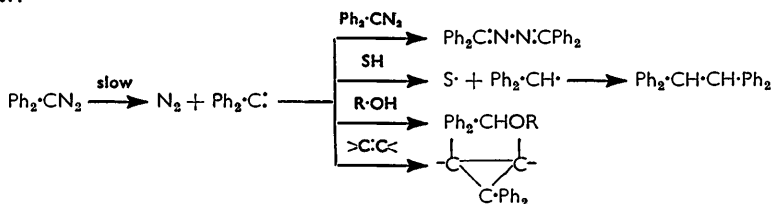


452. *Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part III.*¹ *Thermal Decomposition of Diphenyldiazomethane in Acetonitrile*²

By D. BETHELL, D. WHITTAKER, and (in part) J. D. CALLISTER

The thermal decomposition of diphenyldiazomethane in acetonitrile with and without added water and ethanol has been investigated. Reactions were carried out under nitrogen in sealed glass tubes coated internally with polytetrafluoroethylene to minimise surface reactions. In aqueous and ethanolic acetonitrile, where diphenylmethanol and its ethyl ether are the main products, kinetic and product studies indicate slow formation of diphenylcarbene which is partitioned between the hydroxylic compound and unchanged diphenyldiazomethane. In anhydrous acetonitrile, benzene, and toluene, the results suggest that the products, notably benzophenone azine and tetraphenylethane, are formed by partitioning of two reactive intermediates. The electronic state of the carbene intermediates in these reactions is discussed.

THERMAL and photolytic decomposition of diphenyldiazomethane has been the subject of a considerable number of investigations and it is generally agreed that the first step is formation of diphenylcarbene.³ The thermal reaction in aprotic (*e.g.*, hydrocarbon) solvents gives benzophenone azine and tetraphenylethane as the principal identifiable products,⁴ whilst in hydroxylic solvents the appropriate derivative of diphenylmethanol accompanies the azine.⁵ In the presence of olefins, 1,1-diphenylcyclopropanes are formed, and the non-stereospecific nature of this process has led to the conclusion that the carbene reacts in the triplet (diradical) form.⁶ Kinetic studies of the decomposition of diphenyldiazomethane in xylene⁷ and in 1-methylnaphthalene⁸ at about 100° have shown that the reaction is first-order in diazo-compound: this has been interpreted as supporting the rationalisation of the reaction products in terms of intermediate formation of diphenylcarbene, *viz.*:



Starting from the proposition that carbenes are electrophiles, we sought to determine the relative rates of competing reactions of diphenylcarbene and compare them with values already determined for analogous reactions of the related diphenylmethyl cation in acetonitrile.^{1,9}

EXPERIMENTAL

Materials.—Diphenyldiazomethane was prepared as previously described⁹ except that double the amount of yellow mercuric oxide was used. Recrystallised from light petroleum, methanol, and finally acetonitrile, it had *m. p.* 29°. Titration with benzoic acid showed it to

¹ Part II, D. Bethell and J. D. Callister, *J.*, 1963, 3808.

² For a preliminary account of part of this work see D. Bethell, J. D. Callister, and D. Whittaker, *Proc. Chem. Soc.*, 1964, 192.

³ J. Hine, "Divalent Carbon," Ronald Press Co., New York, 1964.

⁴ W. E. Parham and W. R. Hasek, *J. Amer. Chem. Soc.*, 1954, **76**, 937.

⁵ H. Staudinger, E. Anthes, and F. Pfenninger, *Ber.*, 1916, **49**, 1928.

⁶ R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Amer. Chem. Soc.*, 1959, **81**, 1008.

⁷ G. Murgulescu and T. Oncescu, *J. Chim. phys.*, 1961, **58**, 508.

⁸ H. Reimlinger, *Chem. Ber.*, 1964, **97**, 339.

⁹ D. Bethell and J. D. Callister, *J.*, 1963, 3801.

be more than 99% pure. Benzophenone azine, prepared by the method of Szmant and McGinnis,¹⁰ was recrystallised from ethanol, m. p. 163°: λ_{max} (EtOH) 280 μ (ϵ 19,800); shoulder at 312 μ (ϵ 13,500). At 350 μ , $\epsilon = 4100$. Diphenylmethyl ethyl ether, prepared by Linnemann's method,¹¹ had b. p. 142°/16 mm., λ_{max} (EtOH) 255 μ (ϵ 510). Bisdiphenylmethyl ether, m. p. 108—109°, was kindly supplied by Mr. A. F. Cockerill. Tetraphenylethylene was prepared as described earlier.⁹ At 350 μ , $\epsilon = 2600$ in ethanol solution.

Solvents.—Acetonitrile was purified as described previously.⁹ Benzene and toluene were dried over sodium and fractionated.

