1118. *Nucleophilic Substitution at a Metal-bearing Carbon Atom. Part II.*[1] *Kinetics and Mechanism of the Reaction between Mercuric Chloride and Diazodiphenylmethane*

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The reaction between diazodiphenylmethane and mercuric chloride in dry tetrahydrofuran leads to formation of $ClHg{\cdot}CPh_2Cl$, and $ClHg{\cdot}CPh_2{\cdot}CPh_2Cl$ depending on the reaction conditions. Both products are excessively reactive to hydrolysis, yielding mercury and benzophenone or benzpinacolone, respectively. Detailed kinetic studies support the view that the reaction between diazodiphenylmethane and mercuric chloride involves polar rather than free radical intermediates.

THE reaction between diazoalkanes and metal halides is a particularly useful synthetic route to carbon-functional organometallic compounds.[2] Mercuric derivatives have been widely employed for this purpose [3,4] and the reaction is generally represented as follows:

$$R^1R^2CN_2 + HgX_2 \longrightarrow XHgCR^1R^2X + N_2$$

$$XHgCR^1R^2X + R^1R^2CN_2 \longrightarrow Hg(CR^1R^2X)_2 + N_2$$

Yields of organomercury compounds are essentially quantitative when the reaction is performed in ether, but the formation of a di- or mono-alkyl-mercury derivative depends critically upon the nature of the diazoalkane. A detailed kinetic study of one of these reactions was necessary in order fully to understand the reaction mechanism.

Hellerman and Newman [4] showed that mercuric chloride reacts with diazodiphenylmethane in diethyl ether to give the thermally unstable compound chlorodiphenylmethylmercuric chloride (I), *i.e.*,

$$\underset{}{Ph_2CN_2 + HgCl_2} \longrightarrow \underset{\text{(I)}}{ClHgCPh_2Cl} + N_2 \qquad \underset{\text{(II)}}{ClHg{\cdot}CPh_2{\cdot}CPh_2Cl}$$

Preliminary experiments indicated that the rate of this reaction was convenient for kinetic studies whereas the corresponding reaction with diazomethane was much too rapid to follow at room temperature.

EXPERIMENTAL

Mercuric chloride and mercuric bromide were AnalaR grade materials used without further purification.

Tetrahydrofuran (General Purpose Reagent) was made both anhydrous and free from peroxide by refluxing it for several hours with calcium hydride, and then distilling from the solid through a glass-bead fractionating column. A middle fraction of constant boiling point 65° at 760 mm. was collected, and used.

Acetonitrile (General Purpose Reagent) was purified by refluxing over phosphorus pentoxide for several hours, followed by distillation through a Vigreux column. A middle fraction of constant b. p. 81·5° at 760 mm. was collected.

Diazodiphenylmethane and diazodi-(*p*-methoxyphenyl)methane were prepared by the method of Smith and Howard,[5] and purified to constant melting point by repeated recrystallisation from methanol.

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[1] Part I, A. Ledwith and L. Phillips, *J.*, 1962, 3796.

[2] D. Seyferth, *Chem. Rev.*, 1955, **55**, 1155.

[3] A. Ledwith, L. Phillips, and J. Whittleston, unpublished work; P. Pfeiffer, R. Schulze-Bentrop, K. H. La Roche, and E. Schmitz, *Chem. Ber.*, 1952, **85**, 232; P. Pfeiffer and A. Jager, *Chem. Ber.*, 1947, **80**, 1.

[4] L. Hellerman and M. D. Newman, *J. Amer. Chem. Soc.*, 1932, **54**, 2859.

[5] L. I. Smith and K. L. Howard, *Org. Synth.*, 1944, **24**, 53.

Kinetic Measurements.—The reaction was followed by observing the rate of disappearance of the diazodiphenylmethane absorption maximum at 529 mμ. Molar extinction coefficients obtained in the present work were $\varepsilon_{529} = 94$ l. mole^{-1} in tetrahydrofuran and 101·6 l. mole^{-1} in toluene. Beer's law plots of absorbance *versus* concentration of diazodiphenylmethane were strictly linear in the concentration range employed. A Unicam S.P. 500 spectrophotometer was used to measure the absorbance at various times and this technique has been used previously for studying reactions of diazodiphenylmethane.[6]

RESULTS

Hellerman and Newman [4] reported that treatment of mercuric chloride with diazodiphenylmethane in ether resulted in the evolution of nitrogen, and precipitation of a white amorphous solid which had the appropriate mercury content for chlorodiphenylmethylmercuric chloride (I) and which was excessively unstable in moist air. These observations were confirmed early in the present work but it was later found that the reaction could be more conveniently effected in dry tetrahydrofuran, a solvent in which the product (I) remained soluble. Consequently, tetrahydrofuran was used as solvent for all kinetic measurements.

