Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part IX.[1] Kinetics and Mechanism of the Decomposition of Diaryldiazomethanes catalysed by Zinc Halides [2]

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The kinetics and products of decomposition of diphenyldiazomethane, 9-diazofluorene, and of some of their substituted analogues induced by zinc chloride, bromide, and iodide in acetonitrile solution have been investigated.

With zinc chloride or bromide, diphenyldiazomethane yields after work-up a mixture of benzophenone and benzophenone azine, the proportions depending on the initial concentration of diazoalkane and the nature (but not the concentration) of the zinc halide. The kinetics and product proportions are consistent with rate-limiting formation of a dipolar diphenylmethylene–zinc halide complex, $Ph_2\overset{+}{C},\overset{-}{Zn}X_2$. This intermediate reacts with a further diazoalkane molecule yielding the azine and zinc halide or gives rise to ketone, plausibly by way of an α-halogenoalkylzinc halide formed by rearrangement.

The principal products from reaction of diazofluorene are fluorenone, fluorenone azine, and 9,9'-bifluorenylidene. The proportions of products are affected by the presence of oxygen as well as by the factors mentioned for diphenyldiazomethane. The kinetic form of the reaction is similar to that for diphenyldiazomethane but under given conditions, diazofluorene reacts 5—10 times more slowly.

When zinc iodide is used, the products isolated from reactions of both diazo-compounds are qualitatively the same as those found using the other zinc halides. However, kinetic experiments show that the reactions take place in two phases, one fast and one slow. Comparison of the results with those from the reaction of 9-iodofluoren-9-ylzinc iodide (prepared from 9,9-di-iodofluorene and zinc–copper couple) with diazofluorene suggest that the organometallic reagent is one product of the fast step in the diazofluorene–zinc iodide reaction and that its reaction with unchanged diazofluorene is the second, slower phase.

Quantitative aspects of the reactivities of the zinc halides and of the diazoalkanes are discussed.

UNLIKE their decomposition in the presence of Brønsted acids,[3] the reaction of diazoalkanes with Lewis acids has not received detailed kinetic and mechanistic study. On the other hand, the reaction between electrophilic metal halides and diazoalkanes has long been recognised as a convenient synthetic route to α-halogenoalkyl metal compounds,[4] a class of compound which can show carbenoid reactions, usually towards olefins, but which in certain instances can act as sources of the carbenes themselves.[5]

In this paper we describe in detail [2] an investigation of the kinetics and mechanism of the reaction of diaryldiazomethanes with zinc chloride, bromide, and iodide. These metal halides were chosen for our first venture in this area of diazoalkane chemistry principally because the results should be relevant to the chemistry of the Simmons–Smith reaction, in which olefins are converted into cyclopropanes by treatment with methylene iodide and zinc–copper couple.[6] The reactive intermediate, formulated as ICH_2ZnI [in equilibrium with $(ICH_2)_2Zn,ZnI_2$], reacts directly with the olefin in the rate-limiting step of the reaction.[7] Bis(halogenomethyl)zinc compounds can also be obtained by reaction of diazomethane with zinc halides and these too are capable of the methylene transfer reaction.[8] By using the relatively stable aliphatic diazo-compounds diphenyldiazomethane, 9-diazofluorene, and some of their substituted analogues, and by studying the kinetics of their decomposition in the presence of zinc halides, we hoped to learn more about the mechanism of formation of the α-halogenoalkylzinc intermediates and to confirm the identity of the product with that from the conventional Simmons–Smith procedure, *i.e.*, the reaction of a *gem*-di-iodide with zinc–copper couple.

RESULTS

Products.—Diphenyldiazomethane. The decomposition of diphenyldiazomethane in acetonitrile solutions of zinc halides in air produces, after hydrolytic work-up, mixtures of benzophenone azine and benzophenone together with small amounts of an unidentified material which appears to be polymeric. The proportions of ketone and azine were estimated spectrophotometrically and are given in Table 1. They were unaffected when a reaction was carried out under nitrogen or when the concentration of the zinc halide was changed (Table 1). However, changing the halogen causes a decrease in the proportion of azine in the sequence Cl > Br > I. The fraction of azine in the product also decreases as the initial concentration of diazo-compound is reduced. The last observation is consistent with partitioning of an intermediate between two reaction pathways, only one of which shows a kinetic dependence on the concentration of diazoalkane, namely, that leading to azine [equation (1)]. If r represents k_2/k_3, then it can be shown [9] that the

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[1] Part VIII, D. Bethell, A. R. Newall, and D. Whittaker, *J. Chem. Soc.* (*B*), 1971, 23.

[2] Preliminary account, D. Bethell and K. C. Brown, *Chem. Comm.*, 1967, 1266.

[3] For a review, see R. A. More O'Ferrall, *Adv. Phys. Org. Chem.*, 1967, **5**, 331.

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

[5] W. Kirmse, 'Carbene, Carbenoide und Carbenanaloge,' Verlag Chemie, Weinheim, 1969, ch. 5.

[6] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 1958, **80**, 5323; 1959, **81**, 4256; H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, 1964, **86**, 1347.

[7] E. P. Blanchard and R. D. Smith, *J. Amer. Chem. Soc.*, 1964, **86**, 1337.

[8] G. Wittig and K. Schwarzenbach, *Angew. Chem.*, 1958, **71**, 652; *Annalen*, 1961, **650**, 1; G. Wittig and F. Wingler, *ibid.*, 1962, **656**, 18; *Chem. Ber.*, 1964, **97**, 2146; H. Hoberg, *Annalen*, 1962, **656**, 15; S. H. Goh, L. E. Closs, and G. L. Closs, *J. Org. Chem.*, 1969, **34**, 25.

