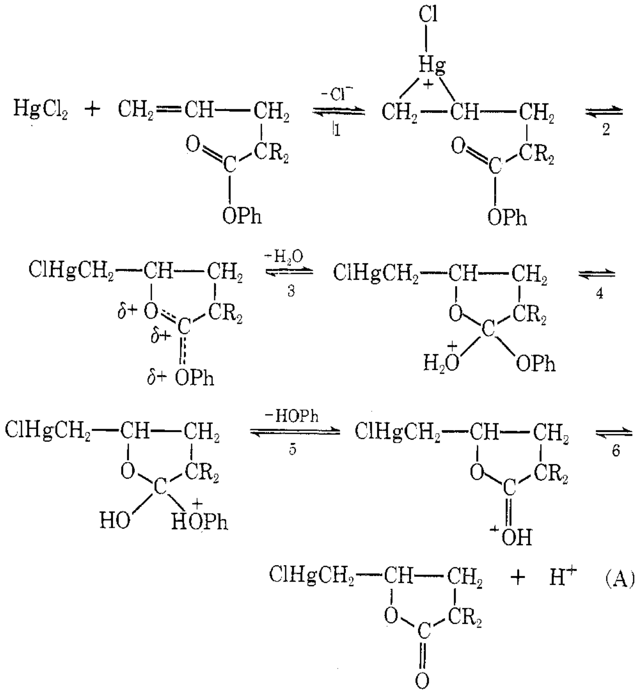

(A)

when the substituent is an electron-releasing group. This suggests that the rate-determining step is the departure of the phenol (step 5), since a better leaving groups departs quicker. If the rate-determining step were the nucleophilic attack of the carbonyl oxygen on the mercurinium ion (step 2), the velocity of the reaction would decrease when the substituent is an electron-attracting group and increase when the substituent is an electron-releasing group. The experimental observations do not support the latter statement.

With the phenyl allyl para-substituted phenylacetates esters the presence of electron-withdrawing groups in the para position of the phenyl ring decreases the rate of the reaction while the presence of electron-donating groups at the same position causes an increase in the reaction rate. In these esters the leaving group remains the same, but step 2 is shifted to the right by the increase in the electron density of the carbonyl group. This further supports the postulate that the rate-determining step for the chloromercuriolactonization reaction is the loss of the substituted phenol.

Registry No.—$HgCl_2$, 7487-94-7; phenyl allyldiphenylacetate, 51231-12-0.

References and Notes

(1) Supported in part by the Fund for Overseas Research Grants and Education.

(2) Fellow of the Fundação de Amparo à Pesquisa do Estado de São Paulo.

(3) J. Bourdais and C. Mahieu, *C. R. Acad. Sci., Ser. C,* **263**, 84 (1966).

(4) R. L. Rowland, W. L. Perry, and H. L. Friedman, *J. Amer. Chem. Soc.*, **73**, 371 (1951).

(5) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(6) Sadtler, I. R. Standard Spectra Catalog No. 23090.

(7) P. N. Craig and I. H. Witt, *J. Amer. Chem. Soc.*, **72**, 4952 (1950).

(8) M. Carissimi, I. Grasso, F. Grumelli, E. Milla, and F. Ravena, *Il Farmaco, Ed. Sci.*, **17**, 390 (1962).

(9) P. E. Pfeffer and L. S. Silbert, *J. Org. Chem.*, **35**, 2607 (1968).

(10) H. Hamell and R. Levine, *J. Org. Chem.*, **15**, 162 (1950).

(11) A. Factor and T. C. Traylor, *J. Org. Chem.*, **33**, 2607 (1968).

(12) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963.

(13) S. V. Arakelyan, M. T. Dangyan, and A. A. Abetisyan, *Izv. Akad. Nauk. Arm. SSR, Khim. Nauki*, **15**, 435 (1962).

(14) E. E. van Tamelen and M. Shamma, *J. Amer. Chem. Soc.*, **76**, 2315 (1954).

(15) E. Hankanen, T. Moisio, and P. Karvonen, *Acta Chem. Scand.*, **19**, 370 (1965); *ibid.*, **23**, 531 (1969).

(16) W. H. MacFadden, E. A. Day, and H. J. Diamond, *Anal. Chem.*, **37**, 89 (1965).

(17) G. F. Wright, *Ann. N. Y. Acad. Sci.*, **65**, 436 (1957).

(18) K. L. Mallik and M. N. Das, *J. Amer. Chem. Soc.*, **82**, 4269 (1960).

