol) of *p*-fluorocumene, 3.1284 g (20.23 mmol) of *p*-chlorocumene, and 1.0993 g (2.50 mmol) of $PhHgCCl_2Br$. The mixture was stirred (magnetic stirrer) at room temperature under nitrogen for 10 min and then transferred to a constant-temperature bath operated at 80.45 ± 0.03°. The mixture was stirred at this temperature for exactly 4 hr and then cooled in an ice bath. The reaction mixture was transferred to a 15-ml centrifuge tube and centrifuged. The supernatant liquid was separated and the solid washed twice with 5 ml of hexane to extract all of the occluded insertion products. The hexane was evaporated at reduced pressure and the residue was combined with the reaction solution. Glc analysis of this solution (10% SE-30 at 150°, 20 psi helium, MIT isothermal unit) followed.

Suitable control experiments were carried out to verify the applicability of the work-up procedure and analytical method.[40]

The relative rate constants thus determined are shown in Table V. The best straight line relating log k_Z/k_H to σ, σ^0, and σ^+ values (log $k_Z/k_H = \sigma\rho + C$) was obtained by linear regression by the method of least squares. The results are shown in Table III.

Competition between 2-Phenylbutane and 2-Phenylbutane-α-d_1 for Phenyl(bromodichloromethyl)mercury. A 25-ml round-bottomed flask equipped with a magnetic stirring assembly and a reflux condenser topped with a nitrogen inlet tube was charged with 3.9908 g (29.73 mmol) of 2-phenylbutane and 4.0083 g (29.64 mmol) of 2-phenylbutane-α-d_1 (96.7% deuterated) and 4.5502 g (10.32 mmol) of the mercury reagent. The mixture was stirred under nitrogen at room temperature for 10 min and then at 80.45 ± 0.03° for 4 hr. The reaction mixture was cooled to 0° and filtered through a sintered glass funnel, and the precipitate was washed with hexane. The combined filtrate and washings were concentrated at reduced pressure and then trap-to-trap distilled at 0.37 mm (pot temperature to 100°). A few milliliters of hexane was added to the distillate which then was chilled to −40° and filtered. The hexane was removed from the filtrate at reduced pressure. A sample of the insertion product was isolated by glc. *Anal.* Calcd for $C_{11}H_{13}DCl_2$: atom % excess D, 7.14. Found: 1.94 (equivalent to 27.2% deuteration). The relative rate was adjusted to 100% 2-phenylbutane-α-d_1 by the following calculation.

$$k_H/k_D = \frac{\text{mmol (product H)}}{\text{mmol (product D)}} \times \frac{\text{mmol (starting D)}0.967}{\text{mmol (starting H)} + \text{mmol (starting D)}0.033} = \frac{72.8}{27.2}\left(\frac{29.64 \times 0.967}{29.73 + 29.64 \times 0.033}\right) = 2.50$$

Other related competition reactions are summarized in Table VI.

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[40] Y. M. Cheng, Ph.D. Thesis, Massachusetts Institute of Technology, 1972.

Reduction of 1,1-Dichloro-2-methyl-2-phenylbutane with Triphenyltin Hydride. A 25-ml round-bottomed flask was charged with 2.80 g (13 mmol) of the dichloride and 5.0 g (14.6 mmol) of triphenyltin hydride under nitrogen. The mixture, which immediately became turbid, was stirred (magnetic stirrer) and heated at 78° under nitrogen for 12 hr. The resulting clear mixture was distilled to give 2.24 g (95%) of 1-chloro-2-methyl-2-phenylbutane, bp 62–62.5° (0.4 mm), n^{25}D 1.5213. Glc analysis (10% DC-200 fluid at 120°) showed that a single component was present. *Anal.* Calcd for $C_{11}H_{15}Cl$: C, 72.31; H, 8.28; Cl, 19.41. Found: C, 72.56; H, 8.11; Cl, 19.48. Nmr: δ 0.70 (t, J = 7.8 Hz, 3 H), 1.40 (s, 3 H), 1.95 (q, J= 7.8 Hz, 2 H), 3.58 (s, 2 H), and 7.18 ppm (s, 5 H).

A similar reduction of the optically active insertion product, (+)-1,1-dichloro-2-methyl-2-phenylbutane, $[\alpha]^{25}$D +1.88° (9.22 mmol), was carried out with 10.6 mmol of triphenyltin hydride to give 1.22 g (73%) of (+)-1-chloro-2-methyl-2-phenylbutane, n^{25}D 1.5213, d_4^{25} 1.0295, $[\alpha]^{25}$D +8.55° (neat), pure by glc, with an identical nmr spectrum. *Anal.* Calcd for $C_{11}H_{15}Cl$: C, 72.31; H, 8.28; Cl, 19.41. Found: C, 72.18; H, 8.23; Cl, 19.29.

In another such reaction, starting with (+)-1,1-dichloro-2-methyl-2-phenylbutane with $[\alpha]^{25}$D +1.95°, an 85% yield of (+)-1-chloro-2-methyl-2-phenylbutane with $[\alpha]^{25}$D +8.28° (neat) was obtained, n^{25}D 1.5212.