Kinetic Procedure.—To prevent interference by oxygen, all reactions were carried out under nitrogen purified by Fieser's procedure.¹² Solutions for kinetic experiments were prepared by dilution of an aliquot part of a stock solution in anhydrous organic solvent with purified solvent in a volumetric flask containing, where appropriate, a weighed quantity of water or ethanol. Purified nitrogen saturated with solvent vapour was bubbled into the solution through a sintered glass disc for 1 hr. Portions of the solution were then transferred under nitrogen to reaction tubes which had been freed of oxygen by at least three cycles of evacuation and flushing with nitrogen. The reaction mixture was frozen by immersing the tube in an alcohol–solid carbon dioxide bath and three further cycles of evacuation and flushing with nitrogen carried out, the tube being finally sealed under vacuum by means of a tap. Tubes were allowed to warm up to room temperature and then transferred to a thermostat at the appropriate reaction temperature. After 3 min. a tube was removed for analysis, its removal being taken as zero time for the run: negligible reaction occurred during this warming-up period. Tubes were removed at intervals and cooled in water for 5 min. before opening. The change in optical density at 526 and 350 μ of a sample of the reaction mixture diluted with absolute ethanol was measured using a Unicam S.P. 500 quartz spectrophotometer. The reaction was followed for at least two half-lives. First-order rate coefficients (k_{obs}) were determined graphically from plots of $\log(D_t - D_\infty)$ against time, where D_t is the optical density at 526 μ of the diluted sample at time t and D_∞ that corresponding to complete reaction. Rate coefficients were reproducible within 5% usually, somewhat greater variation being found for reactions in aromatic solvents where a slight turbidity developed.

Reactions in Pyrex tubes yielded apparently satisfactory rate constants by this procedure, but the optical density of the samples at 350 μ , from which the concentration of azine was calculated, showed a serious random variation (Table 1). This was particularly marked for reactions in aqueous acetonitrile. It could be further increased by etching the interior of the tubes with concentrated aqueous alkali or by adding glass wool to the reaction mixture, procedures which increased the rate of disappearance of diazo-compound considerably and modified the product composition.

TABLE 1

Sample data for the thermal decomposition of diphenyldiazomethane in aqueous acetonitrile at 85.0°

Time (min.)	Coated tubes (4.07M-H ₂ O present)		Uncoated tubes (4.29M-H ₂ O present)	
	[Ph ₂ CN ₂] (M)	10 ³ [Azine] (M)	[Ph ₂ CN ₂] (M)	10 ³ [Azine] (M)
0	0.0594	0.88	0.0662	1.45
30	0.0437	1.25	0.0474	2.10
60	0.0339	1.42	0.0362	1.84
90	0.0274	1.61	0.0244	3.18
120	0.0183	1.66	0.0190	1.94
150	—	—	0.0122	2.69
∞	0.0000	1.80	0.0000	3.00

Graphically, $k_{\text{obs}} = 0.94 \times 10^{-2} \text{ min.}^{-1}$,

$k_{\text{obs}} = 1.08 \times 10^{-2} \text{ min.}^{-1}$

To eliminate that fraction of the reaction which was occurring on the glass surface, all tubes were coated internally with polytetrafluorethylene (PTFE). The insides of the tubes were etched by introducing a mixture of lead shot and carborundum powder into the tubes which were clamped horizontally and vibrated rapidly for 2 hr. After cleaning with hot, concentrated

¹⁰ H.H. Szmant and C. McGinnis, *J. Amer. Chem. Soc.*, 1950, **72**, 2390.

¹¹ E. Linnemann, *Annalen*, 1865, **133**, 17.

¹² L. F. Fieser, "Experiments in Organic Chemistry," 3rd edn., D. C. Heath and Co., Boston, 1957, p. 299.

nitric acid and then water, the tubes were filled with an aqueous dispersion of PTFE (Imperial Chemical Industries Limited "Fluon," Grade S.C.1) and allowed to drain. The coating was left to dry at room temperature and finally sintered by heating in an annealing oven to 350° for 15 min. Etching made the tubes very brittle: precautions were taken against implosion of tubes during the filling operations but none in fact occurred. Reactions were slightly (*ca.* 10%) slower in coated than uncoated tubes but showed a steady increase in the optical density of the solution at 350 m μ (Table 1). Addition of a large quantity of PTFE powder to a reaction mixture produced only a slight increase in the azine yield from which we conclude that, in coated tubes, the reaction is almost entirely homogeneous.

Product Analysis.—The yield of benzophenone azine was calculated from the optical density at 350 m μ of diluted samples of reaction solutions, a correction being applied for the small amount of azine present initially. In cases where tetraphenylethylene was also formed a further correction had to be applied to take account of its absorption at 350 m μ .

