709. *Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part I. Decomposition of Diaryldiazomethanes in Acetonitrile Catalysed by Perchloric Acid.*

By D. Bethell and J. D. Callister.

Decomposition of diaryldiazomethanes in anhydrous or slightly aqueous acetonitrile catalysed by perchloric acid involves rate-determining protonation of the diazo-compound, the resultant diazonium ion decomposing rapidly. Evidence is advanced that the final reaction products, tetra-arylethylene and diarylmethanol, arise by competition between the available nucleophilic species for intermediate diarylmethyl cations. The relative nucleophilic reactivities of certain substituted diphenyldiazomethanes have been evaluated and a possible mechanistic interpretation of them is put forward.

It was found by Roberts, Watanabe, and McMahon[1] that diphenyldiazomethane in acetonitrile is converted by a catalytic amount of toluene-*p*-sulphonic acid into tetraphenylethylene. The reaction takes place in high yield and can be used to assess the purity of samples of the diazo-compound. Preliminary kinetic experiments gave puzzling results and were not pursued.[2] A plausible mechanism for the reaction has, however,

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[1] Roberts and Watanabe, *J. Amer. Chem. Soc.*, 1950, **72**, 4869; Roberts, Watanabe, and McMahon, *ibid.*, 1951, **73**, 760.

[2] Roberts, personal communication.

been advanced by Huisgen.[3] This involves formation of a diphenylmethyl cation which then attacks a molecule of unchanged diazo-compound to yield the dimeric olefin:

$$Ph_2CN_2 \longrightarrow Ph_2CH{\cdot}N_2^+ \longrightarrow Ph_2CH^+ + N_2$$
$$Ph_2CH^+ + Ph_2CN_2 \longrightarrow Ph_2CH{\cdot}CPh_2^+ \longrightarrow Ph_2C{:}CPh_2$$

Similar mechanisms have recently been suggested to account for the products of reaction of triphenylmethyl perchlorate with several aliphatic diazo-compounds in aprotic media.[4] Dimeric olefins are also formed in the thermal decomposition of certain aliphatic diazo-compounds,[5] *e.g.*, 4,4′-dimethoxydiphenyldiazomethane (see below) in inert solvents, conditions under which the reactive intermediate is likely to be the diarylcarbene rather than the carbonium ion. The formulation of this reaction as attack by the carbene on a molecule of unchanged diazo-compound with elimination of nitrogen is probably preferable to a mechanism involving dimerisation of the carbene.[6]

As a preliminary to a quantitative comparison of the reactivities of carbonium ions and carbenes, we have reinvestigated the kinetics and mechanism of the acid-catalysed decomposition of diaryldiazomethanes in acetonitrile solution. In this paper we report the relatively uncomplicated results which we have obtained with perchloric acid as the catalyst. Part II (succeeding paper) describes the changes which occur when arenesulphonic acids replace perchloric acid in the system. We conclude that diphenylmethyl cations are formed in these reactions as reactive intermediates. The carbonium ions subsequently attack the available nucleophiles of which the diazo-compound itself is one.

EXPERIMENTAL

Materials.—Solvents. Acetonitrile was purified by careful distillation from phosphorus pentoxide through a 10-in. helix-packed column. The fore-run was contaminated with hydrogen cyanide and discarded. The purified solvent gave no precipitate with aqueous silver nitrate, and Karl Fischer titration showed that it contained *ca.* 0·01% of water. Determination of the rate of decomposition of diphenyldiazomethane catalysed by toluene-*p*-sulphonic acid under standard conditions in samples from batches of purified solvent afforded a further check on their purity. Solutions of perchloric acid in acetonitrile were prepared by dilution of a 70% aqueous solution with purified acetonitrile. Since the required concentration of acid was very low, a negligible amount of water was introduced by this procedure. Such solutions are, however, unstable,[7] the acidity, as determined by indicator measurements, decreasing with time. All experiments were therefore carried out with freshly prepared solutions which appeared to change very little during 3—6 hr.

Diaryldiazomethanes. The method used was similar to that of Smith and Howard,[8] and is exemplified by the following preparation.