[9] D. Bethell and J. D. Callister, *J. Chem. Soc.*, 1963, 3801.

concentration of azine at the end of the reaction is given by equation (2). Values of r derived from the yields of azine in this way are in Table 1. The high sensitivity of r to small changes in the azine yield being borne in mind [*cf.* the first three entries in Table 1(*b*)], r is roughly constant for a given halide over the range of diazoalkane concentrations examined.

TABLE 1

Effect of initial reactant concentration on product proportions in the decomposition of diphenyldiazomethane catalysed by zinc halides in acetonitrile at 30 °C

$10^3[Ph_2CN_2]_0$/M	$10^3[ZnX_2]_0$/M	Products (%)[a]		
		$Ph_2C{:}N{\cdot}N{:}CPh_2$	$Ph_2C{:}O$	r
(*a*) X = Cl				
6·72	6·80	72 (74)[b]	23 (22)[b]	510
6·83	0·68	72	22	530
8·04	6·80	71		450
8·51	0·68	73	18	580
16·1	6·80	78		390
42·5	0·68	93	6	670
42·5	1·98	90	10	450
				Av. 510 ± 90
(*b*) X = Br				
7·35	4·20	65	25	360
7·35	6·30	71	25	500
7·35	10·1	72	25	520
7·66	2·10	59	17	250
22·4	2·27	80	13	300
38·1	2·10	79	6	160
				Av. 350 ± 140
(*c*) X = I				
7·40	4·93	29		60

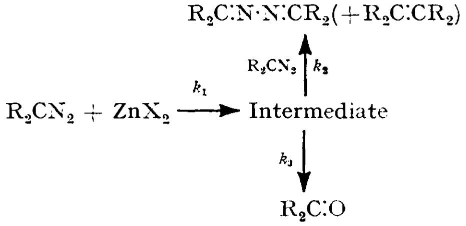
[a] In all Tables, percentage yields refer to percentage of $[Ph_2CN_2]_0$ converted into that product. [b] Reaction carried out in nitrogen atmosphere: all other results refer to reactions in air.

TABLE 2

Effect of initial reactant concentration on product proportions in the decomposition of 9-diazofluorene catalysed by zinc halides in acetonitrile at 30 °C under nitrogen (Fl = fluorenylidene)

$10^3[FlN_2]_0$/M	$10^2[ZnX_2]$/M	Products (%)		
		Fl:Fl	Fl:N·N:Fl	Fl:O
a) X = Cl				
43·2	1·22	32·2	19·0	11·5
26·9	1·22	32·0	17·5	20·8
26·9	0·24	17·6	15·8	27·4
5·4	1·22	10·0	10·9	18·6
(*b*) X = Br				
42·1	1·11	49·5	22·5	9·2
42·1	1·11	35[a]	24[a]	
42·1	1·11	25[b]	24[b]	
24·0	1·11	40·5	21·3	10·6
5·98	1·11	27·8	14·3	11·3
4·80	1·11	23·3	12·0	9·6
2·96	1·11	15·5	11·3	10·2
1·48	1·11	5·5	8·2	13·1
0·74	1·11	5·7	6·4	14·9
(*c*) X = I				
40·6	1·23	17·2	6·5	48
18·5	1·23	10·4	9·1	61
13·2	1·64	4·4	5·6	47
9·2	0·18	<1	4·9	45

[a] Reaction carried out in air. [b] Reaction carried out in pure oxygen atmosphere.



$$\begin{tikzcd} & R_2C{:}N{\cdot}N{:}CR_2(+R_2C{:}CR_2) \\ R_2CN_2 + ZnX_2 \arrow[r, "k_1"] & \text{Intermediate} \arrow[u, "R_2CN_2"', "k_2"] \arrow[d, "k_3"'] \\ & R_2C{:}O \end{tikzcd} \qquad (1)$$

$$[Ph_2C{:}N{\cdot}N{:}CPh_2] = \tfrac{1}{2}\{[Ph_2CN_2]_0 - 1/2r \,.\, \ln\,(2r[Ph_2CN_2]_0 + 1)\} \qquad (2)$$

9-*Diazofluorene*. The major products from the decomposition of diazofluorene induced by zinc halides in acetonitrile under nitrogen are 9,9′-bifluorenylidene and fluorenone and its azine, together with small amounts of fluorenol and 9,9-dihalogenofluorenes. The remainder of the initial concentration of diazofluorene is accounted for by an unidentified material which appears to be polymeric. Analysis of the major components was carried out by quantitative t.l.c. on silica and the results are in Table 2. The yields of fluorenone recorded incorporate the yields of 9-fluorenol and 9-halogenofluorenes which are converted into the ketone before development. The yield of ' dimeric ' products, bifluorenylidene and fluorenone azine, are greatest for the highest initial concentrations of diazofluorene in a fashion analogous to the reaction of diphenyldiazomethane. However, the olefin : azine ratios varies from *ca.* 2 at high initial diazoalkane concentration to less than unity at low concentrations. Plainly the dimeric products are not formed by competing modes of attack of a single intermediate on the diazo-carbon or on the terminal nitrogen atom of unchanged diazofluorene. This is confirmed by the fact that in air or oxygen the bifluorenylidene yield, but not the yield of azine, is reduced. The azines are produced more readily by zinc bromide than zinc chloride, the iodide being the least effective in this respect as for diphenyldiazomethane.