The products of each experiment were determined by evaporating to dryness a sample of the mixture after completion of the reaction, dissolving the residue in deuteriochloroform, and measuring the proton magnetic resonance (p.m.r.) spectrum of this solution using a Varian A-60 spectrometer. By comparison with spectra of authentic specimens a partial analysis of the products could be obtained. The identity of products was confirmed by adding authentic material to the solution and observing the coincidence of peaks. The yield of tetraphenylethylene was determined from the spectrum by comparison of the area of its aromatic proton peak with that of the methine proton peak of the diphenylmethanol (or its ethyl ether) which was also present. The presence of numerous small peaks in the aromatic region of the spectrum of the mixture of products increases the error of the determination, so that values given for the percentage of diazo-compound forming tetraphenylethylene are $\pm 1\%$. Since the azine yield has to be corrected for the presence of olefin, its accuracy is reduced when tetraphenylethylene is present. Qualitative analyses of the products of reactions in the solvents studied are detailed below.

(i) *Anhydrous acetonitrile.* Benzophenone azine, tetraphenylethane, succinonitrile, and bisdiphenylmethyl ether were identified by p.m.r. spectroscopy which also showed the presence of two major (*ca.* 10%) and several minor unidentified products. Column chromatography of the mixture on alumina yielded samples of all the identified products except succinonitrile, together with samples of two unidentified products. The first of these, a pale yellow oil eluted with benzene, had an infrared spectrum almost identical with that of benzene. It proved impossible to free it from solvent which leads us to suppose that it was polymeric. The other unidentified material was a brown gum eluted with ethyl acetate from which it too was difficult to separate. Its infrared spectrum indicated that it contained aromatic groups. The bisdiphenylmethyl ether, which was found in traces in the products of all reactions in "anhydrous" solvents is attributable to traces of water which could trap a significant fraction of the reaction intermediate at the concentrations of diphenyldiazomethane used in these experiments (see below). When the reaction was carried out in etched, uncoated tubes or in the presence of glass wool, the azine yield was increased and tetraphenylethane, succinonitrile, one major, and several minor unidentified products were absent. In the presence of oxygen, the main product was benzophenone.

(ii) *Aqueous acetonitrile.* The products varied with water concentration. Below 1M-water, benzophenone azine, diphenylmethanol, and bisdiphenylmethyl ether were found by ultraviolet and p.m.r. spectroscopy and isolation. Between 1M- and 4M-water, the reaction gave only azine and diphenylmethanol, but at higher water concentrations, traces of tetraphenylethylene were detected. In air, the reaction products were benzophenone and diphenylmethanol only.

(iii) *Ethanollic acetonitrile.* Benzophenone azine, diphenylmethyl ethyl ether, and a trace of diphenylmethane were detected by p.m.r. spectroscopy.

(iv) *Benzene.* The p.m.r. spectrum of the products showed the presence of azine and a trace of bisdiphenylmethyl ether. Several other unidentified products were present but none of these contained aliphatic protons. In particular, tetraphenylethane was absent.

(v) *Toluene.* Benzophenone azine, bisdiphenylmethyl ether, tetraphenylethane, 1,1,2-triphenylethane, and bibenzyl were detected spectroscopically. Several other unknown products were also present, but none contained aliphatic protons.

Evaluation of Reactivity Ratios.—Reactivity ratios (r_H) governing the partitioning of reaction intermediates between attack on a second molecule of diazo-compound (to give azine and/or

tetraphenylethylene) and attack on some other molecule (water, ethanol) were determined using the equation previously derived,⁹ viz.

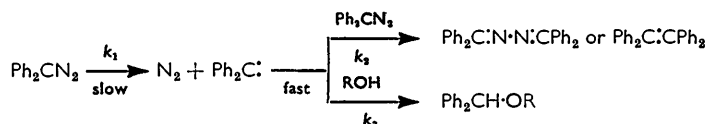
$$y_{\infty} = \frac{[\text{H}_2\text{O}]}{2r_{\text{H}}} \log_e \left(\frac{2r_{\text{H}}a_0}{[\text{H}_2\text{O}]} + 1 \right)$$

where y_{∞} is the concentration of diazo-compound converted into products other than azine or ethylene after completion of the reaction, $[\text{H}_2\text{O}]$ is the constant concentration of water present, and a_0 is the initial concentration of diphenyldiazomethane. The equation was adapted for use in anhydrous solvents by putting $r_{\text{H}} = r_{\text{H}}^0$ and $[\text{H}_2\text{O}] = 1$, r_{H}^0 then having the units l. mole⁻¹. Simple algebraic modification of this equation enabled r_{H} and r_{H}^0 to be calculated on a KDF.9 electronic computer.