An intimate mixture of 4,4′-dichlorobenzophenone hydrazone (5 g.), prepared by the method of Szmant and McGinnis,[9] and yellow mercuric oxide (4·5 g.) was suspended in light petroleum (b. p. 40—60°; 25 ml.) and shaken for 12 hr. The dark red solution was filtered and concentrated. On cooling, dark red needles of 4,4′-*dichlorodiphenyldiazomethane* crystallised. Recrystallised twice from light petroleum (yield, 80%), it had m. p. 70° (Found: C, 59·4; H, 3·0. $C_{13}H_8Cl_2N_2$ requires C, 59·3; H, 3·1%).

The diazo-compounds prepared and some of their physical properties are listed below:

R in R_2CN_2	M. p. (solvent)	Recorded m. p.	Ref.	$\lambda_{max.}$ (mμ) (in MeCN)	ε
Ph	29° (methanol)	29°	8	526	100
p-C_6H_4Cl	70 (light petroleum)	—	—	526	120
p-C_6H_4Me	100—101 (ether)	101	10	540	100
p-$C_6H_4{\cdot}OMe$	99—100 (ether)	99—101, 110	11, 4	560	70

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[3] Huisgen, *Angew. Chem.*, 1955, **67**, 439.

[4] Whitlock, *J. Amer. Chem. Soc.*, 1962, **84**, 2807.

[5] Staudinger and Kupfer, *Ber.*, 1911, **44**, 2197.

[6] See, *e.g.*, Swain and Thornton, *J. Amer. Chem. Soc.*, 1961, **83**, 4033.

[7] Kolthoff, Bruckenstein, and Chantooni, *J. Amer. Chem. Soc.*, 1961, **83**, 3927.

[8] Smith and Howard, *Org. Synth.*, Coll. Vol. III, p. 351.

[9] Szmant and McGinnis, *J. Amer. Chem. Soc.*, 1950, **72**, 2890.

[10] Staudinger and Goldstein, *Ber.*, 1916, **49**, 1923.

[11] Barrott, Gillibrand, and Lamberton, *J.*, 1951, 1282.

For kinetic purposes, the diazo-compounds were repeatedly recrystallised until a constant rate of decomposition under given conditions was attained. Even after six recrystallisations, the *p*-methyl- and *p*-methoxy-substituted compounds, although apparently analytically pure, did not yield reproducible rate coefficients. It was possible, however, to establish that the kinetic form of their perchloric acid-catalysed decomposition was the same as for the other two compounds. The product proportions in the competition experiments were not sensitive to these minor impurities.

Satisfactorily pure diazo-compounds were stored in solution in anhydrous acetonitrile at 0°. These solutions were stable for several weeks but slowly decomposed thermally to give the corresponding ketazine, except in the case of 4,4'-dimethoxydiphenyldiazomethane which yielded the tetra-arylethylene.

Tetra-arylethylenes. Substituted tetraphenylethylenes were isolated in almost quantitative yield on decomposition of the corresponding diazo-compound catalysed by perchloric acid in anhydrous acetonitrile (Table 3 below). Some properties are here tabulated.

R in $[(p\text{-R}\cdot\text{C}_6\text{H}_4)_2\text{C}:]_2$	M. p.	Recorded m. p.	Ref.	$\lambda_{\text{max.}}$ (mμ) (in EtOH)	ε
H	224°	222°	12	308	13,100
Cl	216—217	216—217	13	315	14,500
Me	151	151	10	315	14,100
MeO	179—180	177	14	325	17,000

Diarylmethanols. Authentic specimens of the alcohols were generally prepared by reduction of the corresponding ketone with zinc dust in aqueous ethanol or sodium borohydride in methanol. 4,4'-Dimethoxydiphenylmethanol was, however, prepared from *p*-methoxyphenylmagnesium bromide and *p*-methoxybenzaldehyde. M. p.s were as follows: diphenylmethanol, 68° (lit.,[15] 68°); 4,4'-dichlorodiphenylmethanol, 94° (lit.,[16] 94°); 4,4'-dimethyldiphenylmethanol, 68—69° (lit.,[17] 69°); 4,4'-dimethoxydiphenylmethanol, 72° (lit.,[18] 72°).