Kinetics.—Catalysts by zinc chloride and bromide. Rates of disappearance of diazo-compounds were followed spectrophotometrically at the wavelength of their maximum absorption in the visible region or in the i.r. region at *ca.* 2060 cm^{-1}.

The decomposition of diphenyldiazomethane in acetonitrile solution containing a large excess of zinc bromide or chloride obeyed a first-order kinetic law over the first 75% reaction. During the third half-life some deviation from this simple behaviour was observed, instantaneous rate coefficients decreasing progressively with time. This is to be expected if the diazoalkane is removed both in the primary reaction with zinc halide and in a subsequent reaction with a reactive intermediate giving benzophenone azine [equation (1)]. As previously shown,[10] this leads to the kinetic equation (3), where r is the reactivity ratio obtained from the product analyses. By use of the r-value appropriate

$$\ln\left\{\frac{[Ph_2CN_2]}{[Ph_2CN_2]_0}\left(\frac{2r[Ph_2CN_2]_0 + 1}{2r[Ph_2CN_2] + 1}\right)^{\frac{1}{2}}\right\} = k_1't = k_1[ZnX_2]t \qquad (3)$$

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[10] D. Bethell, D. Whittaker, and J. D. Callister, *J. Chem. Soc.*, 1965, 2466.

to the zinc halide concentration and equation (3), values of the pseudo-first-order rate coefficient for the reaction of diphenyldiazomethane with zinc halide ($k_1' = k_1[ZnX_2]$) can be derived. Instantaneous values of k'_1 remained constant for up to five half-lives, although at very low initial concentration of zinc halide some decrease was found in the late stages of reaction, indicating perhaps appreciable consumption of the catalyst.

TABLE 3

Rate coefficients for the disappearance of diphenyldiazomethane in acetonitrile solutions of zinc halides at 30 °C

$[Ph_2CN_2]_0$ = *ca.* 0·01M

$10^3[ZnCl_2]/(M)$	0·68	1·98	6·80	25
k_{obs}/min^{-1}	0·021	0·066	0·204	0·272 *
k_1'/min^{-1}	0·011	0·033	0·12	
$10^3[ZnBr_2]/(M)$	0·21	2·10	2·27	4·20
k_{obs}/min^{-1}	0·012	0·128	0·147	0·220
k_1'/min^{-1}		0·084	0·081	0·14
$10^3[ZnBr_2]/(M)$	4·40	6·30	20·2	33·7
k_{obs}/min^{-1}	0·272	0·320	0·310 *	0·47 *
k_1'/min^{-1}		0·195		
$10^3[ZnI_2]/(M)$	0·99	4·92		
k^f_{obs}/min^{-1}	1·0	>1·0		
k^s_{obs}/min^{-1}	0·03	0·16		

* 4,4′-Dichlorodiphenyldiazomethane: reaction followed spectrophotometrically at 515 nm.

Kinetic data for the decomposition of diphenyldiazomethane are summarised in Table 3. Values of k_{obs} are rate coefficients obtained graphically from the initial linear portion of plots of log ($D_t - D_\infty$) against t. These and the derived k_1' values are proportional to the zinc halide concentration. Average values for the derived second-order velocity constants are 16·8 l mol^{-1} min^{-1} for zinc chloride and 35·0 l mol^{-1} min^{-1} for zinc bromide. The effect of having a *p*-chloro-substituent in the two aromatic rings of the diazo-compound is to reduce $k_{obs}/[ZnX_2]$ by factors of 2·9 (zinc chloride) and 4·0 (zinc bromide). Translated into the parameters of the Hammett equation, these figures would correspond to ρ-values of *ca.* −1·0 for zinc chloride and *ca.* −1·3 for zinc bromide.

TABLE 5

Effect of 2-substituents on the rate coefficients for disappearance of 9-diazofluorene in acetonitrile solutions of zinc halides at 30 °C

$[FlN_2]_0$ = 0·013−0·030M

Substituent	$10^2[ZnCl_2]/M$	$\frac{10^2k_{obs}}{min^{-1}}$	$10^2[ZnBr]_2/M$	$\frac{10^2k_{obs}}{min^{-1}}$	$\frac{k_{obs}/[ZnX_2]}{l\ mol^{-1}\ s^{-1}}$ ZnCl$_2$	$\frac{k_{obs}/[ZnX_2]}{l\ mol^{-1}\ s^{-1}}$ ZnBr$_2$
Br	12·2	4·65	3·37	2·02	0·38	0·60
	4·90	1·87	1·35	0·80		
CN	12·2	1·12	3·37	0·52	0·091	0·154
	4·90	0·44	1·68	0·26		
Et	2·45	9·6	1·35	10·8	3·9	8·1
	1·22	4·8	0·67	5·4		
OMe	4·90	9·37	1·35	6·07	1·95	4·5
	2·45	4·87	0·67	3·04		
H					2·4 [a]	3·9 [a]

[a] From Table 4.

The kinetic form of the decomposition of 9-diazofluorene induced by zinc chloride and bromide is similar to that of diphenyldiazomethane. Results are in Table 4. The presence of oxygen in the system did not affect the reaction rate. Since, for reasons given above, the formation of azines is thought to be a more complex process than in the reaction of diphenyldiazomethane, values of k_1 could not be derived for diazofluorene by use of equation (3). However, provided that the initial concentration of diazofluorene in the kinetic experiments is small and yields of bifluorenylidene and fluorenone azine low, values of k_{obs} should be fair approximations to k_1'. On this basis, diphenyldiazomethane is more reactive than diazofluorene by a factor of 7 when the catalyst is zinc chloride and by a factor of 9 for zinc bromide catalysis.