RESULTS AND DISCUSSION

Reactions in Aqueous Acetonitrile.—Kinetics and products. We deal with these media first because of the relative simplicity of the reaction under these conditions. A complete analysis of the products was possible (see Experimental section) and showed the absence of what may be termed "free-radical products," e.g., tetraphenylethane and succinonitrile.

In aqueous acetonitrile the disappearance of diphenyldiazomethane followed first-order kinetics at all water concentrations. The observed velocity constants varied little in the range 0—10M-water (Table 2, Figure) and, moreover, *decreased* in that range of water concentrations where products of the reaction of the diazo-compound with water rise from zero to >90% of the total product. These observations suggest that the rate- and product-determining steps are separate as indicated in the following formulation:



According to this scheme the rate of disappearance of the diazo-compound is given by

$$v = -d[\text{Ph}_2\text{CN}_2]/dt = k_1[\text{Ph}_2\text{CN}_2] + k_2[\text{Ph}_2\text{C:}][\text{Ph}_2\text{CN}_2] \quad (1)$$

and, assuming the establishment of a steady-state concentration of the intermediate carbene, this becomes

$$v = k_1[\text{Ph}_2\text{CN}_2] \left\{ 1 + \frac{k_2[\text{Ph}_2\text{CN}_2]}{k_2[\text{Ph}_2\text{CN}_2] + k_3[\text{ROH}]} \right\}$$

The water concentration $[\text{ROH}]$ remaining constant during each reaction, integration and application of limiting conditions yields the kinetic equation

$$\log_e \left\{ \frac{[\text{Ph}_2\text{CN}_2]}{[\text{Ph}_2\text{CN}_2]_0} \left(\frac{2r_{\text{H}}[\text{Ph}_2\text{CN}_2]_0/[\text{ROH}] + 1}{2r_{\text{H}}[\text{Ph}_2\text{CN}_2]/[\text{ROH}] + 1} \right)^{\dagger} \right\} = -k_1 t \quad (2)$$

where $r_{\text{H}} \equiv k_2/k_3$ and the subscript refers to $t = 0$. Evaluation of r_{H} showed that, in all the cases studied, $r_{\text{H}}/[\text{ROH}]$ never exceeded unity. With $[\text{Ph}_2\text{CN}_2]_0$ always less than 0.13M, the variation from unity of the square-root term in equation (2) during the first 75% reaction never exceeded 10%. Thus, values of k_{obs} , derived as indicated in the Experimental section, can be equated with k_1 , the velocity constant for carbene formation from the diazo-compound. This is not possible for reactions in anhydrous media.

In a solvent of fixed composition, the proportion of diazo-compound which formed azine increased with increasing $[\text{Ph}_2\text{CN}_2]_0$. By use of the equation derived in Part I,⁹ assuming that molecules of diazo-compound and water compete for a reactive intermediate derived from diphenyldiazomethane, the product proportions can be transformed into values of r_{H} . The approximate constancy of these values with changing $[\text{Ph}_2\text{CN}_2]_0$ at

TABLE 2

Thermal decomposition of diphenyldiazomethane in aqueous acetonitrile at 85.0°

[Ph ₂ CN ₂] ₀ (M)	[Water] (M)	10 ² k _{obs} (min. ⁻¹)	k _D /k _H	Products (%) *			r _H
				Ether	Azine	Ethylene	
0.0668	—	0.97	—	—	24.9	—	—
0.0668	0.665	0.794	—	16.7	3.8	—	—
0.0668	0.674 D ₂ O	0.75	0.95	?	3.4	—	—
0.0668	1.02	0.76	—	—	4.5	—	0.75
0.0668	1.05 D ₂ O	0.70	0.93	—	4.2	—	0.74
0.0594	2.22	0.68	—	—	1.9	—	0.74
0.0594	4.07	0.94	—	—	3.2	—	2.28
0.0594	6.06	1.09	—	—	1.7	2.0	3.96
0.0507	10.15 D ₂ O	1.40	0.90	—	?	?	—
0.0507	10.32	1.55	—	—	2.0	1.9	8.37
0.1187	—	1.09	—	—	38.7	—	—
0.1086	0.429	0.93	—	33.1	11.9	—	0.56 †
0.1335	0.434 D ₂ O	0.82	0.94	?	12.2	—	—
0.1086	0.540 D ₂ O	0.73	0.90	?	11.1	—	—
0.1262	0.658	0.76	—	22.9	3.6	—	0.21 †
0.1262	2.16	0.84	—	—	3.0	—	0.55
0.1262	2.16 D ₂ O	0.79	0.94	—	2.8	—	0.52
0.1262	4.07	1.07	—	—	3.5	—	1.17
0.1086	5.98	1.28	—	—	2.4	3.8	3.69

* Throughout this Paper, product yields are quoted as % of diazo-compound converted into that product. † These r_H-values were calculated on the assumption that all the diazo-compound not converted into azine had formed alcohol, not a mixture of alcohol and ether. They are consequently minimum values.