Kinetic Procedure.—Solutions for kinetic experiments were prepared by dilution of an aliquot part of a stock solution of the diazo-compound in anhydrous acetonitrile with purified solvent in a volumetric flask containing, where appropriate, a weighed quantity of water. The reactants were brought to thermostat temperature (29·5° ± 0·1° in all cases), and the reaction initiated by addition of the requisite volume of the freshly prepared solution of perchloric acid. A portion of the reaction mixture was quickly transferred to a stoppered silica optical cell (10 mm.) kept at 29·5° in the thermostat-controlled cell-holder of a Unicam S.P. 500 quartz spectrophotometer. The change in optical density of the solution at the wavelength of the absorption maximum of the diazo-compound in the visible region was followed over at least three half-lives. First-order velocity constants (k_1) were determined graphically from plots of log $(D_t - D_\infty)$ against time, where D_t is the optical density of the solution at time t, D_∞ being the value when the reaction was complete. In all cases excellent straight lines were obtained up to at least 85% reaction. Some typical examples are shown in the Figure. Rate constants were reproducible within 5%, although greater uncertainty should probably be attached to results at very low water concentrations.

Product Analysis.—In anhydrous acetonitrile the diazo-compounds were converted by perchloric acid into the corresponding tetra-arylethylene essentially quantitatively, as determined both from the ultraviolet spectrum of the reaction mixture after completion of the reaction and by isolation of the product. Added water reduced the yield of olefin, producing instead the sovolysis product (diarylmethanol). Isolation of the two products showed that there were no appreciable side reactions. For the evaluation of reactivity ratios, the product proportions were determined by measurement of the optical density of a suitably diluted aliquot portion of the reaction mixture (from the kinetic experiments or experiments at similar concentrations) at the long-wavelength absorption maximum of the tetra-arylethylene. The

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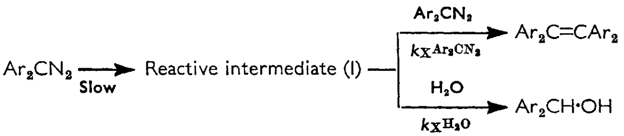
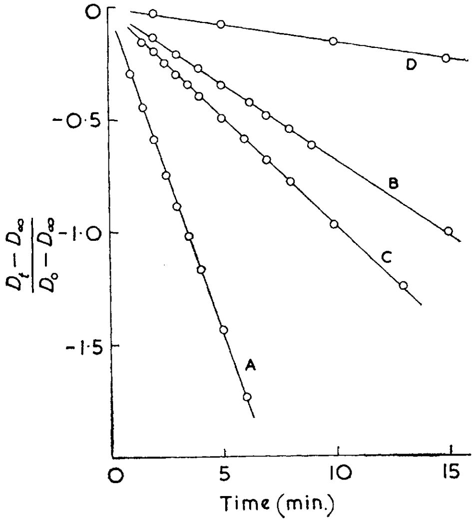
[12] Schlenk and Bergmann, *Annalen*, 1928, **463**, 15.
[13] Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2947.
[14] Bergmann, Magat, and Wagenberg, *Ber.*, 1930, **63**, 2576.
[15] Zechmeister and Rom, *Annalen*, 1929, **468**, 117.
[16] Montagne, *Rec. Trav. chim.*, 1905, **24**, 114.
[17] Ador and Crafts, *Ber.*, 1874, **7**, 1184.
[18] Schnackenberg and Scholl, *Ber.*, 1903, **36**, 655.

diarylmethanols do not absorb at this wavelength and, though the azines do, the shape of the absorption spectrum of the solution and the failure to isolate any azine in preparative experiments indicate that under our conditions there is no interference from this source. In Table 3, yields of olefin (q) determined by this spectrophotometric procedure are recorded. The probable accuracy of the values is ±1%. Product proportions were unaffected by changes in the catalyst concentration.