It was also observed, however, that in tetrahydrofuran as solvent the reaction did not appear to be complete when a stoicheiometric equivalent of diazodiphenylmethane had been added to the mercuric chloride in solution, and appreciably more than one molar equivalent of diazo-compound was required before the reaction ceased. Moreover, if the reaction was carried out by adding mercuric chloride slowly to a solution of diazo-compound, the latter being kept always in excess, then very nearly two equivalents of diazo-compound reacted with one of mercuric chloride.

TABLE 1

Typical kinetic run in dry tetrahydrofuran

(Temp. = 25·0°. Initially: $[(C_6H_5)_2CN_2] = 0{\cdot}00754$M; $[HgCl_2] = 0{\cdot}03600$M.)

Time (sec.)	Optical density at 529 mμ	$10^3[(C_6H_5)_2CN_2]$ (M)	$10^3[HgCl_2]$ (M)	$10k_2$ (l. mole^{-1} sec.$^{-1}$)
0	0·703	7·54	36·00	
50	0·405	4·34	32·80	3·23
60	0·350	3·75	32·21	3·44
70	0·310	3·32	31·78	3·49
80	0·277	2·97	31·43	3·49
90	0·244	2·62	31·08	3·55
100	0·218	2·34	30·80	3·56
110	0·196	2·10	30·56	3·56
120	0·174	1·87	30·33	3·58
130	0·157	1·68	30·14	3·58
140	0·138	1·48	29·94	3·62
150	0·127	1·36	29·82	3·57
160	0·117	1·25	29·71	3·53
170	0·104	1·12	29·58	3·54
180	0·097	1·04	29·50	3·48
190	0·087	0·93	29·39	3·50
200	0·078	0·84	29·30	3·49
210	0·073	0·78	29·24	3·45
225	0·063	0·68	29·14	3·43
240	0·060	0·64	29·10	3·30
270	0·046	0·49	28·95	3·27
			Average:	3·48

The product of this latter reaction always precipitated even when tetrahydrofuran was used as solvent and the compound decomposed as soon as it was freed from a protective covering of solvent. Initially it was considered that compound (II) was a bis-organo-mercurial formed by alkylation of the second Hg–Cl linkage, *i.e.*, $Hg(CPh_2Cl)_2$; however although complete characterisation was not achieved it seems more probable (see later) that this compound was a 2-chloroethyl derivative of mercury, *i.e.*, (II).

In order to eliminate all possibility of formation of compound (II) during the kinetic measurements, the reactions were performed always with a molar ratio $[HgCl_2]/[Ph_2CN_2] \geqslant 4$.

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[6] D. Bethell and J. D. Callister, *J.*, 1963, 3801, 3808; C. K. Hancock and J. S. Westmorland, *J. Amer. Chem. Soc.*, 1958, **80**, 545.

Characterisation of both (I) and (II) was most conveniently effected by studying the products of the very easy hydrolysis—molar equivalents of water in tetrahydrofuran being sufficient to cause rapid decomposition. The hydrolysis of compound (I) could be represented by the equation:

$$\mathrm{ClHgCPh_2Cl + H_2O \longrightarrow Hg^0 + Ph_2C{=}O + 2HCl}$$

and the yield of benzophenone was always quantitative. However, when the reactions were performed using excess of mercuric chloride then the product was mercurous chloride, formed by the reaction

$$\mathrm{Hg^0 + HgCl_2 \longrightarrow 2HgCl}$$

Mercury was shown to be the primary product by performing the reaction in the presence of excess of lithium chloride which forms complexes with any free mercuric chloride and leaves the product mercury free to be isolated. Hydrolysis of compound (II) was even more rapid and could be represented thus:

$$\mathrm{ClHg{\cdot}CPh_2{\cdot}CPh_2Cl + H_2O \longrightarrow Hg^\circ + 2HCl + Ph{\cdot}CO{\cdot}CPh_3}$$

In this case the isolation of benzpinacolone rather than two moles of benzophenone provided clear evidence for the structure of (II). The kinetics and mechanism of these hydrolysis reactions form the basis for Part III of this series.[7]

Under the conditions prescribed the reaction between mercuric chloride and diazodiphenylmethane in dry tetrahydrofuran was uniformly bimolecular and proceeded to completion as evidenced by the quantitative isolation of the hydrolysis products described above.

