Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part 13.[1] Mechanistic Studies on the Reaction of Diaryldiazomethanes with Singlet Molecular Oxygen

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The reaction of 9-diazofluorene, diazodiphenylmethane. and *p*-substituted diazodiphenylmethanes with singlet ($^1\Delta_g$) molecular oxygen to give mainly the corresponding ketone, has been studied in the solvents acetonitrile, chloroform, and methanol. In most cases singlet oxygen was generated photochemically using Methylene Blue as sensitiser, but the thermal decomposition of triphenyl phosphite ozonide was used for some experiments. Quantitative studies of the Methylene Blue-sensitised photo-oxidation of 9-diazofluorene. diazodiphenylmethane. and 9.10-dimethylanthracene (standard) at concentrations below 10^{-3}M established that the diazo-compounds decomposed only by reaction with singlet oxygen. The low relative reactivity of diazodiphenylmethane (*ca.* 12) compared with 9-diazofluorene, the insensitivity of the rate constant to solvent polarity. and the low value of the Hammett ρ for the reactions of a series of *para*-substituted diazodiphenylmethanes all suggest that the charge separation in the reactant is increased very little on passing to the transition state. It is argued that the process is one of concerted cycloaddition yielding a heterocyclic intermediate (2). This species then decomposes with loss of N_2O (detected mass spectrometrically) to give the ketone. By labelling 9-diazofluorene specifically at the terminal nitrogen with ^{15}N and examining the exhaust gases from the photo-oxidation. it is shown that 1.3-cycloaddition takes place rather than the 1,2-mode of addition reported for the isoelectronic acceptor diphenylketen. The relevance of the results to the mechanism of direct photo-oxidation of diazoalkanes is discussed.

PREVIOUSLY [2] it has been shown that singlet molecular oxygen reacts very readily with fluorenyl anions (FIX$^-$) giving fluorenone and the oxyanion XO$^-$. We speculated that diazoalkanes (which can be represented as carbanions, or more accurately *N*-ylides, in one canonical form) should also react rapidly with singlet oxygen,† and, further, with relatively stable diazoalkanes, that a photo-excited triplet species might be capable of sensitising [4] the formation of singlet oxygen. Thus previous studies of diazoalkane photo-oxidation,[5] all of which were interpreted in terms of carbene formation followed by reaction of the divalent carbon species with triplet oxygen, could be be complicated by this additional mode of reaction.

This paper describes experiments undertaken to investigate the photo-oxidation of diazoalkanes and its mechanisms, with particular reference to the involvement of singlet oxygen. The diazoalkanes used were diazodiphenylmethane, several of its *para*-substituted derivatives, and 9-diazofluorene. Acetonitrile was the solvent in most experiments, but the effect of changing to chloroform and methanol was investigated. In almost all cases singlet oxygen was generated by Methylene-Blue photosensitisation, thus ensuring that the reactive species was in the $^1\Delta_g$ state.[6] However, in some experiments triphenyl phosphite ozonide was used as a non-photochemical source of singlet oxygen.[7] A few experiments on the photo-oxidation induced by direct irradiation of the diazoalkane were also carried out.

Our conclusions are based largely on structural and environmental influences on the reactivity of diazoalkanes with singlet oxygen. The reactivity results were obtained either by determination of the so-called β value, the ratio of the rate constants for quenching of

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† During the course of this work, the correctness of this idea was established when Higley and Murray [3] reported evidence for such a reaction under conditions almost identical with our own.

[1] Part 12, D. Bethell, M. R. Brinkman, J. Hayes, and K. McDonald, *J.C.S. Perkin II*, 1976, 966.

[2] D. Bethell and R. G. Wilkinson, *J.C.S. Chem. Comm.*, 1970, 1178.

[3] D. P. Higley and R. W. Murray, *J. Amer. Chem. Soc.*, 1974, **96**, 3330.

[4] *Cf.* H. Prinzbach and J. H. Hartenstein, *Angew. Chem. Internat. Edn.*, 1962, **1**, 507; 1963, **2**, 477; J. N. Bradley and A. Ledwith, *J. Chem. Soc.* (*B*), 1967, 96.

[5] (*a*) P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, 1962, **84**, 3408; (*b*) W. Kirmse, L. Horner, and A. W. Hoffmann, *Annalen*, 1958, **614**, 19; (*c*) W. Kirmse, *ibid.*, 1963, **666**, 9; (*d*) R. W. Murray and A. Suzui, *J. Amer. Chem. Soc.*, 1971, **93**, 4963; 1973, **95**, 3343; (*e*) G. A. Hamilton and J. R. Giacin, *ibid.*, 1966, **88**, 1584.