(19) A. K. Chaudhuri, K. L. Mallik, and M. N. Das, *Tetrahedron*, **19**, 1981 (1946).

(20) H. J. Lucas, R. R. Hepner, and S. Winstein, *J. Amer. Chem. Soc.*, **61**, 3102 (1939).

(21) W. Kithching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

(22) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **78**, 815 (1959).

(23) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 7 (1963).

(24) J. L. Maged, T. Ri, and H. Eyring, *J. Chem. Phys.*, **9**, 419 (1941).

(25) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(26) P. N. Craig, *J. Amer. Chem. Soc.*, **74**, 129 (1952).

(27) R. T. Arnold, M. Moura Campos, and K. L. Lindsay, *J. Amer. Chem. Soc.*, **75**, 1044 (1953).

Mercuric Chloride Promoted and Cobaltous Chloride Promoted Reactions of 1-Phenylethyl Chloride[1,2]

Carlos Monge, Jr., John L. Palmer, and A. F. Diaz*

Department of Chemistry, University of California, San Diego, La Jolla, California 92037

Received January 28, 1974

The ionization of 1-phenylethyl chloride in anhydrous acetone is efficiently promoted by $HgCl_2$ and $CoCl_2$. The reactions measured by loss of optical activity and radiochlorine exchange provide results which are consistent with the intervention of ion-pair intermediates. In the case with $HgCl_2$ the kinetics are complicated and are consistent with the presence of two molecules of $HgCl_2$.

In the previous papers of this series we described the $HgCl_2$-promoted reactions of fairly reactive alkyl chlorides which ionized to form cations with intermediate stability such as the benzhydryl[3a] and the norbornyl[3b,c] cations. In these cases, the reactions are well behaved, showing a clean first-order dependence on the $HgCl_2$ concentration, and the importance of ion-pair intermediates was stressed. It seemed appropriate to extend this study to alkyl chlorides whose ionization reactions are more endothermic and where the cation is relatively less stable, especially since previous reports on studies with compounds of this type bring out the fact that the kinetic dependence of the reaction on $HgCl_2$ is complicated.[4-6] Thus, the hydrolysis and accompanying loss of optical activity of 1-phenylethyl chloride in aqueous acetone shows complicated kinetics and the two reactions are reported to proceed *via* different reaction pathways.[5] We now wish to present the results of a study on the $CoCl_2$-promoted and $HgCl_2$-promoted reactions of 1-phenylethyl chloride (RCl).

Table I
Summary of k Values for 1-Phenylethyl Chloride[a] in Acetone Containing $CoCl_2$ at 50.0°

$[CoCl_2]$, 10^2 M	10^6 k, sec^{-1}		10^4 k, M^{-1} sec^{-1}	
	k_α	k_e	k_α	k_e
0.853	31.7		37.2	
0.900		21.1 ± 2.0		23.5
1.003	37.2 ± 0.4		37.2	
1.160		28.1 ± 1.4		24.3
1.640		37.2 ± 3.4		23.1
2.002		54.9 ± 0.9		27.5
2.098	82.8 ± 0.6		39.5	
3.556	131		37.1	
			Av 37.8 ± 0.8	24.6 ± 1.4
			$k_\alpha/k_e = 1.54 \pm 0.09$	

[a] *Ca.* 0.09 and 0.01 M RCl used for k_α and k_e measurements, respectively.

Table II
Summary of k Values for 1-Phenylethyl Chloride[a] in Acetone

Temp, °C	$[H_2O]$, M	$[HgCl_2]$, 10^2 M	10^6 k, sec^{-1}			k_{rac}/k_e
			k_α	k_e	k_t	
50.0		0.204		0.788 ± 0.014		
50.0		0.530		2.66 ± 0.27		
50.0		1.00	8.23 ± 0.4	5.60 ± 0.35		1.47
50.0		1.00	8.20[b]			
50.0		5.00	54.3 ± 1.2	47.2 ± 2.2		1.15
50.0		10.1	153 ± 4	129 ± 3		1.19
50.0		10.0	134[b]			
50.0	2.22	2.50	42.3 ± 1.7 (k_{rac}) 31.7	20.3 ± 0.3	10.6 ± 1.2	1.56
50.0	2.22	5.00	104 ± 9 (k_{rac}) 64.3	41.5 ± 1.5	39.7 ± 3.1	1.54
25.0	2.22	120.0		~2.5[d]	~950[d]	
20.0[c]	2.78	30.0	95.0 ± 5.1		90.1 ± 2.2	
20.0[c]	2.78	120.0	1050 ± 30		905 ± 40	

[a] [RCl] was 0.02–0.1 M for exchange runs and 0.1–0.3 M for polarimetric runs. [b] Calculated from Satchell's data (ref 4). [c] Recalculated values using the data of Read and Taylor (ref 5). [d] Good values are difficult to measure at these experimental conditions.