TABLE 3

Thermal decomposition of diphenyldiazomethane in ethanolic acetonitrile at 85.0°

[Ph ₂ CN ₂] ₀ (M)	Ethanol (M)	10 ² k _{obs} (min. ⁻¹)	Products (%)		
			Ketazine	Ethylene	r _H
0.0594	0.96	0.76	1.5	0.3	0.32
0.0594	3.43	0.96	2.8	0.8	2.16

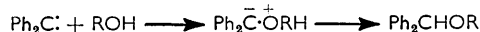
constant water concentration is taken to justify the assumptions involved. It is noteworthy that r_H-values (and rates of disappearance of diazo-compound) in ethanolic acetonitrile (Table 3) were not significantly different from those in aqueous acetonitrile of the same concentration of hydroxylic compound. It would seem that the intermediate carbene is incapable of discriminating between water and ethanol, a result in marked contrast with the fourfold greater reactivity of ethanol compared with water toward diphenylmethyl cations.¹

Mechanism of the reaction of diphenylcarbene with hydroxylic molecules: The value of r_H did not change significantly when deuterium oxide replaced water in our reactions. There are two possible explanations of this absence of kinetic isotope effect on the product-determining step: (i) reaction of diphenylcarbene and a hydroxylic molecule occurs on every collision; (ii) in the transition state of reaction of diphenylcarbene with a hydroxylic molecule, no loosening of the O-H bond occurs.

We believe that the first explanation can be excluded. Although carbenes show low discrimination in their reactions with other molecules, there is no reason to suppose that these reactions involve zero activation energy. Thus, although diphenylcarbene apparently reacts equally readily with water and ethanol, the non-unit values of r_H and their variation with water concentration indicate that the carbene is capable of some measure of selection between available reaction partners. Moreover, even for very reactive carbenes (*e.g.*, CH₂^{*}), small, but nevertheless significant, kinetic isotope effects (k_H/k_D in the range 1 to 2) have been observed in insertion and addition reactions.¹³ We

¹³ J. W. Simon and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1963, **85**, 1023; *J. Phys. Chem.*, 1964, **68**, 1322; M. J. Goldstein and S. J. Baum, *J. Amer. Chem. Soc.*, 1963, **85**, 1885; J. P. Chesick and M. R. Willcott, *J. Phys. Chem.*, 1963, **67**, 2850.

conclude therefore that, if reaction of diphenylcarbene with water involved breaking of the O-H bond, this would be slower using deuterium oxide, favouring azine formation and so resulting in a larger value of r_H . Reaction of diphenylcarbene with water and ethanol would thus appear to involve attack on the oxygen atom with subsequent proton transfer from the oxonium to the carbanionic centre, *viz.*



The first step, which competes with reaction of the carbene with unchanged diazo-compound, should occur *via* a transition state which involves little change in the interaction of ROH with other solvent molecules. There should therefore be a negligible *solvent* deuterium isotope effect on the product-determining steps.¹⁴

The above interpretation contrasts sharply with the conclusion reached by Kirmse¹⁵ concerning the mechanism of reaction of diphenylcarbene, produced by photolysis of diphenyldiazomethane, with alcohols. The ability of alcohols to suppress the oxidation of the intermediate carbene by molecular oxygen was found to increase with increasing acidity of the alcohol. Added azide ion did not affect the oxidation but did lead to the production of diphenylmethyl azide, the ratio of azide to ether produced being similar to that from alcoholysis of diphenylmethyl halides in the presence of azide ion. Kirmse's interpretation of these results was that the carbene behaves as a nucleophile, abstracting a proton from the alcohol to give a diphenylmethyl cation which is then partitioned between the available nucleophilic species, azide ion, alcohol, and presumably alkoxide ion. The formation of diphenylmethyl cations for which the available nucleophiles can compete freely cannot, however, be occurring in our experiments since it has already been shown that carbonium ions of this type react with diaryldiazomethanes to form tetra-arylethylenes only.^{1,9} An alternative interpretation of Kirmse's observations is that the diazo-compound and alcohol form a hydrogen-bonded complex which promotes reaction of the carbene formed by photolysis with the alcohol. Such complexes, for which there is independent evidence,¹⁶ should be favoured by increased acidity of the alcohol. They should be less important at the higher temperature of our experiments. The origin of the difference in behaviour of diphenylcarbene produced thermally and photolytically merits further investigation.