Evaluation of Reactivity Ratios (r_{X}).—The procedure is an adaptation of that of Swain, Scott, and Lohmann.[19] We assume (see Discussion) that the reaction path is of the general form:



and that solute species are not associated in acetonitrile. Support for the latter assumption, in the case of hydroxylic solutes at least, has been provided by Mitra's infrared studies[20] on hydrogen bonding between phenol or methanol and nitriles: in acetonitrile the hydroxylic compounds were hydrogen-bonded only to solvent molecules up to solute concentrations as high as 4M. If x and y are the concentrations of olefin and alcohol, respectively, at time t, and a is the concentration of diazo-compound, then we have:



Specimen first-order kinetic behaviour: diphenyldiazomethane, 2·22M-H_2O, (A) 2·8 × 10^{-4}M-$HClO_4$ and (B) 0·7 × 10^{-4}M-$HClO_4$; 4,4′-dichlorodiphenyldiazomethane, 0·7 × 10^{-4}M-$HClO_4$, (C) 0·77M-H_2O and (D) 2·22M-H_2O.

$$\mathrm{d}x/\mathrm{d}t = k_{\mathrm{X}}^{\mathrm{Ar_2CN_2}}a[\mathrm{I}]$$

and

$$\mathrm{d}y/\mathrm{d}t = k_{\mathrm{X}}^{\mathrm{H_2O}}[\mathrm{H_2O}][\mathrm{I}].$$

Division yields

$$\mathrm{d}x/\mathrm{d}y = k_{\mathrm{X}}^{\mathrm{Ar_2CN_2}} \,.\, a/k_{\mathrm{X}}^{\mathrm{H_2O}} \,.\, [\mathrm{H_2O}].$$

Now $a = a_0 - 2x - y$, where a_0 is the initial concentration of diazo-compound.

Thus
$$\frac{\mathrm{d}x}{\mathrm{d}y} = \frac{k_{\mathrm{X}}^{\mathrm{Ar_2CN_2}}}{k_{\mathrm{X}}\mathrm{H_2O}} \cdot \frac{a_0 - 2x - y}{[\mathrm{H_2O}]} = \frac{r_{\mathrm{X}}}{[\mathrm{H_2O}]} \cdot (a_0 - 2x - y)$$

If we assume that [H_2O] remains constant during the reaction, the equation may be integrated

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[19] Swain, Scott, and Lohmann, *J. Amer. Chem. Soc.*, 1953, **75**, 136.
[20] Mitra, *J. Chem. Phys.*, 1962, **36**, 3286.

by making the substitution $u = 2x + y$. In this way, the concentration of solvolysis product in the reaction mixture at the end of the reaction may be obtained:

$$y_\infty = \int_{u=0}^{u=a_0} \left\{\frac{2r_X(a_0 - u)}{[H_2O]} + 1\right\}^{-1} \cdot du = \frac{[H_2O]}{2r_X} \log_e \left(\frac{2r_X a_0}{[H_2O]} + 1\right).$$

Since y_∞ is known from the product analysis and a_0 can be determined exactly by extrapolation of the optical density of the reaction mixture at the absorption maximum of the diazo-compound to $t = 0$, r_X can be obtained either numerically or graphically.

The effect of errors in the estimate of the percentage yield of alcohol (p) on the derived value of r_X increases, broadly speaking, as p increases and r_X decreases. In Table 3, the percentage error in r_X is from one to five times that in p for almost all the entries. Values of r_X were never calculated when p exceeded 95%.

Indicator Experiments.—The effect of added water on the acidity of solutions of perchloric acid in acetonitrile was examined by determining the extent of protonation of an electrically neutral indicator (B). Water has such a profound effect on the ability of acid solutions in acetonitrile to protonate bases that it proved difficult to find an indicator to cover the whole range of water concentrations required. *m*-Nitroaniline had proved convenient in a related investigation for a different acid catalyst (see Part II) and was used here although it was completely protonated by even dilute solutions of perchloric acid in *anhydrous acetonitrile*. The ionisation ratio, R (= $[BH^+]/[B]$), was determined spectrophotometrically at 400 mμ.