Results

Cobaltous Chloride. Optically active 1-phenylethyl chloride was prepared from the resolved carbinol with thionyl chloride. The prepared solution in acetone was placed in an all-glass 1-dm cell thermostated at 50.0°, and the rate of loss of optical activity was measured using a Perkin-Elmer polarimeter, Model 141.

$$\left.\begin{array}{lll} d\text{-RCl} \longrightarrow dl\text{-RCl} & k_{rac} \\ d\text{-RCl} \longrightarrow dl\text{-ROH} & k_t \end{array}\right\} k_\alpha \qquad (1)$$

The infinity readings were *ca.* zero rotation but difficult to read because of the yellow color which developed during the reaction. The data were treated using a first-order rate expression where α_0, α_t, and α_∞ are the polarimetric readings initially, at time t, and at t_∞, respectively.

$$k_\alpha = \frac{2.303}{t}\log\frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \qquad (2)$$

In those runs with $CoCl_2$ the integrated first-order rate constants, k_α, were well behaved up to 60% reaction. These k values are summarized in Table I. The k_α values seem to be linearly depended on $[CoCl_2]$ in the concentration range studied, providing a second-order rate constant equal to $37.8 \pm 0.8 \times 10^{-4}$ sec^{-1}.

The rates of chlorine exchange between RCl and radiochlorine-labeled $CoCl_2$ were sampled up to 40–45% reaction using the sealed ampoule technique. In anhydrous acetone, the exchange proceeds to completion, where at 8 reaction half-lives the distribution of radiochloride between RCl and $CoCl_2$ is 98% of the calculated amount.

The exchange reactions showed good second-order kinetics. The integrated second-order rate constants were calculated using eq 3,[3c] where γ is the fraction of radioactivity measured in the organic layer at time t. The pseudo-first-order rate constants are given by the product of k_{2e} and the salt concentration (eq 4). The k_e values seem to be linearly related to the $CoCl_2$ concentration and are significantly lower than the corresponding k_α values. The second-order exchange rate constant has a value of $24.6 \pm 1.4 \times 10^{-4}$ M^{-1} sec^{-1}. These values are summarized in Table I.

$$k_{2e} = \frac{2.303}{t([RCl] + 2[CoCl_2])}\log\left[1 - \gamma\frac{[RCl] + 2[CoCl_2]}{[RCl]}\right] \qquad (3)$$

$$k_e = k_{2e}2[CoCl_2] \qquad (4)$$

Mercuric Chloride. The racemization of 1-phenylethyl chloride in anhydrous acetone containing $HgCl_2$ was followed as described above. These reactions are considerably slower than with $CoCl_2$ and the k_α values showed a slight downward drift during a run where the initial k values are decreased by *ca.* 5% at 30% reaction. This decrease is most likely due to the slow decomposition of 1-phenylethyl chloride under the reaction conditions to produce styrene and HCl, which renders $HgCl_2$ inactive. The amount of decomposition at 50% racemization is *ca.* 1.3% with 0.1 M $HgCl_2$. Thus, only the initial k values, *i.e.*, up to *ca.* 15% reaction, are listed in Table II for comparison with the other k values.

The k_{rac} values do not plot linearly with $[HgCl_2]$ but instead the slope increases with increasing $HgCl_2$ concentration as reported by Satchell.[4] These values are fit to within 3% by eq 5, which shows the sum of two kinetic terms, one first order in $HgCl_2$ and the other second order in $HgCl_2$. This equation was obtained by a series of successive approximations. For the purpose of comparing our results with Satchell's, k_{rac} values for 1-phenylethyl chloride with $HgCl_2$ at 50.0° were calculated using the values at 25.0° published by Satchell.[4b] The calculations were made using ΔH^* values equal to 15.7 and 16.9 kcal for the second-order and third-order terms, respectively, obtained from the reaction of 1-phenylethyl chloride with $HgBr_2$. The resulting kinetic expression at 50° calculated from Satchell's values is given in eq 6, which provides k_{rac} values equal to 8.2×10^{-6} and 134×10^{-6} sec^{-1} at 0.01 and 0.05 M $HgCl_2$, respectively. These values agree well with our results and are listed in Table II.