The representation of the reaction of diphenylcarbene with hydroxylic compounds given above implies that the divalent carbon species reacts in its singlet form, which we shall represent by $\text{Ph}_2\text{C}\uparrow$, *i.e.*, with the spins of its non-bonded electrons paired. Recent electron spin resonance investigations¹⁷ on diphenylcarbene obtained by photolysis of diphenyldiazomethane at low temperatures indicate, however, that it is a ground-state triplet (represented by $\text{Ph}_2\text{C}\uparrow\uparrow$). Moreover the non-stereospecificity of the addition of diphenylcarbene to olefins and the sequence of olefin reactivities have been taken to show that it reacts in the triplet form.^{6*} Our formulation thus needs justification: this we do as follows.

Electrophilic behaviour is that expected of a singlet carbene: radical properties (*e.g.*, hydrogen-atom abstraction) are to be anticipated for the triplet form. Thus, dichlorocarbene, which adds stereospecifically to olefins, reacts more readily with the more highly alkylated double bonds.³ Diphenylcarbene in the absence of powerful nucleophiles, *e.g.*,

* Stereospecific 1,1-diphenylcyclopropane formation has been reported by Closs and Closs¹⁸ in the reaction of diphenyldibromomethane with methyl-lithium in the presence of olefins. The precise nature of the species which adds to the olefin has yet to be defined.

¹⁴ C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, **1961**, **83**, 3207.

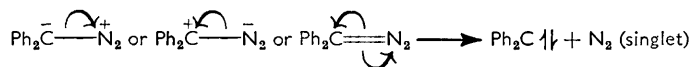
¹⁵ W. Kirmse, *Annalen*, **1963**, **666**, 9.

¹⁶ H. Bredereck, R. Sieber, and L. Kamphenkel, *Chem. Ber.*, **1956**, **89**, 1169; T. Wieland and R. K. Rothaupt, *ibid.*, p. 1176; A. Ledwith, personal communication.

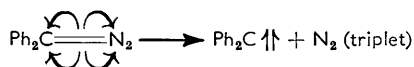
¹⁷ R. W. Brandon, G. L. Closs, and C. A. Hutchison, *J. Chem. Phys.*, **1962**, **37**, 1878; R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, **1962**, **84**, 3214; A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, p. 4990.

¹⁸ G. L. Closs and L. E. Closs, *Angew. Chem.*, **1962**, **75**, 431.

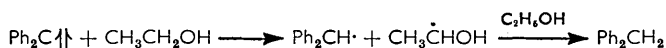
in anhydrous acetonitrile or light petroleum, affords tetraphenylethane. Now diphenylcarbene formation from diphenyldiazomethane is most simply represented



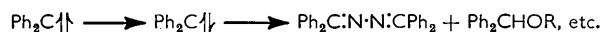
rather than



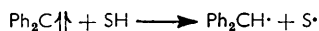
Thus, the triplet would seem to arise by spin inversion from the singlet (see below). Our observation of reactions of diphenylcarbene with hydroxylic compounds and diphenyldiazomethane analogous to those of diarylmethyl cations suggests electrophilic behaviour with both these intermediates. The presence of quite small amounts of water completely suppresses the formation of "radical products," *e.g.*, tetraphenylethane and succinonitrile, while with ethanol the only "radical product" was a trace of diphenylmethane formed presumably by the reaction



These findings can be rationalised in two ways. According to the simpler of these, the strong nucleophiles, water, ethanol, and diphenyldiazomethane, capture singlet diphenylcarbene before it can undergo spin inversion to the triplet state. In the absence of hydroxylic compounds, spin inversion can compete more successfully with reaction of the singlet with unchanged diazo-compound and "radical products" accompany benzophenone azine. Since their nucleophilic activity is likely to be much less than that of water and ethanol, olefins should be less able to capture singlet diphenylcarbene before it undergoes spin inversion.* Alternatively, as suggested by our results in anhydrous media (see below), the singlet-triplet interconversion may be reversible, the reaction path



being more favourable than the alternative paths available to the triplet carbene, *e.g.*,



Olefins being less nucleophilic than hydroxylic compounds, cyclopropane formation *via* the singlet carbene would no longer be favoured relative to direct reaction of olefin with the triplet form. Our observations and interpretations of them are thus not incompatible with the earlier results.

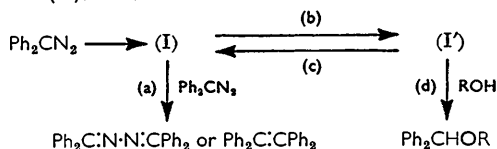
Solvent Effects on Rates and Products.—The variation in k_1 and in r_{H} with changing water (or ethanol) concentration, shown in the Figure, display an interesting similarity. While it is possible, by making reasonable assumptions about the variation of solvation energies of the several reactants and transition states with solvent composition, to rationalise this similarity, it is equally possible that the likeness is coincidental. Thus, while the variation in velocity constant seems a genuine medium effect, the somewhat surprising increase in r_{H} at the higher water concentrations could stem from a failure of our assumption⁹ that hydroxylic molecules are not self-associated.