TABLE 4

Rate coefficients for the disappearance of 9-diazofluorene in acetonitrile solutions of zinc halides at 30 °C [a]

$10^2[FlN_2]/M$	2·69	2·40	2·69	
$10^2[ZnCl_2]/M$	2·45	1·47	0·49	
$10^2k_{obs}/min^{-1}$	5·90	3·50	1·13	
$10^2[FlN_2]/M$	0·0016	0·041	2·02	2·69
$10^2[ZnBr_2]/M$	1·42	1·13	1·11	0·34
$10^2k_{obs}/min^{-1}$	5·55 [b]	4·40 [b]	4·34	1·41 [c]
$10^2[FlN_2]/M$	0·014	2·02		
$10^2[ZnBr_2]/M$	0·22	0·22		
$10^2k_{obs}/min^{-1}$	0·82 [b]	0·79		
$10^2[FlN_2]/M$	2·71	2·71	0·007	0·007
$10^2[ZnI_2]/M$	1·23	0·49	0·20	0·10
$10^2k^f_{obs}/min^{-1}$	>60	90	39 [d]	20 [d]
$10^2k^s_{obs}/min^{-1}$	*ca.* 14	4·0		

[a] Disappearance of diazofluorene followed by i.r. spectroscopy unless specified otherwise. [b] Reactions followed spectrophotometrically in the visible region. [c] Reaction under nitrogen. [d] Reactions followed by the appearance of a peak at 360 nm.

The effect on the reactivity of diazofluorene of introducing a variety of substituents into the 2-position is shown in Table 5. The rate of both the zinc chloride and the zinc bromide-catalysed reactions is increased by electron-repelling substituents. Correlations of the results by the Hammett equation by use of σ_m-values for the substituents gives ρ-values of −2·45 (correlation coefficient 0·982) for zinc chloride catalysis and −2·49 (correlation coefficient 0·989) for zinc bromide catalysis. This is to be compared with a ρ-value of −1·6 for proton transfer to 2-substituted diazofluorenes in aqueous ethanol.[11] For a given substituted diazofluorene, zinc bromide is 1·5—2·3 times more efficient than zinc chloride in bringing about decomposition. The corresponding value for diphenyldiazomethane is 2·1.

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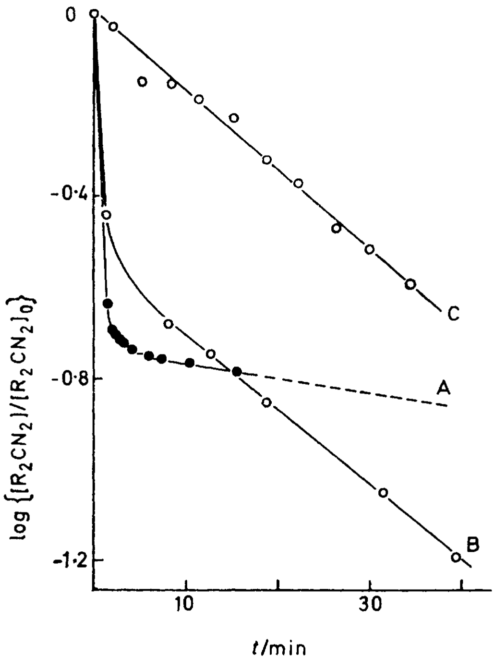
[11] K. D. Warren, *J. Chem. Soc.*, 1963, 598.

Catalysis by zinc iodide. The decomposition of both diphenyldiazomethane and diazofluorene shows a quite different kinetic form when zinc iodide is used instead of the chloride or bromide as the catalyst. A very rapid initial reaction consumes some 75% of the diazoalkane whereafter a much slower disappearance of the remainder ensues. This is illustrated in the Figure. Values of observed pseudo-first-order rate coefficients for the two stages of reaction, symbolised as k^f_{obs} and k^s_{obs} are given in Tables 3 and 4. Because of the rapidity of the first stage, some values of k^f_{obs} are recorded as minimum values and this prevents the establishment of the dependence of k^f_{obs} on the initial concentration of zinc iodide. (See, however, below.) However, the value of k^s_{obs} appears to be approximately proportional to the initial catalyst concentration.



First-order kinetic plots for the decomposition of diazoalkanes induced by zinc iodide and by 9-iodofluoren-9-yl zinc iodide in acetonitrile solution at 30 °C: A, $[Ph_2CN_2]_0$, $7{\cdot}5 \times 10^{-3}$M; $[ZnI_2]_0$, $1{\cdot}0 \times 10^{-5}$M; B, $[FlN_2]_0$, $2{\cdot}7 \times 10^{-2}$M; $[ZnI_2]_0$, $5{\cdot}0 \times 10^{-3}$M; C, $[FlN_2]_0$, $1{\cdot}8 \times 10^{-2}$M; $[IFlZnI]_0$, $5{\cdot}1 \times 10^{-3}$M (Fl = fluorenylidene)

During the decomposition of diazofluorenes promoted by zinc iodide, repetitive scanning of the u.v.-visible spectrum of reaction solutions showed the appearance of an absorption peak having $\lambda_{max.}$ 360 nm. This absorption increased as the diazoalkane decomposed and was quite stable after completion of the reaction. Dilution of the reaction solution with ethanol or chromatography led to decomposition of the species responsible for the absorption and only bifluorenylidene, fluorenone, and fluorenone azine could be isolated. With reaction solutions in which the concentration of zinc iodide was much larger than that of diazofluorenes, the appearance of the absorption at 360 nm followed a first-order kinetic law with a rate coefficient proportional to the zinc iodide concentration and corresponding, in magnitude, to that of the fast stage of the diazoalkane decomposition (Table 4).