$$k_{rac}(\mathrm{sec}^{-1}) = 7.4 \times 10^{-4}[\mathrm{HgCl_2}] + 78 \times 10^{-4}[\mathrm{HgCl_2}]^2 \quad (5)$$

$$k_{rac}(\mathrm{sec}^{-1}) = 7.6 \times 10^{-4}[\mathrm{HgCl_2}] + 58 \times 10^{-4}[\mathrm{HgCl_2}]^2 \quad (6)$$

$$k_e(\mathrm{sec}^{-1}) = 4.9 \times 10^{-4}[\mathrm{HgCl_2}] + 78 \times 10^{-4}[\mathrm{HgCl_2}]^2 \quad (7)$$

The polarimetric rates measured with $HgCl_2$ in acetone containing 2.22 M H_2O were again treated using first-order kinetics. In this case, the k_α values show a very dramatic drift due to the solvolytic reaction. Thus only the initial k values (up to 10% reaction) are included in the summary in Table II. The effect of adding 2.22 M H_2O to the reaction solution is to increase k_α, while the nonlinear dependence on $[HgCl_2]$ still prevails.

The rates of radiochlorine exchange between RCl and $HgCl_2^*$, followed as described above, were sampled up to 70 and 80% reaction. In anhydrous acetone, the exchange proceeds to near completion, where at 6 reaction half-lives the distribution of radiochlorine between RCl and $HgCl_2$ is 96.5% of the calculated amount. The integrated second-order rate constants calculated as above were constant within a run. The k_e values are significantly lower than the corresponding k_α values and the differences vary with the $HgCl_2$ concentration. As in the racemization reaction, the k_e values do not plot linearly with $[HgCl_2]$ but again deviate upward from linearity with increasing $HgCl_2$ concentration. These values can be fit to within 3% by the two-term expression given in eq 7.

The exchange rate constants for the reactions measured in the presence of 2.22 M H_2O were calculated using eq 8, where the value of $e^{-k_t t}$ at time t calculated using the measured k_t. Inspection of Table II brings out the fact that, in contrast to the reaction in anhydrous acetone, the k_e values are now linearly related to $[HgCl_2]$.

$$\frac{k_e}{2[\mathrm{HgCl_2}]} = k_{2e}\frac{2.303}{([\mathrm{RCl}] + 2[\mathrm{HgCl_2}])t}\log\left[1 - \gamma\frac{[\mathrm{RCl}] + 2[\mathrm{HgCl_2}]}{[\mathrm{RCl}]e^{-k_t t}}\right] \quad (8)$$

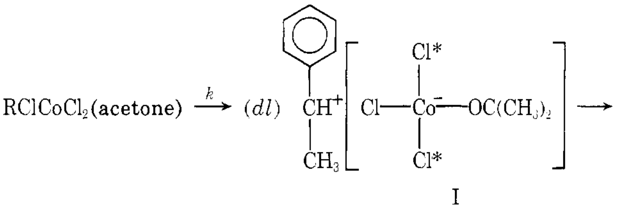
The rate of solvolysis of 1-phenylethyl chloride in acetone containing 2.22 M H_2O and $HgCl_2$ was followed by titrating the produced HCl with sodium methoxide to a Bromophenol Blue end point. The reaction followed good second-order kinetics and proceeded to 97% completion. The pseudo first-order k_t values given by the product of the second-order k and $[HgCl_2]$ are listed in Table II.

$$\mathrm{RCl} + \mathrm{H_2O} + \mathrm{HgCl_2} \longrightarrow \mathrm{ROH} + \mathrm{H^+} + \mathrm{HgCl_3^-} \quad k_t \quad (9)$$

Discussion

Scheme I

$$\mathrm{RCl} + \mathrm{CoCl_2(acetone)_2} \overset{k}{\rightleftharpoons} \mathrm{RClCoCl_2(acetone)}$$



dl-RCl* (10)

Table III
Comparison of Racemization and Exchange Rate Constants for 1-Phenylethyl Chloride in Acetone at 50.0°