RESULTS AND DISCUSSION

Mechanism of the Decomposition of Diaryldiazomethanes Catalysed by Perchloric Acid.—The acid-catalysed decomposition of diaryldiazomethanes in acetonitrile yields the corresponding tetra-arylethylene under anhydrous conditions, irrespective of the initial concentration of diazo-compound. However, thermal decomposition of the same compounds, with the exception of 4,4′-dimethoxydiphenyldiazomethane,* furnishes the ketazine when the intial diazo-compound concentration is high (~0·1M), and a mixture of ketazine and tetra-arylethane when the concentration is the same as that in the kinetic experiments reported here.[21] It should be added that thermal decomposition in dilute solution in air leads mainly to the substituted benzophenone. These results may be rationalised in terms of the intermediate formation of carbenes and diarylmethyl radicals [22] and contrast sharply with the results from the acid-catalysed reactions. Accordingly, we feel confident that a carbene mechanism need not be considered further in this instance and we interpret our experimental results as arising from reactions involving ionic intermediates.

Perchloric acid is the only acid known to be completely dissociated in acetonitrile.[7] The resultant simplicity of the (freshly prepared) catalyst–solvent system is reflected in the uncomplicated kinetic results. No evidence was found for the kinetic irregularities observed in other systems at low acid concentrations.[1,23]

The experimental results in Table 1 show that: (*a*) The rate of reaction is of the first order in diazo-compound and perchloric acid. (*b*) *p*-Chloro-substituents reduce the reaction rate. (*c*) Addition of water reduces the reaction rate without affecting the kinetic form. Increasing amounts of water result, however, in an increasing proportion of diarylmethanol in the product (Table 3). (*d*) The reaction shows a solvent isotope effect—$k_1^{H_2O}/k_1^{D_2O} = 3{\cdot}3$ for diphenyldiazomethane, the value remaining constant within the experimental uncertainty with changing water concentration. For 4,4′-dichlorodiphenyldiazomethane, $k_1^{H_2O}/k_1^{D_2O} = 2{\cdot}8$.

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* *Added in Proof.*—It has now been found that, under rigorously acid-free conditions, thermal decomposition of this compound yields ketone and azine in similar fashion to the other diaryldiazomethanes.

[21] Bethell and Callister, unpublished experiments.

[22] Parham and Hasek, *J. Amer. Chem. Soc.*, 1954, **76**, 935.

[23] Warren, *J.*, 1961, 2561.

TABLE 1.

Kinetic results for perchloric acid-catalysed decomposition of diaryldiazomethanes in acetonitrile at 29·5°.

Diphenyldiazomethane

10^4[$HClO_4$] M.	[H_2O]M.	10^2[Ar_2CN_2]$_0$M.	k_1 (min.$^{-1}$)	
0·70	Nil	—	Very fast	
,,	0·22	1·32	2·10	
,,	0·66	1·40	0·978	$\frac{k_1^{H_2O}}{k_1^{D_2O}} = 3·25$
,,	,, D_2O	1·41	0·301	
,,	1·11	1·41	0·423	
,,	2·22	1·38	0·159	
,,	,,	1·40	0·163	$\frac{k_1^{H_2O}}{k_1^{D_2O}} = 3·41$
,,	,, D_2O	1·41	0·0472	
,,	4·44	1·29	0·0478	
,,	,,	1·46	0·0470	
1·40	2·22	1·41	0·320	
2·80	2·22	1·45	0·671	

4,4′-Dichlorodiphenyldiazomethane

10^4[$HClO_4$] M.	[H_2O]	10^2[Ar_2CN_2]$_0$M.	k_1 (min.$^{-1}$)	
0·70	Nil	0·83	1·13	
,,	0·22	1·23	0·913	
,,	0·77	1·23	0·225	
,,	1·11	1·32	0·106	
,,	2·22	1·26	0·0366	$\frac{k_1^{H_2O}}{k_1^{D_2O}} = 2·79$
,,	,, D_2O	1·22	0·0131	
,,	4·44	1·22	0·0115	