The rate of reaction is given by $-\mathrm{d[Ph_2CN_2]}/\mathrm{d}t = -\mathrm{d[HgCl_2]}/\mathrm{d}t = k_2\mathrm{[Ph_2CN_2][HgCl_2]}$ and results from a typical kinetic run are given in Table 1. The second-order rate coefficient k_2 was independent of the ratio $\mathrm{[Ph_2CN_2]/[HgCl_2]}$ and representative values obtained at different temperatures are shown in Table 2.

TABLE 2

The reaction between $\mathrm{Ph_2CN_2}^a$ and $\mathrm{HgCl_2}^a$ in dry tetrahydrofuran

Temp. (°C)	$10k_2$ [b] (l. mole^{-1} sec.$^{-1}$)	$\Delta H^\ddagger$ (kcal. mole^{-1})	$\Delta S^\ddagger$ (e.u.)
4·8	0·847		
25·0	3·44	9·6	−18·5
35·0	5·38		

[a] Initially $\mathrm{[HgCl_2]/[Ph_2CN_2]} \geqslant 4$, with $\mathrm{[Ph_2CN_2]}$ normally in the range (3·0—10·0) × 10^{-3}M. [b] These values are the mean of several determinations at each temperature and reproducibility was better than 2%.

In order to determine whether the reaction involved polar or free radical intermediates, the effects of adding small amounts of water and acetonitrile (polar additives), and several free radical traps, are shown in Tables 3 and 4.

TABLE 3

Effect of polar additives on the reaction between $\mathrm{Ph_2CN_2}$ and $\mathrm{HgCl_2}$ in tetrahydrofuran

$10^3\mathrm{[Ph_2CN_2]}$ (M)	$10^2\mathrm{[HgCl_2]}$ (M)	Additive	[Additive] (M)	$10k_2$ (l. mole^{-1} sec.$^{-1}$)
9·0	3·71	None	0	0·860 [a]
9·0	3·71	MeCN	0·378	1·20 [a]
9·0	3·71	MeCN	0·764	1·56 [a]
9·0	3·71	MeCN	1·534	2·25 [a]
9·0	3·71	MeCN	2·285	2·94 [a]
8·5	3·73	None	0	0·899 [b]
8·5	3·73	$\mathrm{H_2O}$	0·109	0·953 [b]
8·5	3·73	$\mathrm{H_2O}$	0·500	1·21 [b]
8·5	3·73	$\mathrm{H_2O}$	1·020 [c]	1·55 [b]

[a] Temp. = 5·1°. [b] Temp. = 6·0°. [c] Increase in $\mathrm{[H_2O]}$ above this point caused too rapid solvolysis of the product (I).

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[7] Part III, A. Ledwith and L. Phillips, to be published.

TABLE 4

The effect of free-radical traps on the reaction between Ph_2CN_2 and $HgCl_2$ in dry tetrahydrofuran at 25·0°

$[Ph_2CN_2] = 4{\cdot}25 \times 10^{-3}$M, $[HgCl_2] = 2{\cdot}12 \times 10^{-2}$M.

Additive	[Additive] (M)	Weight (g.) of Hg_2Cl_2 obtained *
None	0	0·500 [a]
αα′-Diphenyl-β-picrylhydrazyl	0·05	0·499
Styrene	0·05	0·496
Benzophenone	0·05	0·500

* Upon subsequent hydrolysis of the product.

[a] Theoretical weight, 0·500 g.

Reaction between Mercuric Chloride and Diazodi(p-*methoxyphenyl*)*methane*.—This reaction was much faster than the corresponding reaction with the unsubstituted diazo-compound and could not be studied kinetically. In addition the reaction product was much less stable than compound (I).

Reaction between Diazodiphenylmethane and other Mercury Compounds.—Mercuric bromide reacted readily with diazodiphenylmethane and qualitative observations established that the reaction was at least three times faster than the reaction with $HgCl_2$. Quantitative measurements were not possible because of the rapid decomposition of the reaction product.

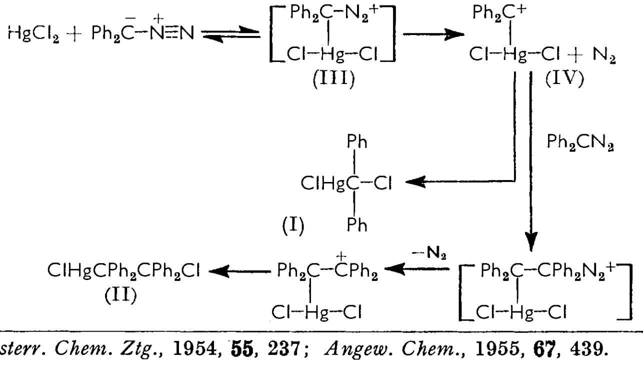
Significantly ethylmercuric chloride, chloromethylmercuric chloride and preformed chlorodiphenylmethylmercuric chloride (I) did not react with diazodiphenylmethane, whereas reaction occurred readily with diazomethane.