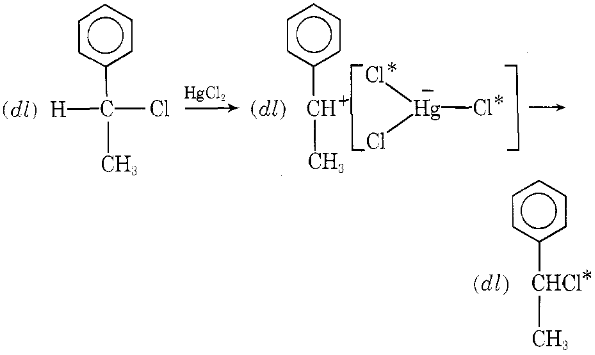
$[HgCl_2]$, M	k	$10^6 k$, sec^{-1} k_{rac}	k_e	k_{rac}/k_e	Per cent of reaction
0.01	Observed	8.23	5.60	1.47	
	Monomer	7.4	4.9	1.51	90
	Dimer	0.83	0.5	(1.2)	10
0.1	Observed	153	129	1.19	
	Monomer	74	49	1.51	48
	Dimer	79	80	0.99	52

In considering the reactions of 1-phenylethyl chloride promoted by $CoCl_2$ and by $HgCl_2$ in acetone at 50° the reaction in the absence of salt is neglected, since even in CH_3NO_2 at 100° k_α is only 1.2×10^{-5} sec^{-1}.[7] The $CoCl_2$-promoted ionization reaction of 1-phenylethyl chloride in anhydrous acetone at 50.0° is reminiscent of the $HgCl_2$-promoted reactions of p-chlorobenzhydryl chloride in the same solvent.[3a] Thus $CoCl_2$ efficiently promotes the ionization reaction and is *ca.* 4–5 times a better catalyst than $HgCl_2$ at 0.01 M salt concentration in anhydrous acetone. The promoted reaction shows a linear dependence on $CoCl_2$ concentration where the racemization and exchange reactions differ in the ratio $k_{rac}/k_e = 1.54 \pm 0.09$. As in the case with $HgCl_2$, racemization and exchange in the promoted reaction proceed *via* ion pairs, $R^+//CoCl_3^-$, like I, which do not exchange the anion with the other $CoCl_2$ present in solution and which will equilibrate the two faces of the cation when and only when the three chlorine atoms on cobalt become equivalent. Therefore the probability of incorporating radiochlorine into the regenerated RCl is ⅔ as given by the constitution of the chlorine atoms on the anion.

The solution of $CoCl_2$ in anhydrous acetone is blue, suggesting the tetrahedral arrangement of two chlorine atoms and two acetone molecules around the cobalt atom. Thus, the overall reaction must involve a rapid and reversible displacement of acetone on cobalt by RCl followed by the rate-determining ionization of the RCl complex to give an intermediate like I which generates racemic RCl (Scheme I).

In the reactions with $HgCl_2$, both k_{rac} and k_e deviate upwardly from linearity with increasing $HgCl_2$ concentration. The k_α values are greater than the k_e values where the k_{rac}/k_e ratio decreases from 1.47 at 0.01 M $HgCl_2$ to 1.19 at 0.1 M $HgCl_2$. The ratio of 1.47 at the lower $HgCl_2$ concentration approximates the 3:2 ratio observed previously,[3a] suggesting a similarity in the nature of the ion pairs which give rise to racemization and exchange in the two systems. The ratio at the higher concentration is more difficult to interpret; however, if a kinetic dissection of the overall reaction is interpreted as the presence of two discrete reactions[5] which proceed *independently,* one being the reaction promoted by monomeric $HgCl_2$ (k_2) and the other a reaction involving two molecules of $HgCl_2$ (k_3), then the data will be easier to understand.

From such a dissection one calculates with the aid of eq 5 that at 0.1 M $HgCl_2$ the ionization of 1-phenylethyl chloride occurs *ca.* 48% with monomeric $HgCl_2$, where the k_{rac}/k_e ratio is 1.5 (Table III). Thus, racemization and exchange proceed *via* intermediates like I which do not dissociate and do not exchange with the rest of the $HgCl_2$ present in solution.



(11)

The remaining 52% of the reaction is promoted by $HgCl_2$ involving two molecules where the k_{rac}/k_e ratio is 1. In this reaction the rates of racemization and exchange are equal. Efficient ion-pair dissociation in the reaction with the dimeric form of $HgCl_2$ will make the rates of racemization and exchange equal. Chemical capture of the ion pair II (Scheme II) by $HgCl_2$ will permit the chlorine atoms originally from RCl to become randomized with the total inorganic chloride pool (eq 12) before the ions recombine to regenerate racemic RCl. In line with this explanation is the expectation that an ion like $(HgCl_3HgCl_2)^-$ in the ion pair II will be more susceptible to dissociation and exchange than the anion in an ion pair like I. Therefore, at 0.1 *M* $HgCl_2$ the racemization in excess of exchange observed in the overall reaction appears to be wholly accountable by the reaction with monomeric $HgCl_2$.