These results are all consistent with a rate-determining proton-transfer to the diazo-compound. Such a mechanism is well-established for acid-catalysed decompositions of aliphatic diazo-compounds in hydroxylic solvents, where the chemical outcome of the reaction is solvolysis.[1,23] Most importance is to be attached to the results relating to the influence of water and deuterium oxide on the rate and products. The large solvent isotope effect in particular is compelling evidence for rate-determining proton-transfer, and it is significant that the present value (3·3) is very close to the values obtained for the reaction of diphenyldiazomethane with benzoic acid [24a] (3·6) and acetic acid [24b] (3·5) in ethanol. In the reaction with carboxylic acids, effectively simultaneous attachment of hydrogen and the carboxylate group occurs in the rate-determining step through either a cyclic transition state [2] or intermediate formation of an ion pair.[25] An analogous reaction between H_3O^+ and the diazo-compound can be formulated, but our observation (Table 3) that replacement of H_2O by D_2O has only a small effect on the ratio of tetra-arylethylene to diarylmethanol in the product suggests that the rate- and product-determining steps of the solvolysis are distinct. Moreover, added water reduces the reaction rate, indicating that the hydrolysis reaction is not providing an additional kinetic pathway for the decomposition of the diazo-compound. This rate reduction is qualitatively similar to the effect of water on the ability of the reaction medium to protonate *m*-nitroaniline (Table 2). Both effects may be explained by progressive replacement of $CH_3{\cdot}CNH^+$ by H_3O^+ as

TABLE 2.

Effect of added water on the extent of protonation of *m*-nitroaniline by solutions of perchloric acid in acetonitrile.

Nominal acid concn.: 2·8 × 10^{-4}M. Indicator concn.: 4·7 × 10^{-4}M.

[H_2O] (M)	0	0·22	1·11	2·22	4·44
R	1·74	1·33	0·14	$0·08_4$	$0·05_1$
$10^{-3}R$/[H^+]	Very large	33·8	0·65	0·34	0·20

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[24] (*a*) Roberts, Regan, and Allen, *J. Amer. Chem. Soc.*, 1952, **74**, 3679; (*b*) Roberts and Regan, *ibid.*, p. 3695.

[25] Roberts, Watanabe, and McMahon, *J. Amer. Chem. Soc.*, 1951, **73**, 2521; Huisgen and Rüchardt, *Annalen*, 1956, **601**, 1.

the proton transfer agent. The effects are more pronounced in acetonitrile than in ethanol,[1,23] in keeping with the lower basicity of the former than of hydroxylic solvents.

A satisfactory interpretation of our results is in terms of a reactive intermediate for which the nucleophiles present in the reaction solution compete. Warren [23] has adduced evidence that, in the case of acid-catalysed decomposition of 9-diazofluorene in aqueous ethanol, the important intermediate is the 9-fluorenylcarbonium ion rather than the related diazonium ion. We have arrived at a similar conclusion in the present instance. The product proportions (see Table 3) permit the calculation of relative reactivities r_{X} ($\equiv k_{\text{X}}{}^{\text{Ar}_2\text{CN}_2}/k_{\text{X}}{}^{\text{H}_2\text{O}}$) of the X-substituted diphenyldiazomethane and water towards the hypothetical intermediate. The ratio is constant, within the experimental uncertainty, over a considerable range of water concentrations. Now, if the important intermediate were the diazonium ion, then decomposition to the carbonium ion would be expected to compete with reaction with the nucleophiles. Since it seems unlikely that both carbonium ions and diazonium ions would be partitioned between the available nucleophiles in exactly the same way, variation of r_{X} with changing water concentration would be observed. The observed constancy of r_{X} and the fact that the values obtained in the present investigation are very similar to those (Part II) for sulphonic acid-catalysed decomposition of diaryldiazomethanes at low water concentrations in acetonitrile, where there is evidence that the diazo-nitrogen is lost before the rate-determining step, lead us to conclude that the available nucleophiles compete for the diarylmethyl cation.

TABLE 3.

Olefin yields (q%) and reactivity ratios (r_x) for perchloric acid-catalysed decomposition of $(p\text{-X}\cdot\text{C}_6\text{H}_4)_2\text{CN}_2$ in aqueous acetonitrile at 29·5°.

$[(p\text{-X}\cdot\text{C}_6\text{H}_4)_2\text{CN}_2]_0 \sim 1{\cdot}4 \times 10^{-2}$M.; [Catalyst] $2{\cdot}8 \times 10^{-4}$M.