An alternative explanation of the approximately linear increase in r_{H} with increasing

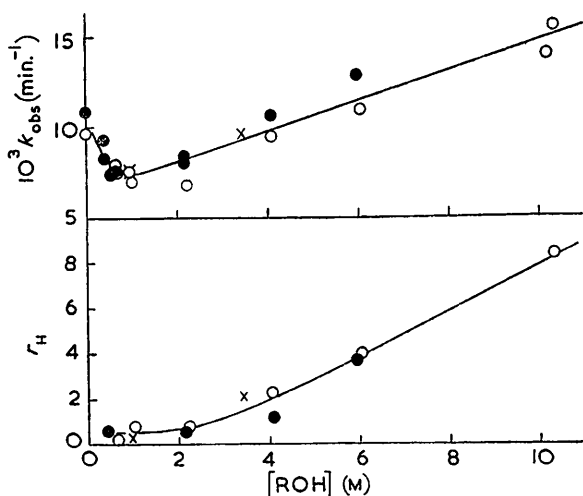
* Reimlinger⁸ reported that diphenyldiazomethane is only 1.14 times more reactive than tetramethylethylene towards dichlorocarbene and therefore suggested that it is the triplet form of diphenylcarbene which reacts with diphenyldiazomethane to form azine and with olefin to form 1,1-diphenylcyclopropane. The force of this argument is reduced, however, by the fact that diphenylcarbene reacts at the terminal nitrogen atom of the diazo-compound, while dichlorocarbene apparently reacts at the diazo-carbon atom. It would be interesting to know whether $\text{Ph}_2\text{C}:\text{N}:\text{N}:\text{CCl}_2$ is stable under the reaction conditions, cf. $\text{PhCH}\cdot\text{N}:\text{N}:\text{CHPh}$.¹⁹

¹⁹ H. E. Zimmerman and S. Somasekhara, *J. Amer. Chem. Soc.*, 1960, **82**, 5865.

water concentration above 2M is that, in this region, water does not compete with unchanged diazo-compound for a single intermediate (I) but rather the intermediate either reacts with a diphenyldiazomethane molecule or undergoes a unimolecular transformation giving a second intermediate (I'), *viz.*,



At low water concentrations it is not unreasonable that $k_d[\text{ROH}] \ll k_c$: steps (a) and (d) would then be in competition, and r_{H} would be independent of water concentration as found. At higher water concentrations the rate of step (d) would increase relative to that



Variation of k_{obs} and r_{H} with concentration of hydroxylic additive (ROH); \circ , R = H, $[\text{Ph}_2\text{CN}_2]_0 \approx 0.06\text{M}$; \bullet , R = H, $[\text{Ph}_2\text{CN}_2]_0 \approx 0.12\text{M}$; \times , R = C_2H_5 , $[\text{Ph}_2\text{CN}_2]_0 \approx 0.06\text{M}$

of step (c) and, when $k_c \ll k_d[\text{ROH}]$, step (b) would compete with step (a), the yield of azine and olefin becoming independent of the water concentration. As indicated earlier, if (I) and (I') are carbenes, (I') must be in the singlet state: (I) must therefore be a triplet. There are two major objections to this scheme: (i) it is difficult to account for formation of triplet diphenylcarbene from diphenyldiazomethane other than *via* the singlet; (ii) there is no obvious reason why the singlet carbene (I') cannot react with diphenyldiazomethane to give azine. Accordingly we reject this explanation.

We also draw attention to our repeated observation of slightly lower rate constants for the reaction in the presence of deuterium oxide compared with water at the same concentration. While the differences in rate are of the same order of magnitude as the experimental uncertainty, we feel that the consistency with which deuterium oxide-containing media gave the lower rate constant signifies a real, but unexplained, effect.

Reaction in Anhydrous Acetonitrile and Other Aprotic Solvents.—We have been unable to elucidate fully the structures of all the products from the thermal decomposition of diphenyldiazomethane in acetonitrile. Such deductions as we are able to make about the reaction mechanism must therefore be regarded as tentative.

Rates of disappearance of the diazo-compound and azine yields were determined as before. In anhydrous solvents, however, the yields of azine were so large that k_{obs} was no

TABLE 4

Thermal decomposition of diphenyldiazomethane in acetonitrile at 85.0°

$[\text{Ph}_2\text{CN}_2]_0$ (M)	$10^2 k_{\text{obs}}$ (min. ⁻¹)	$10^2 k_1$ (min. ⁻¹)	Yield of ketazine (%)	r_{H}^0 (l. mole ⁻¹)
0.1187	1.09	0.83	38.7	6.3
0.0668	0.97	0.75	24.9	5.5
0.0533	1.04	0.93	19.7	5.0
0.0297	0.94	0.84	14.9	6.2
0.0148	0.96	0.95	7.0	5.2