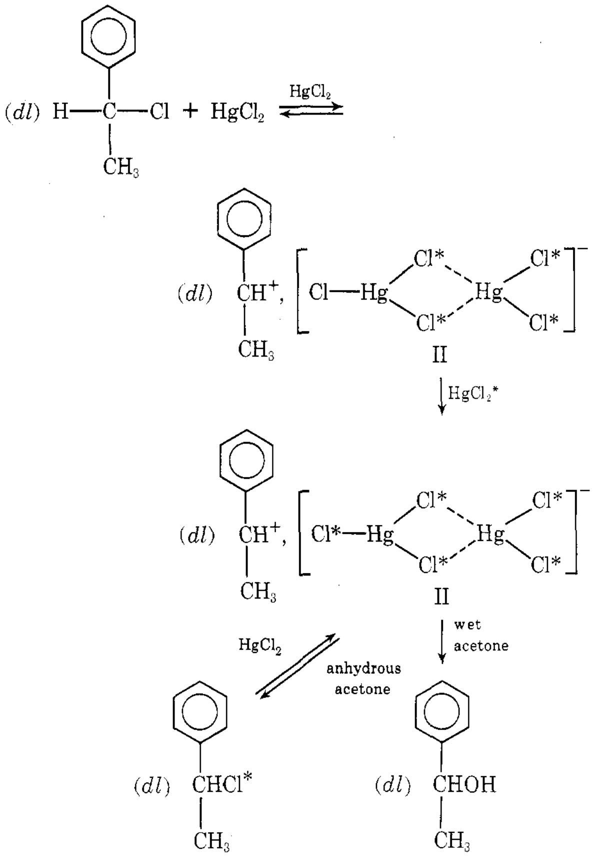
This kinetic behavior is in sharp contrast to that observed with the less endothermic benzhydryl chloride system, where k_α is linear in $[HgCl_2]$ up to 0.15 *M*. In the present case the termolecular term contributes 10% of the overall reaction already at 0.01 *M* $HgCl_2$.

This reaction was further studied in wet acetone, since the presence of a nucleophile such as water which can yield a chemical product will further test this theory on the relative susceptibilities of the two intermediates toward chemical capture. The presence of 2.22 *M* H_2O causes a small rate increase in the overall reaction. In considering our data no correction is made for the unpromoted reaction, since its contribution is small, where the value of k_t is *ca.* 1×10^{-6} sec^{-1}.[8,9] At 0.05 *M* $HgCl_2$, the k_t/k_α ratio indicates that *ca.* 35% of the reaction intermediates give rise to product ($f = 0.35$) and *ca.* 65% return to regenerate RCl. The intermediates that return to RCl must have the same constitution as I and must involve the reaction with monomeric $HgCl_2$, since k_{rac} and k_e are linear in $[HgCl_2]$ and the k_{rac}/k_e ratio is 3:2 (1.50 ± 0.04). See Table II.

While it is not clear how product is formed, one may expect by analogy with the benzhydryl system that those intermediates that dissociate will collapse to give product almost exclusively.[3a] Therefore, return to RCl from intermediates like II is effectively eliminated owing to efficient chemical capture of the intermediates by H_2O (eq 12). It seems consistent that the racemization process, loss of optical activity in *excess* of that which occurs *via* ion pair *dissociation* as measured either by exchange (anhydrous acetone) or solvolysis (wet acetone), involves the reaction with monomeric $HgCl_2$ to produce an ion pair like I. The role of the second molecule of $HgCl_2$ is depicted by Satchell as one of specific solvation rather than promotion of the ionization reaction by incipient dimer formation.[4]

Thus, while in the $HgCl_2$-promoted reactions of *p*-chlorobenzhydryl chloride, dissociation of the intermediates

Scheme II



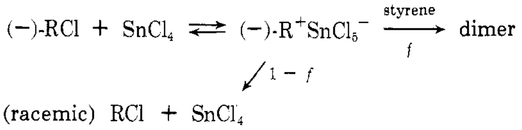
(12)

was increased by solvent variation,[3a] with 1-phenylethyl chloride in anhydrous acetone, dissociation is increased by specific solvation of the $HgCl_3^-$ anion of the ion pair by a second molecule of $HgCl_2$.