[6] A. U. Khan and D. R. Kearns, A.C.S. Advances in Chemistry Series, No. 77, 1965, p. 155.

[7] (*a*) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, 1968, **90**, 537, 4161; 1969, **91**, 5358; (*b*) P. D. Bartlett and G. D. Mendenhall, *ibid.*, 1970, **92**, 210; (*c*) A. P. Schaap and P. D. Bartlett, *ibid.*, 1970, **92**, 6055.

singlet oxygen (k_q) to that for reaction with an acceptor species (k_A) derived from plots of the reciprocal of the quantum yield (or its equivalent) against the reciprocal of the acceptor concentration, or from competitive reactions. Additionally, we have investigated the products of the reaction, the influence of singlet oxygen quenchers, and finally the fate of a ^{15}N-label specifically located at the terminal position in 9-diazofluorene, when the diazoalkane reacts with singlet oxygen.

RESULTS

Reaction of Singlet Oxygen with Diazodiphenylmethane and 9-Diazofluorene.—Under the conditions used in the present investigation, Methylene Blue sensitised photo-oxidation did not take place to a measurable extent at concentrations above 10^{-3}M in oxygen-saturated acetonitrile. For example, with $[Ph_2CN_2]_0 = 1 \times 10^{-2}$M, there was no decomposition after 7 min irradiation at 650 nm of Methylene Blue (O.D. 1.1 at 650 nm). At diazoalkane concentrations below 10^{-3}M, however, photo-oxidation occurred smoothly. In acetonitrile the diazoalkane was quantitatively converted into benzophenone; in methanol, however, small amounts of other products were also formed, but these were not identified. 9-Diazofluorene behaved similarly in all respects, yielding fluorenone at low concentrations and showing no photo-oxidation at concentrations $>10^{-3}$M for irradiation times up to 25 min.

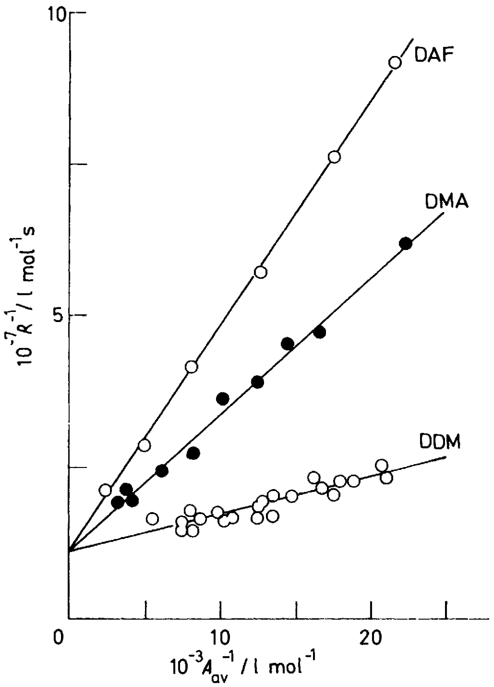

FIGURE 1 Dependence of the rate of photo-oxidation of 9-diazofluorene (DAF), diazodiphenylmethane (DDM), and 9,10-dimethylanthracene (DMA) on concentration. For DDM, the abscissa scale is twice that shown. Linear regression analysis gives the following intercepts (10^{-7} l mol^{-1} s) and slopes (10^{-3} s): DAF, 1.13 ± 0.01, 3.71 ± 0.08; DDM, 1.09 ± 0.02, 0.313 ± 0.009; DMA, 1.14 ± 0.07, 2.23 ± 0.05

The exhaust gases from the photochemical reactor were passed through two traps, the first at −95 °C (toluene–liquid nitrogen) and the second at −131 °C (n-pentane–liquid nitrogen). The contents of the second trap after reactions in acetonitrile were investigated mass spectrometrically and showed peaks at *m/e* 44, 41, 40, 39, 38, 32, 31, 30, 29, and 28. Of these, the peaks at *m/e* 44, 32, and 28 were present in the background spectrum. The group of peaks *m/e* 41—38 correspond to ions produced from residual acetonitrile; their intensity varied from run to run. Authentic nitrous oxide shows peaks at *m/e* 44 (N_2O^+), 30 (NO^+), and 28 (N_2^+). The presence of the peak at *m/e* 30 (accurate masses, 29.999 from Ph_2CN_2, 29.999 from FlN_2) indicates that the exhaust gases from the photolysis contain N_2O (NO^+ requires *m/e* 29.997 99).