Effect of Solvent on the Reaction between $HgCl_2$ *and* Ph_2CN_2.—Although reaction between mercuric chloride and diazodiphenylmethane was very easy to demonstrate in almost any organic solvent, only in the case of ethers could the reaction product be isolated. Solvents such as dichloromethane, acetonitrile, and acetone caused immediate decomposition of compound (I).

DISCUSSION

Diphenyldiazomethane reacted readily with mercuric chloride to give chlorodiphenylmethylmercuric chloride (I). This material was extremely unstable thermally, and was immediately hydrolysed by traces of hydroxylic compounds to give a quantitative yield of benzophenone. Conventional free-radical traps had apparently no effect on the course of the reaction and it seems most likely that compound (I) is formed by a polar reaction path. Formation of (I) occurs *via* a reaction which is kinetically first-order in both diazodiphenylmethane and mercuric chloride. The rate-determining process must therefore involve either initial, rapid, pre-equilibrium between the two reactants followed by slow breakdown of the adduct, or a primary reaction between diazodiphenylmethane and mercuric chloride followed by rapid elimination of nitrogen and formation of compound (I). Although the latter path is favoured, the former alternative cannot be completely eliminated.

In view of the known tendency of mercuric halides to co-ordinate with nucleophiles it seems most likely that the reaction follows a mechanism such as that proposed initially by Huisgen,[2,8] *i.e.*,



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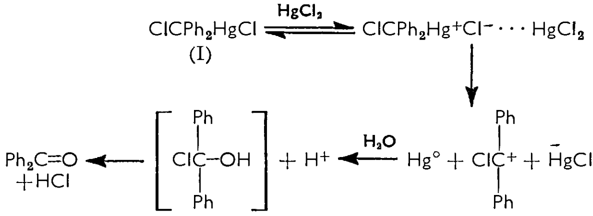
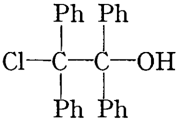
[8] R. Huisgen, *Österr. Chem. Ztg.*, 1954, **55**, 237; *Angew. Chem.*, 1955, **67**, 439.

Support for this reaction path was found by observing the effect of water and acetonitrile as additives (Table 3). Water has the greater ability to solvate ions and to promote ionisation. However, the data of Table 3 show that, while the rate coefficient increases linearly on addition of both water and acetonitrile, for a given molar concentration of additive the rate increase is higher for acetonitrile than for water. Dipolar aprotic solvents such as acetonitrile are more effective than typical protic solvents (ROH) in solvating highly polarised intermediates and transition states.[9] Consequently the relative efficiencies of acetonitrile and water in increasing the rate of reaction between diazodiphenylmethane and mercuric chloride are readily understood since the rate-determining process, leading to the dipolar intermediates (III) and (IV), most probably involves a highly polarised transition state similar to (III). The formation of such a transition state will be more favoured in the system containing acetonitrile.

Additional evidence for the mechanism suggested above is provided by the formation of compound (II). Thus although there was no significant reaction between diazodiphenylmethane and preformed compound (I), reaction between diazodiphenylmethane and mercuric chloride resulted, under optimum conditions, in the utilisation of 2 moles of diazo-compound for one of mercuric chloride. This result demonstrates that diazodiphenylmethane can react readily with an intermediate involved in the formation of compound (I). Presumably the dipolar intermediate (IV) is the reactant, as shown above. In this respect the present reaction differs markedly from the corresponding reaction between diazodiphenylmethane and zinc iodide, where the only products are benzophenoneazine and tetraphenylethylene.[10] Other factors in favour of the polar mechanisms are the increased rate observed upon changing from mercuric chloride to the more electrophilic bromide and the much bigger increase in rate when diazodiphenylmethane is replaced by the much more nucleophilic molecule di-(p-$MeOC_6H_4$)CN_2.

Several reaction paths are possible for the rapid hydrolysis of compounds (I) and (II) but detailed kinetic studies suggest[7] that in both cases the rate determining process involves mercury-chlorine fission, *i.e.*,



The analogous reaction for compound (II) leads to formation of a pinacol-type intermediate[11] such as  $Cl{-}C(Ph)_2{-}C(Ph)_2{-}OH$ which would rapidly solvolyse and rearrange to benzpinacolone under the reaction conditions.

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[9] A. J. Parker, *Quart. Rev.*, 1962, **16**, 163.
[10] D. E. Applequist and H. Babad, *J. Org. Chem.*, 1962, **27**, 288.
[11] C. J. Collins, *Quart. Rev.*, 1960, **14**, 357.