Preparation of Methyl 3-Methyl-3-phenylpentanoate from 1-Chloro-2-methyl-2-phenylbutane. A 50-ml three-necked flask equipped with a pressure-equalizing dropping funnel topped with a nitrogen inlet tube was flame-dried under nitrogen and charged with 0.25 g (36 mg-atoms) of Li in the form of a dispersion in oil. The oil was washed out with hexane and THF, and the lithium then was covered with 3 ml of dry THF and cooled to −10°. Five drops of 1-chloro-2-methyl-2-phenylbutane was added and then 3 drops of iodomethane. The mixture turned brown; it was stirred for 30 min and then cooled to −78°. The rest of the 1-chloro-2-methyl-2-phenylbutane (1.00 g, 5.5 mmol) was added dropwise with stirring over a 10-min period. The reaction mixture was stirred at −78° for 6 hr and then was poured onto a slurry of crushed Dry Ice in dry diethyl ether. The resulting mixture was allowed to warm slowly to room temperature and acidified with 6 *N* HCl. The ethereal layer was separated and the aqueous layer extracted with ether. The combined ether layers were dried over $MgSO_4$ and the solvent was removed at reduced pressure. A few milliliters of dry ether was added to the residue and treatment with ethereal diazomethane followed. Evaporation of the reaction mixture at reduced pressure was followed by trap-to-trap distillation of the residue at 0.75 mm (pot temperature to 105°). The distillate, n^{25}D 1.5024, 65% yield, was pure by glc (10% UC-W98 at 130°) and was identified as the title compound. *Anal.* Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.74; H, 8.64. Nmr: δ 0.67 (t, J = 7.9 Hz, 3 H), 1.48 (s, 3 H), H), 1.76 (q, J = 7.9 Hz, 2 H), 2.55 (s, 2 H), 3.46 (s, 3 H), and 7.23 (s, 5 H); ir (neat) $\nu_{C=O}$ 1735 cm^{-1}.

This procedure was followed in the reaction of 6.3 mmol of (+)-1-chloro-2-methyl-2-phenylbutane, $[\alpha]^{25}$D +8.55°, with 0.3 g of lithium (dispersion). After the reaction mixture had been poured onto Dry Ice and acidified, the ether extracts were evaporated and the residue was distilled (trap-to-trap) at 0.4 (pot temperature to 142°) to give a light yellow oil, 0.79 g (62% yield). A 100-mg aliquot of this oil was crystallized from pentane at −78° to give white needles, mp 38.5–42°, $[\alpha]^{25}$D +13.6° (*c* 3.47 in $CHCl_3$). The remaining acid was esterified with diazomethane in ether solution to give 0.60 g (46%) of (+)-methyl 3-methyl-3-phenylpentanoate, bp 76–78.5° (0.5 mm), n^{25}D 1.5022, d^{25}_4 0.9925, $[\alpha]^{25}$D +12.27° (neat). Cram, *et al.*,[12] reported bp 96° (1 mm), n^{25}D 1.5018, and $[\alpha]^{25}$D +12.7° (neat). *Anal.* Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.88; H, 8.81.

In another such reaction sequence starting with (+)-1-chloro-2-methyl-2-phenylbutane, $[\alpha]^{25}$D +8.28°, this ester was obtained in 50% yield, n^{25}D 1.5020, $[\alpha]^{25}$D +12.16° (neat).

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Homotropilidene–Palladium Dichloride Complexes

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Abstract: Homotropilidenes (barbaralone, dihydrobullvalene, bicyclo[5.1.0]octa-2,5-diene, bullvalene, and benzobullvalene) react with bis(benzonitrile)palladium dichloride to form complexes. The dihydrobullvalene complex is shown to have a bicyclic structure derived from addition of palladium dichloride across a vinylcyclopropane unit on the basis of the nmr spectrum and borohydride reduction to bicyclo[3.3.2]deca-2,7-diene. The other homotropilidene complexes have similar structures, although barbaralone and bicyclo[5.1.0]octa-2,5-diene also appear to form π-olefin complexes having the cyclopropane intact under certain conditions. In the presence of hydroxylic solvents or upon treatment with silver acetate, the palladium dichloride complexes are converted into derivatives having oxygen substituents in place of chloride. The acetoxy complex obtained from the barbaralone–palladium dichloride adduct is characterized by borohydride reduction to 4-acetoxybicyclo[3.3.1]nona-2,7-dien-9-one and the isomeric 2,6-dien-9-one. The bullvalene–palladium dichloride adduct rearranges to a complex of bicyclo-[4.2.2]deca-2,4,7,9-tetraene at 0°. A similar rearrangement occurs with the benzobullvalene complex in refluxing chloroform. A mechanism based on cyclopropyl carbinyl intermediates is proposed.

Interest in homotropilidene–metal complexes has centered on the possibility of metal-moderated Cope rearrangements and metal-induced skeletal rearrangements. Irreversible rearrangements have been observed in the presence of iron (bullvalene, semibullvalene, dibenzosemibullvalene),[3] palladium (bullval-

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