We believe that the new aborption is due to the formation of 9,9′-di-iodo-9,9′-bifluorenyl for the following reasons. (i) A similar absorption at 360 nm is observed when an acetonitrile solution of 9,9-di-iodofluorene is allowed either to decompose in daylight or, better, to react with an equimolar amount of diazofluorene. (ii) None of the isolable products of any of the reactions nor iodine have absorption maxima at 360 nm. (iii) Treatment of 9,9′-dibromo-9,9′-bifluorenyl with potassium iodide in acetone yielded an unstable iodine-containing solid. A freshly prepared sample dissolved in ethanol had its long wavelength absorption maximum at 360 nm (ε *ca.* 400, a molecular formula $C_{26}H_{16}I_2$ being assumed). The solid decomposed quantitatively to bifluorenylidene on attempted chromatography on alumina; 9,9′-dibromo-9,9′-bifluorenyl can be chromatographed unchanged.

Reactions of 9-*Iodofluoren*-9-*ylzinc Iodide*.—To elucidate further the mechanism of the zinc iodide-promoted decomposition of diazofluorene, 9-iodofluoren-9-ylzinc iodide was prepared by treatment of 9,9′-di-iodofluorene with zinc–copper couple in acetonitrile. Aliquot portions of the filtered solution, which were contaminated with a little bifluorenylidene, gave only fluorenone on hydrolysis. Addition of an aliquot portion to a solution of diazofluorene in acetonitrile led to a smooth decomposition of the diazoalkane. Quantitative t.l.c. analysis of the product mixture showed that the diazoalkane had been converted into fluorenone (63%), bifluorenylidene (31%), and fluorenone azine (7%). When the reaction was carried out under oxygen-free nitrogen the same products were formed to the extent of 31, 60, and 10% respectively.

The rate of decomposition of diazofluorene brought about by the organometallic reagent was measured by use of the i.r. technique (Figure, line C). Results are in Table 6. The reaction is catalytic, since the diazoalkane, initially in substantial excess, is completely decomposed. The disappearance of the diazoalkane fits the kinetic equation $v = k_{obs}[FlN_2] = k[FlN_2][IFlZnI]$ (Fl = fluorenylidene) with a mean value of k of 8·1 l mol^{-1} min^{-1}. This may be compared with the average value of $k^s_{obs}/[ZnI_2]$ for the slow phase of the zinc iodide-promoted decomposition of diazofluorene of 9·7 l mol^{-1} min^{-1}. Bearing in mind the experimental uncertainty, particularly as regards the concentration of 9-iodofluoren-9-ylzinc iodide, we believe that this similarity in rate coefficients, clearly demonstrated in the Figure (lines B and C), indicates that the same chemical process is being observed in both sets of experiments.

TABLE 6

Rate coefficients for the disappearance of 9-diazofluorene induced by iodofluorenylzinc iodide at 30 °C

$10^2[FlN_2]$/M	1·84	2·30	1·02 [a]
$10^2[IFlZnI]$/M	0·51	0·072	0·013
10^2k_{obs}/min^{-1}	4·0	0·61	48

[a] Diphenyldiazomethane: reaction followed spectrophotometrically at 526 nm.

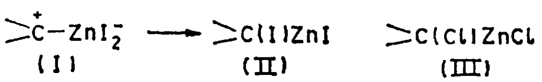
9-Iodofluoren-9-ylzinc iodide also induces the decomposition of diphenyldiazomethane. A first-order dependence of k_{obs} on [IFlZnI] being assumed, as in the case of diazofluorene, k is $3{\cdot}7 \times 10^3$ l mol^{-1} min^{-1}, some 400 times greater than for diazofluorene. The value of $k^s_{obs}/[ZnI_2]$ for diphenyldiazomethane is $3{\cdot}1 \times 10^3$ l mol^{-1} min^{-1}.

Cyclopropane formation was not observed when acenaphthylene and cyclohexene were treated with 9-iodofluoren-9-ylzinc iodide. Irradiation of the organometallic reagent, prepared in ether and added to a large excess of cyclohexene, with light from a tungsten lamp gave mainly bifluorenylidene together with a trace of fluorenone and a little fluorene, identified by its mass spectrum and ^{1}H n.m.r. spectrum.

DISCUSSION

In attempting to interpret our findings we shall make the simplifying assumption that the decomposition of diphenyldiazomethane and of diazofluorene take place by essentially the same mechanism. We justify this assumption by pointing to the similarities in kinetic form, effect of substituents, relative reactivity of catalysts, and dependence of product proportions on reactant concentration. For both diazoalkanes we envisage a reaction scheme similar to that of equation (1). In this scheme, the rate-limiting step is the reaction of a diazoalkane molecule with a molecule of catalyst to give a reactive intermediate. This species can react rapidly with a further diazoalkane molecule, giving the corresponding azine or dimeric olefin, or can react in other ways not involving a further diazoalkane molecule yielding eventually the related ketone. The discussion is focused on three inter-related aspects of this reaction scheme: (i) the constitution and structure of the partitioned intermediate; (ii) the nature of the competing reactions of the intermediates; and (iii) the mechanism of formation of the intermediate.