In quantitative experiments, the (initial) rate of decrease of the diazoalkane concentration (R/mol l^{-1} s^{-1}) was determined spectrophotometrically as a function of the average diazoalkane concentration (A_{av}) over the irradiation interval. Graphs of R^{-1} against A_{av}^{-1} were straight lines as shown in Figure 1 for Methylene Blue sensitised photo-oxidations in acetonitrile of diazodiphenylmethane and 9-diazofluorene. Also included in Figure 1 is a similar plot for the photo-oxidation of 9,10-dimethylanthracene which is known to react readily with singlet oxygen giving the 9,10-*endo*-peroxide. It is to be noted that all three compounds yield graphs having the same intercept within experimental error, although with different slopes. No appreciable decomposition of diazoalkane takes place in the absence of light, or oxygen, or Methylene Blue.

These results are consistent only with reaction of the acceptor molecules with singlet molecular oxygen ($^1O_2$). The rate of disappearance of an acceptor A is given by equation (1) where K, the rate of generation of singlet oxygen, is

$$R = \frac{-\mathrm{d}A}{\mathrm{d}t} = \frac{\mathrm{d}[^1O_2]}{\mathrm{d}t} \cdot \frac{k_A A}{k_A A + k_q} = \frac{K k_A A}{k_A A + k_q} \quad (1)$$

constant if the intensity of absorbed light and the triplet oxygen concentration remain constant and if the changes in reactant and product concentration do not cause changes in the efficiency of the processes leading to singlet oxygen formation. With oxygen-saturated solutions containing low concentrations of diazoalkane, this is so. At higher diazoalkane concentrations, however, the formation of singlet oxygen is impaired somewhat as shown by the observation (Table 1) that the photo-oxidation of 9,10-dimethylanthracene is inhibited to an extent greater than expected from the competitive consumption of singlet oxygen by the diazoalkane. From equation (1) it can be seen that plots of R^{-1} against A^{-1} should be linear provided that measurements are restricted to a period over which the instantaneous acceptor concentration can be satisfactorily

TABLE 1

Effect of 9-diazofluorene (DAF) concentration on the Methylene Blue sensitised photo-oxidation of 9,10-dimethylanthracene (DMA) in oxygen saturated acetonitrile

$10^4[DMA]_0$/M	$10^4[DAF]_0$/M	10^9R_{obs} [a]	10^9R_{calc} [b]
1.67	1.67	24.3	(24.3)
1.67	20	5.5	7.6
1.67	100	0.0	1.9

[a] Observed average rate of DMA consumption (mol l^{-1} s^{-1}) over the irradiation interval. Values were reproducible to within 10%. [b] Calculated average rate of DMA consumption using rate constants for reactions of DMA and DAF with $^1O_2$ derived from experiments at low acceptor concentration, together with the rate constant for quenching of $^1O_2$.

replaced by an average value A_{av}. The ratio of the slope to the intercept then gives k_q/k_A (= β), the value decreasing with increasing reactivity of the acceptor. The intercept itself gives the rate of production of singlet oxygen under the reaction conditions independent of the acceptor used.*

Additional evidence that singlet oxygen is responsible for the photo-oxidation of 9-diazofluorene comes from the observation that R falls to *ca.* 11% of its original value when diazabicyclo[2.2.2]octane (DABCO) (10^{-3}M) is added to a reaction mixture. Similarly DABCO reduced the rate of photo-oxidation of 9,10-dimethylanthracene by a factor of *ca.* 5. DABCO is known to be an effective quencher of singlet oxygen.[10]

Direct irradiation of the diazoalkane was also investigated. With diphenyldiazomethane concentrations below 10^{-3}M, no decomposition occurred over extended periods of irradiation at 545 nm in 10 cm cells. Irradiation at 311 nm gave smooth disappearance of the diazo-compound, but R showed no detectable dependence on the oxygen concentration in the saturating gas (O_2, air, nitrogen) and the photo-oxidation product, benzophenone, was accompanied by the corresponding ketazine. The absence of a clear dependence of R on the oxygen concentration provides evidence to substantiate earlier interpretations [5] of such photolyses in terms of carbene formation; photo-oxidation then results from trapping of the carbene by ground-state oxygen.[11] This conclusion is confirmed by the observation that DABCO reduces R by an amount small enough to lie within the experimental error of the measurements. However, in experiments in which 9-diazofluorene or diazodiphenylmethane (2×10^{-4}M) were irradiated (311 nm) in the presence of oxygen, 9,10-dimethylanthracene (5×10^{-5}M) underwent *ca.* 30% photo-oxidation to the *endo*-peroxide, and this was largely suppressed by DABCO (1×10^{-3}M); no reaction was observed in the absence of the diazoalkane when DABCO was excluded.