While we do not intend to extend this study to higher $HgCl_2$ concentrations, it seems informative to discuss at this time the results of Read and Taylor.[5] These authors measured the rates of loss of optical activity and solvolysis of 1-phenylethyl chloride in acetone containing 2.78 *M* H_2O at 20°. Rate constants were calculated using their experimental data and are listed in Table II. The k_t values are more appropriately calculated using the second-order rate expression. Only the k_t values for the first 25-50% reaction are considered since at longer reaction times the *k* values drift down, probably owing to drastic changes in the reaction media arising from the relative low $H_2O/HgCl_2$ concentration ratio. Some of the drift may be due to common-ion rate depression.[10] The polarimetric runs were calculated using eq 2 and omitting the initial extrapolated polarimetic readings. In contrast to the *k* values calculated by the original authors, the run shows good pseudo-first-order *k* values with no apparent drift.

The results at these high $HgCl_2$ concentrations should be readily explicable based on the above discussion. Thus the reaction should proceed mostly *via* intermediates like II which are dissociated and primarily racemic. Accordingly, product formation at 0.3-1.2 *M* $HgCl_2$ is very efficient, $f = 0.91$–0.95, where the amount of ion pair return accompanying the reaction is minimal, $1 - f$ being *ca.* 0.07. In line with this we observe very little exchange accompanying the solvolysis reaction at 1.20 *M* $HgCl_2$ where k_e/k_t equals *ca.* 0.003. However, racemization is not complete in the intermediates, since the final ROH product is slightly inverted.[5] Therefore the results at these high $HgCl_2$ concentration are fit by a mechanism where racemization and hydrolysis occur *via* the same reaction pathway. This interpretation differs from the one originally proposed by the authors where the mechanisms for racemization and hydrolysis were considered distinct.[5]

Ion-pair intermediates are also important in reactions promoted by $SnCl_4$. Thus, the $SnCl_4$-promoted racemization of optically active 1-phenylethyl chloride in CCl_4 containing excess styrene was reported by Heald and Williams.[11] Here, 1-phenylethyl chloride reacts with styrene to form styrene dimer *ca.* 36 times slower than it undergoes racemization, where the addition of styrene has no apparent effect on the rate of racemization. The authors described the reaction as proceeding by an ionization mechanism to produce a carbonium ion pair intermediate which regenerates racemic RCl more efficiently than it combines with styrene to form dimer. In this system, $1 - f$ is *ca.* 0.97.



$$\begin{tikzcd}[column sep=small] (-)\text{-RCl} + \text{SnCl}_4 \arrow[r, shift left] & (-)\text{-R}^+\text{SnCl}_5^- \arrow[l, shift left] \arrow[r, "\text{styrene}", "f"'] \arrow[dl, "1-f"] & \text{dimer} \\ (\text{racemic})\ \text{RCl} + \text{SnCl}_4 & & \end{tikzcd}$$

Experimental Section

Optically active 1-phenylethyl chloride was prepared from the resolved carbinol[12] using thionyl chloride.[13] The reaction mixture was dissolved in pentane and the pentane solution of RCl was washed carefully with aqueous $NaHCO_3$. The solution was dried over K_2CO_3 and the pentane was evaporated at reduced pressure. The alkyl chloride was used as such without further purification, chloride analysis 99.9% Cl, $[\alpha]_{589}$ − 8.8.

Mercuric chloride was sublimed before use. Radiolabeled mercuric chloride was prepared using 0.25 *N* radiolabeled (^{36}Cl) hydrochloric acid as previously described.[3c] Reagent grade $CoCl_2 \cdot 6H_2O$ was dried over P_2O_5 in an Abderhalder drying apparatus at 110° (1 mm) before use. Radiolabeled cobalt(II) chloride was prepared by mixing 1 g of $CoCl_2$ with 0.1 ml of 0.25 *N* radiolabeled (^{36}Cl) hydrochloric acid in 10 ml of dry methanol. The methanol was next removed under reduced pressure and the recovered solid was dried at 110° (1 mm) for 2 days. The salt was neutral to Bromophenol Blue indicator in acetone. The activity of the sample was 2920 cpm/mg.