In the reaction of zinc iodide with the two diazoalkanes, the kinetic form of the reaction suggests that, in the course of the decomposition, the catalyst initially present is progressively converted into another species of much lower catalytic activity. Moreover, the experiments with 9-iodofluorophen-9-ylzinc iodide suggest very strongly that this organozinc halide is indeed the less active catalyst. Since 9-iodofluoren-9-ylzinc iodide is formed from zinc iodide during a period when a much larger concentration of the diazoalkane is being consumed, it follows that the organometallic species is produced in a process competing with some other route for the consumption of the diazo-compound. It seems probable therefore that formation of 9-iodofluoren-9-ylzinc iodide represents the (unimolecular) reaction of the partitioned intermediate which competes with attack on a further molecule of diazoalkane. A plausible formulation of this process would then be (I) ⟶ (II),

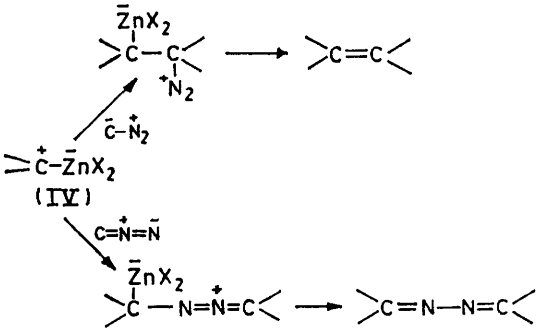


$$>\overset{+}{C}{-}ZnI_2^- \longrightarrow >C(I)ZnI \qquad >C(Cl)ZnCl$$

(I) (II) (III)

and an analogous rearrangement would occur in reactions catalysed by zinc chloride and bromide, the ease of rearrangement decreasing in the sequence I > Br > Cl. However, the fate of structure (III) and its bromo-analogue is not clear: a slow phase in the zinc chloride- and zinc bromide-catalysed reactions is not detectable, and the deviation of the observed kinetics from simple first-order behaviour is smaller than expected on the basis that these organometallic reagents are stable under the reaction conditions and thus effectively inactivate catalyst. It is possible that, rather than attack further diazoalkane, these organozinc halides are oxidised by traces of oxygen (present in the acetonitrile even after deoxygenation) or hydrolysed by traces of water.[12] In either case the zinc must reappear in a form capable of further catalytic action and the organic product on work-up and analysis must be the ketone. Small amounts of 9-bromofluorene and 9,9-dibromofluorene together with fluorenol can be detected by careful analysis of the products of reaction of diazofluorene and zinc bromide: under the normal analytical conditions these appear as fluorenone. Presumably the same sorts of product are formed from diphenyldiazomethane and all, as well as the 9,9′-di-iodo-9,9′-bifluorenyl, find their analogies in the by-products reported in reactions of the Simmons–Smith reagent, iodomethylzinc iodide.[7]

The dimeric products, benzophenone azine from diphenyldiazomethane, and bifluorenylidene and fluorenone azine from diazofluorene are typical of reactions of electrophiles derived from the diazoalkane on unchanged reactant.[1,9,10] This is consistent with the formulation of the partitioned intermediates in the zinc halide reactions as a dipolar species (IV). Reaction at the diazo-carbon atom yields the olefin [equation (4a)] while attack on the terminal nitrogen atom gives the azine [equation (4b)]. In both cases, the zinc halide is regenerated. That azines are more important dimeric products in these reactions of the two diazoalkanes than in Brønsted acid-catalysed reactions may indicate that a more polarisable electrophile is involved in the zinc halide reactions. In this respect the intermediate in the zinc halide reactions resembles the corresponding carbene. Indeed, our formulation of the partitioned intermediate could be termed a zinc–carbene complex, but we do not believe that free carbenes are involved in the present reactions. Some bifluorenylidene may arise by elimination from dimeric halides or dihalides, *e.g.*, 9,9′-di-iodo-9,9′-bifluorenyl, produced by reactions of the intermediate XFl,ZnX with other fluorenyl compounds. Since oxidation of the organometallic intermediate will



(4a)

(4b)

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[12] See, for example, G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' vol. 1, Methuen, London, 3rd edn., 1967.

compete with its other reactions, the decrease in bifluorenylidene yield when oxygen is present is not unexpected.

The kinetic results refer principally to the first step of the reaction leading to the formation of the partitioned intermediate. In bringing about this reaction in acetonitrile solution the order of effectiveness of the zinc halides appears to be $ZnCl_2 < ZnBr_2 \ll ZnI_2$. Somewhat similar sequences of catalytic activity have been described in the racemisation of α-phenylethyl chloride in acetone[13] and in the acetylation of toluene.[14] On the other hand, equilibrium constants for adduct formation with aniline-type indicators seem to vary markedly with solvent, reported sequences of Lewis acidity being $ZnBr_2 > ZnI_2 > ZnCl_2$ (acetone)[15] and $ZnCl_2 \sim ZnBr_2 > ZnI_2$ (ether).[16] Our own equilibrium sequence with use of dibenz[*a,j*]acridine as the indicator suggests that the 1 : 1 complex is formed in acetonitrile with decreasing facility in the order $ZnBr_2 > ZnI_2 > ZnCl_2$ (see Experimental section). Possible causes of such differences between equilibrium and kinetically derived activity sequences have been discussed previously.[15] In the present context the order of catalytic activity seems to us to suggest that the rate-limiting process is co-ordination of the diazoalkane, through the diazo-carbon atom, to zinc $[R_2CN_2 + ZnX_2 \longrightarrow R_2C(N_2^+)\bar{Z}nX_2]$, loss of nitrogen then occurring in a rapid subsequent step giving the partitioned intermediate $R_2\overset{+}{C},\overset{-}{Z}nX_2$. We support our belief in the following way.