X =	H		Cl		CH_3		CH_3O	
$[\text{H}_2\text{O}]$ (M)	q	r_{H}	q	r_{Cl}	q	r_{Me}	q	r_{MeO}
0	95	—	95	—	98	—	100	—
0·11	—	—	40	13	—	—	—	—
0·22	61	36	30	15	$89{\cdot}_4$	385	98·4	3100
0·44	53	35	23	13	—	—	—	—
0·66	40	37						
	41 (39*)	39 ($35{\cdot}_4$*)	21 (20*)	13 (12*)	$76{\cdot}_6$	340	$96{\cdot}_0$	3000
0·77	—	—	14	10	—	—	—	—
1·11	29	36	12	12	67	310	$94{\cdot}_5$	3200
1·80	21	37	—	—	—	—	—	—
2·22	17	37	10 (11*)	15 (24*)	52	300	$91{\cdot}_4$	3200
4·44	10	40	5	16	32	290	—	—
	Av.	37	Av.	13	Av.	32_5	Av.	31_{25}

* Values obtained on using deuterium oxide.

The mechanism of the perchloric acid-catalysed decomposition of diaryldiazomethanes may therefore be represented:

$$\text{Ar}_2\text{CN}_2 + \text{H}^+ \xrightarrow{\text{Slow}} \text{Ar}_2\text{CHN}_2{}^+ \xrightarrow{\text{Fast}} \text{N}_2 + \text{Ar}_2\text{CH}^+ \xrightarrow[\text{Ar}_2\text{CN}_2,\text{H}_2\text{O}]{\text{Fast}} \text{Products}$$

Substituent Effects on the Product-determining Steps.—The values listed in Table 3 indicate that the reactivity ratio r_{X} increases with increasing electron-repulsion by substituents in the aromatic rings. The effect is probably composite since the stability (and hence selectivity) of the carbonium ion as well as the nucleophilic activity of the diazo-carbon atom will be increased simultaneously in this way. The ratio of r-values for substituted and unsubstituted diazo-compounds may be written

$$\frac{r_{\text{X}}}{r_{\text{H}}} = \frac{k_{\text{H}}{}^{\text{Ar}_2\text{CN}_2}}{k_{\text{H}}{}^{\text{Ph}_2\text{CN}_2}} \cdot \frac{k_{\text{X}}{}^{\text{Ar}_2\text{CN}_2}}{k_{\text{H}}{}^{\text{Ar}_2\text{CN}_2}} \cdot \frac{k_{\text{H}}{}^{\text{H}_2\text{O}}}{k_{\text{X}}{}^{\text{H}_2\text{O}}}$$

The first factor on the right-hand side is the relative reactivity of the two diazo-compounds towards the diphenylmethyl cation. The remaining factors are ratios of reactivities of the substituted and unsubstituted carbonium ion intermediates with the two nucleophilic species, and together constitute a measure of the relative selectivities of the two carbonium ions. Swain, Scott, and Lohmann have derived values in the range 1—5 for the relative selectivity of 4,4′-dimethyldiphenylmethyl and diphenylmethyl cations when the competing nucleophiles were azide or chloride ions and water. Thus the ratio r_X/r_H gives the maximum value for the effect of electron-repelling substituents on the nucleophilic activity of diphenyldiazomethane.

It is instructive to compare our results with those recently reported by Oszewski [26] on the acid-catalysed dehydration of 1,1-diaryl-2,2-diphenylethanols. This reaction has been shown to involve rate-determining loss of water from the protonated alcohol, yielding the 1,1-diaryl-2,2-diphenylethyl cation, an intermediate which might plausibly be suggested in the reaction of diphenylmethyl cations with diaryldiazomethanes. Our observation that substituents in the diazo-compound have only a small effect on the reaction rate * suggests to us that the transition state has relatively little carbonium ion character. Further work is in hand in an effort to elucidate fully the substituent effects on the reactivity ratio r_X/r_H.

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* A graph of log (r_X/r_H) against $2\sigma^+$ using Brown's values [27] is linear: the slope (ρ) is $-1{\cdot}309$; standard deviation, 0·150; correlation coefficient, 0·993. Considering *m*-substituents only Oszewski derived a ρ-value of $-3{\cdot}94$ for the dehydration of tetra-arylethanols.

[26] Oszewski, *Diss. Abs.*, 1962, **22**, 2995.

[27] Brown in "Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London, 1958, p. 100.