TABLE 5

Determination of the activation parameters for the thermal decomposition of diphenyldiazomethane in acetonitrile

Initial diphenyldiazomethane concentration = 0.0533M

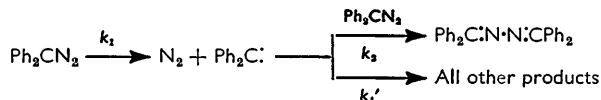
Temp.	$10^2 k_{\text{obs}}$ (min. ⁻¹)	Yield of ketazine (%)
65.0°	0.10	23.4
75.0	0.3411	23.2
85.0	1.04	19.7
95.0	3.17	21.6

 $\Delta H^\ddagger = 27.2 \pm 0.2$ kcal. mole⁻¹ at 85°; $\Delta S^\ddagger = 0.0 \pm 0.4$ e.u. at 85°

longer equivalent to k_1 . Provided that equation (1) still holds good, equation (2) can be modified for use in non-hydroxylic media, giving:

$$\log_e \left\{ \frac{[\text{Ph}_2\text{CN}_2]}{[\text{Ph}_2\text{CN}_2]_0} \left(\frac{2r_{\text{H}}^0[\text{Ph}_2\text{CN}_2]_0 + 1}{2r_{\text{H}}^0[\text{Ph}_2\text{CN}_2] + 1} \right)^{\frac{1}{2}} \right\} = -k_1 t \quad (3)$$

where r_{H}^0 represents the ratio of the velocity constant for azine formation (k_2) relative to the pseudo-first-order velocity constant (k_4') covering all other reactions of the partitioned intermediate. The experimental data fitted equation (3) as well as they fitted a simple first-order law. Results for acetonitrile solutions at different initial concentrations of diphenyldiazomethane at 85.0° and the influence of temperature on the parameters of equation (3) are shown in Tables 4 and 5, respectively. The approximate constancy of the derived values of r_{H}^0 and k_1 support the assumptions made in deriving equation (3) and point to a reaction scheme of the form:



The activation parameters derived from the results of Table 5 are close to those reported for the decomposition of diphenyldiazomethane in xylene.⁷ The very small change in the yield of benzophenone azine over the temperature range 65—95° suggests that the competing processes differ little in activation energy.

As indicated earlier, we believe that benzophenone azine is formed by reaction of singlet diphenylcarbene with diphenyldiazomethane, although the reaction can be formulated in terms of the triplet form.⁸ The following processes merit consideration as the competing reactions of diphenylcarbene, covered by the rate constant k_4' : (i) insertion into the C-H bonds of the solvent; (ii) hydrogen-atom abstraction from the solvent; (iii) spin inversion of singlet to triplet diphenylcarbene. Reaction (i) does not seem to be important: the p.m.r. spectrum of the decomposition products shows a number of signals due to aliphatic protons but none of these shows the splitting due to spin-spin coupling expected for insertion products such as $\alpha\alpha$ -diphenylpropionitrile. Equally, there is no evidence of addition of diphenylcarbene across the multiple bond of the solvent. Hydrogen-atom abstraction [reaction (ii)] is possible, since the radical dimers tetraphenylethane and succinonitrile have both been identified among the products, but seems more likely for triplet than singlet diphenylcarbene. Spin inversion is also a possibility, although for a

Such a possibility, already briefly considered by Zimmerman and Paskovich,²⁴ may at first sight seem unlikely; not only should the multiplicity change lead to a low frequency factor, the interconversion is endothermic. However, in a complex structure such as diphenylcarbene, multiplicity changes are more probable than in simpler structures, and, in solution, the energy separation of singlet and triplet states could well be of comparable magnitude to the activation energy for hydrogen atom abstraction from a solvent molecule.

On the basis of the above scheme,

$$\frac{d[\text{Azine}]}{d[\text{All other products}]} = \frac{k_2[\text{Ph}_2\text{C}'_1][\text{Ph}_2\text{CN}_2]}{(k_5[\text{SH}] + k_6[\text{X}]) [\text{Ph}_2\text{C} \uparrow]} = \frac{k_2[\text{Ph}_2\text{CN}_2]}{k_4} \left\{ 1 + \frac{k_4}{k_5[\text{SH}] + k_6[\text{X}]} \right\}$$

assuming that a steady-state concentration of triplet diphenylcarbene is rapidly established. Thus, $r_H^0 = r_s (1 + 1/r_t)$, where $r_s = k_2/k_4$, is a reactivity ratio for the singlet carbene and r_t is a corresponding ratio for the triplet. The number and precision of our present results do not yet justify their analysis according to this equation.

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²⁴ H. E. Zimmerman and D. H. Paskovich, *J. Amer. Chem. Soc.*, **1964**, **86**, 2149.