The relative reactivity of diphenyldiazomethane and diazofluorene under given conditions of catalyst and concentration is too small to be consistent with the generation of a discrete charge on the central carbon atom. Table 7 lists values of ratios of rate and equilibrium constants for diphenylmethyl and fluorenyl compounds in a variety of reactions. While recognising that several factors determine the magnitude of the rate ratio, we see that diphenylmethyl compounds are more reactive than fluorenyl when the central carbon atom acquires positive charge during the reaction, the reverse being the case when negative charge is developed. Moreover, the greater the charge development the more the ratio differs from unity. In the present instance, the rather small reactivity ratio, *ca.* 10, for the zinc chloride and bromide reactions, suggests electrophilic attack on the diazo-compound and a low degree of charge development on the diazo-carbon atom in the transition state. The value is in fact close to that observed in general (Brønsted) acid-catalysed decomposition where proton transfer to the diazo-carbon atom is rate limiting, *i.e.*, charge development occurs on an adjacent atom.

TABLE 7

Ratios of rate and equilibrium constants for reactions of diphenylmethyl (Dp) and fluorenyl compounds

Derivative	Reaction	Solvent	T/°C	k_{Dp}/k_{Fl}	Ref.
$R_2C(OH)Ph$	$R_2\overset{+}{C}Ph$ formation	H_2O/H^+	25	$10^{4\cdot2}$	*b*
R_2CHBr	Solvolysis	MeOH	50	7010	*c*
	Solvolysis	EtOH	50	3570	*c*
R_2CHCl	Solvolysis	MeOH	50	1600	*c*
R_2CHOTs	Solvolysis	90% aq. THF[a]	0	1500	*d*
R_2CN_2	Benzoate ester formation	MeCN	30	~300	*e*
	Thermolysis	MeCN	110	~25	*e*
	Acid-catalysed solvolysis	93·8% aq. EtOH	25	12	*f*
	$ZnBr_2$-induced decomp.	MeCN	30	9	This work
	$ZnCl_2$-induced decomp.	MeCN	30	7	This work
$R_2C{:}O$	Protonation	H_2O/H^+	25	0·32	*g*
	Reduction by $NaBH_4$	Pr^iOH	25	0·17	*h*
	Oxime formation	70% aq. MeOH	50	0·06	*i*
R_2CH_2	H-isotope exchange	ND_3	120	$3\cdot5 \times 10^{-7}$	*j*
	R_2CH^--formation	Cyclohexylamine		$10^{-11\cdot2}$	*k*
R_2CHPh	$R_2\bar{C}Ph$-formation	Cyclohexylamine		10^{-14}	*k*

[a] THF = Tetrahydrofuran; Ts = toluene-*p*-sulphonyl. [b] D. Bethell and V. Gold, ' Carbonium Ions, An Introduction,' Academic Press, London and New York, 1967, ch. 4. [c] R. Bolton, N. B. Chapman, and J. Shorter, *J. Chem. Soc.*, 1964, 1895. [d] A. Ledwith and D. G. Morris, *J. Chem. Soc.*, 1964, 508, and personal communication. [e] K. C. Brown, unpublished observations. [f] K. D. Warren, *J. Chem. Soc.*, 1961, 2561. [g] R. Stewart, M. R. Granger, R. B. Moodie, and L. J. Muenster, *Canad. J. Chem.*, 1963, **41**, 1065. [h] H. C. Brown, O. H. Wheeler, and K. Ichikawa, *Tetrahedron*, 1957, **1**, 214; G. G. Smith and R. P. Bayer, *ibid.*, 1962, **18**, 323; J. A. Parry and K. D. Warren, *J. Chem. Soc.*, 1965, 4049. [i] J. D. Dickinson and C. Eaborn, *J. Chem. Soc.*, 1959, 3641. [j] A. I. Shatenshtein, *Adv. Phys. Org. Chem.*, 1963, **1**, 155. [k] A. Streitwieser, J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Amer. Chem. Soc.*, 1965, **87**, 384.

EXPERIMENTAL

Materials.—Acetonitrile was purified as described.[9] Diazoalkanes were prepared by mercuric oxide oxidation of the corresponding hydrazones. 9-Diazofluorene and 2-substituted analogues were prepared by methods and had physical properties identical with those reported by Warren.[17] 2-*Ethyl*-9-*diazofluorene*, prepared from 2-*ethylfluorenone hydrazone* [m.p. 123° (Found: C, 81·1; H, 6·4. $C_{15}H_{14}N_2$ requires C, 81·3; H, 6·5%] had m.p. 68—69° (Found: C, 81·2; H, 5·3. $C_{15}H_{12}N_2$ requires C, 81·8; H, 5·5%).

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[13] R. S. Satchell, *J. Chem. Soc.*, 1964, 5464.

[14] G. A. Olah, in ' Friedel–Crafts and Related Reactions,' ed. G. A. Olah, vol. I, Interscience, New York, 1963, p. 861.

[15] D. P. N. Satchell and R. S. Satchell, *Trans. Faraday Soc.*, 1965, **61**, 1118.

[16] D. P. N. Satchell and J. L. Wardell, *J. Chem. Soc.*, 1964, 4296.