The solvents were prepared as previously described.[14]

The polarimetric rate measurements were made in a thermostated 1-dm all-glass cell using a Perkin-Elmer polarimeter, Model 141. The wavelengths used were 589 and 436 nm for runs with $HgCl_2$ and $CoCl_2$, respectively.

The exchange rate measurements were carried out using a sealed ampoule technique as previously described.[3c] The separation of organic chloride from inorganic chloride was afforded using pentane and water. Two-milliliter aliquots from each layer were delivered into 10 ml of Bray's solution[15] and the radioactivity level was measured using a Beckman LS100 Liquid Scintillation Counter.

The titrimetric rate measurements were carried out using a sealed-ampoule technique.[3c] Five-milliliter aliquots were titrated to the blue end point of Bromophenol Blue with 0.01095 *M* sodium methoxide in methanol solution.

Registry No.—$HgCl_2$, 7487-94-7; $CoCl_2$, 7646-79-9; 1-phenylethyl chloride, 72-65-1.

References and Notes

(1) The authors wish to acknowledge the Academic Senate Research Council and the American Cancer Society Institution Grant for their financial support.

(2) Part of this work was previously reported in preliminary form: *Rev. Latinoamer. Quim.*, **4**, 154 (1972).

(3) (a) A. Diaz, L. Reich, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 7598 (1970); (b) J. P. Hardy, A. Ceccon, A. Diaz, and S. Winstein, *ibid.*, **94**, 1356 (1972); (c) J. P. Hardy, A. F. Diaz, and S. Winstein, *ibid.*, **94**, 2363 (1972).

(4) (a) R. S. Satchell, *J. Chem. Soc.*, 5963 (1964); (b) *ibid.*, 5464 (1964); (c) *ibid.*, 767 (1965).

(5) D. R. Read and W. Taylor, *J. Chem. Soc.*, 679 (1940).

(6) (a) R. Anantaraman, *Tetrahedron*, **21**, 535 (1965); (b) *Naturwissenschaften*, **50**, 497 (1963); (c) *J. Sci. Ind. Res., Sect. B*, **21**, 598 (1962); *Z. Phys. Chem.*, **216**, 21 (1961); *J. Amer. Chem. Soc.*, **82**, 1574 (1960); *Proc. Indian. Acad. Sci., Sect. A*, **49**, 111 (1959).

(7) Y. Pocker, W. A. Mueller, F. Naso, and G. Tocchi, *J. Amer. Chem. Soc.*, **86**, 5012 (1964).

(8) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1597 (1957).

(9) E. D. Hughes, C. K. Lingold, and A. D. Scott, *J. Chem. Soc.*, 1201 (1937).

(10) R. Anantaraman and K. Saramma, *Tetrahedron*, **21**, 537 (1965).

(11) K. Heald and G. Williams, *Tetrahedron*, 362 (1954).

(12) E. Dawner and J. Kenyon, *Tetrahedron*, 1156 (1939).

(13) A. McKenzie and G. W. Clought, *Tetrahedron*, **97**, 2564 (1910).

(14) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Amer. Chem. Soc.*, **83**, 618 (1961).

(15) G. A. Bray, *Anal. Biochem.*, **1**, 279 (1960).

Arene–Metal Complexes. VII. Stereoselective Catalytic Deuteration of *syn*-(Dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium[1]

Walter S. Trahanovsky* and Charles Robert Baumann

Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010

Received February 22, 1974

The palladium on charcoal catalyzed deuteration of *syn*-(dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium (1) in dioxane gave a high yield of *syn*-(dibenzobicyclo[2.2.2]octadiene)tricarbonylchromium which was predominantly a d_2 species with both of the deuteriums on the ethano bridge and anti to the tricarbonylchromium moiety. Deuteration of 1 and uncomplexed dibenzobicyclo[2.2.2]octatriene (2) was shown to go without rearrangement to the bicyclo[3.2.1]octane system or significant bridgehead hydrogen exchange. The predominantly anti addition of the deuteriums to 1 appears to be a result of the tricarbonylchromium moiety serving as a blocking group to shield one face of the carbon–carbon double bond.

Tricarbonylchromium groups complexed to benzene rings have been shown to exert electronic and conformational effects.[1a] In this report we describe a study of an addition reaction to a double bond of an arene–tricarbonylchromium complex that has one of its faces shielded by the metal moiety. The results of this study indicate that the metal moiety exerts a steric effect and serves as a blocking group and thus addition occurs predominantly to the unshielded face of the carbon–carbon double bond.

Results

syn-(Dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium (1) was prepared in moderate yield by refluxing the