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Zinc halides. Sticks of commercial anhydrous zinc chloride from a freshly opened container were used without treatment. Zinc bromide was sublimed at 380° and 0·07 mmHg. Zinc iodide was heated at 180 °C for 2 h to remove water and free iodine, residual traces of which were washed out with acetonitrile. Stock saturated solutions of the zinc halides in acetonitrile were prepared and concentrations determined by adding aliquot portions to excess of standard aqueous silver nitrate with back titration with potassium thiocyanate. The stock solutions had the following concentrations: $ZnCl_2$, 0·245M; $ZnBr_2$, 0·067M; ZnI_2, 0·049M. The zinc iodide solution was stable for long periods provided that it was stored in the dark.

9-*Iodofluoren*-9-*ylzinc iodide.* 9,9-Di-iodofluorene (0·5 g) prepared from diazofluorene and iodine in chloroform,[18] and zinc–copper couple [19] (0·12 g) were stirred in oxygen-free acetonitrile (50 ml) in the dark for 24 h. The reaction mixture was drawn through a sintered glass filter (Grade 3) in a nitrogen atmosphere and aliquot portions of the filtrate were withdrawn by syringe. The visible absorption spectrum of the filtrate indicated that it contained some bifluorenylidene (10% based on the initial concentration of 9,9-di-iodofluorene). The amount of bifluorenylidene did not increase when an aliquot portion of the solution of 9-iodofluoren-9-ylzinc iodide was hydrolysed and the organic products analysed by quantitative t.l.c.; the chromatographed products were fluorenone (89% based on initial 9,9-di-iodofluorene) and bifluorenylidene (10%).

9,9′-*Di-iodo*-9,9′-*bifluorenyl.* 9,9′-Dibromo-9,9′-bifluorenyl [20] (0·25 g) and sodium iodide (0·16 g) were stirred in AnalaR acetone (10 ml) at room temperature in the dark for 24 h. The precipitated sodium bromide was filtered off and the solvent removed, leaving a dark solid which quickly decomposed to a black intractable material. Fresh samples were used for the determination of the u.v. spectrum and for examination of chromatographic behaviour on alumina, whereupon quantitative conversion to bifluorenylidene was observed.

Kinetics.—In all cases the rates of reaction were followed by monitoring the decrease in concentration of the diazoalkane. For diphenyldiazomethane, visible spectrophotometry at 526 nm was used as previously described.[21] In the case of diazofluorene and its substituted analogues which have low-intensity absorption at *ca.* 500 nm, the formation of appreciable amounts of bifluorenylidene (ε 25,000 at 450 nm) quickly interfered with spectrophotometric analyses. Accordingly the characteristic i.r. absorption of the diazo-function at *ca.* 2060 cm^{-1} was used to estimate the concentration of diazoalkane. The maximum intensity of absorption of this peak was used to determine the optical density of solutions and these were found to obey Beer's law over the range of concentrations studied. Aliquot portions of reaction solutions containing zinc halides were quenched by addition of AnalaR sodium chloride (*ca.* 20 mg). The liquid was then transferred to a cell having calcium fluoride windows and a path-length of 0·2 mm. The i.r. absorption was measured over the range 2250—1970 cm^{-1} with a Perkin-Elmer 125G grating spectrometer.

Product Analysis.—The reaction of diphenyldiazomethane with the zinc halides gives essentially only benzophenone and its azine. The concentrations of these in reaction product mixtures were determined spectrophotometrically with use of optical densities at 250 and 350 nm of aliquot portions suitably diluted with 95% ethanol. The concentrations so determined are correct to within 1%. In the reaction of the other diazoalkanes, the product mixture is too complex for such analysis and quantitative t.l.c. was used. The procedure was similar to that previously described [21] except that the mixture of products after being spotted on to the chromatographic plate was allowed to stand for a short period before being developed with 1 : 1 benzene–light petroleum.

Measurement of the Lewis Acidity of the Zinc Halides.—An indicator method was employed. Conventional nitroaniline indicators as used in studies on zinc halides in ether [16] and acetone [15] were unaffected in acetonitrile solution, presumably as a consequence of the known strong solvation of the Lewis acids. Indeed, a stable crystalline solvate of composition $ZnCl_2,2MeCN$ has been described.[22] Dibenzacridines were found to undergo a rapid and reversible colour change on treatment with zinc halides in acetonitrile solution. Spectral examination indicated that the complex had an absorption at longer wavelengths than the uncomplexed indicator. However, we do not believe that this necessarily indicates a charge-transfer interaction since protonation of the indicators by use of solutions of perchloric acid in acetonitrile gave similar spectral changes. A Benesi–Hildebrand treatment [23] indicated 1 : 1 stoicheiometry for the complexes and yielded values of their dissociation constants K_d and extinction coefficients. The results (Table 8) show that the stability of the complexes formed between dibenz[*a,j*]acridine and the zinc halides decreases in the sequence $ZnBr_2 > ZnI_2 > ZnCl_2$, while towards zinc bromide the sequence of basicities of dibenzacridines decreases in the sequence [*a,j*] > [*a,h*] > [*c,h*]. The steric effect indicated by the latter sequence further suggests a donor–acceptor (2-electron) rather than charge transfer (1-electron) interaction between the zinc halides and these indicators.

TABLE 8

Complex formation between zinc halides and dibenzacridines in acetonitrile solution at 30 °C

Zinc halide	Dibenzacridine	10^3K_d/l mol^{-1}	ε	λ/nm
$ZnCl_2$	[*a,j*]	116	26,100	424
$ZnBr_2$	[*a,j*]	1·48	23,500	424
	[*a,h*]	17·7	12,400	428
	[*c,h*]	22·9	1630	431
ZnI_2	[*a,j*]	3·06	22,400	424

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