Relative Reactivities.—The relative reactivities of acceptors A—C *etc.* towards singlet oxygen are given by the ratios of their β-values (β_A, β_B *etc*), as shown in equation (2). The relative reactivity of a given pair of acceptors can also be obtained by direct competition by using equation (3), where the subscripts i and f refer to acceptor concentrations before and after irradiation (*ca.* 80% reaction).

$$k_A/k_B = \beta_B/\beta_A \tag{2}$$

$$\frac{k_A}{k_B} = \frac{\log (A_i/A_f)}{\log (B_i/B_f)} \tag{3}$$

Table 2 compares the reactivities in photo-oxidation of 9-diazofluorene and diazodiphenylmethane with that of 9,10-dimethylanthracene as determined by these two procedures. Also included is a value obtained competitively for reactions of the diazoalkanes with triphenylphosphite ozonide. The agreement between the two methods is good for photo-oxidations, confirming the correctness of our interpretation of the reaction in terms of the partitioning of singlet oxygen. The relative reactivities obtained competitively by using triphenyl phosphite ozonide did not show such good agreement, perhaps because the ozonide reacted directly with acceptors to give the same products as singlet oxygen but in different proportions.[7b,c] Finally in Table 2 we note that diazodiphenylmethane is *ca.* 12 times more reactive than 9-diazofluorene [12] and 1.8 times more reactive than diazobis-4-chlorophenylmethane, consistent with electrophilic attack by singlet oxygen on the diazoalkanes.

TABLE 2

Reactivities of some diazodiarylmethanes relative to 9,10-dimethylanthracene towards singlet oxygen in acetonitrile solution

Acceptor, A	$10^4\ \beta_A$/M (n) [a]	k_A/k_B	
		β_B/β_A	Competition [b]
DMA (B)	1.95 ± 0.35 (10)	(1.00)	(1.00)
DAF	3.27 ± 0.60 (6)	0.596	0.587, 0.735 [c,d]
DDM	0.288 ± 0.045 (22)	6.77	8.0, 13.9,[c] 12.2 [c,d]
Cl_2DDM [e]	0.501 ± 0.11 (16)	3.89	4.29

[a] Average values of β_A are given with 95% confidence limits. n = Number of data points used in the correlation. [b] Average values from at least three separate spectrophotometric determinations, all of which agreed to within 10% of the average. [c] $(PhO)_3PO_3$ used as a thermal source of singlet oxygen. [d] $CHCl_3$ as solvent. [e] Diazo-4,4′-dichlorodiphenylmethane.

A wider study of substituent effects on the reactivity of diazodiphenylmethane was undertaken using both acetonitrile and methanol as solvent. For acetonitrile, the competitive procedure was used with 9,10-dimethylanthracene as standard. For methanol, the same technique could not be applied because unidentified by-products interfered with the spectrophotometric analysis at the high conversions normally used. A modification of the β ratio method was used instead since the interference was negligible at the low conversions used for the R^{-1} against A_{av}^{-1} plots; relative reactivities were evaluated from ratios of the slopes of such plots because the intercepts were small and subject to relatively large uncertainties. The results are in Table 3.

TABLE 3

Substituent effects on the reactivity of diazodiphenylmethane towards singlet oxygen

Substituents, X in Ph_2CN_2	k_X/k_H		Σσ
	MeOH [a]	CH_3CN [b]	
H	(1.00)	(1.00)	0
4-Br		0.648 ± 0.032	0.232
4,4′-Cl_2	0.577 ± 0.038	0.537 ± 0.027	0.452
4,4′-Me_2	1.41 ± 0.085	1.65 ± 0.083	−0.340
4-OMe		1.44 ± 0.072	−0.268
ρ	-0.49_2	-0.63_1	
r	0.999	0.995	

[a] Values with probable error from determinations of β assuming a constant intercept. [b] Values with probable error from competitive experiments (see Table 1, footnote *b*).

Both sets of relative reactivities are well correlated by Hammett σ values, giving rather similar, low negative slopes, −0.63 (CH_3CN) and −0.49 (CH_3OH). Again, electrophilic

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* Conventionally, plots of the reciprocal of the quantum yield for photo-oxidation, ϕ^{-1} against A_{av}^{-1} are used, the intercept then giving the quantum yield for production of singlet oxygen (ϕ_0) which is characteristic of the sensitiser. In our hands, actinometry using potassium reineckate [8] did not give very reproducible results, and we have preferred to use R rather than ϕ to evaluate β. Our value for ϕ_0 for Methylene Blue in acetontrile is 0.364 ± 0.044 (95% confidence limits). This is to be compared with Usui's value of 0.52 in methanol and ethanol.[9]

[8] E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, 1966, **88**, 394.

[9] Y. Usui, *Chem. Letters*, 1973, 744.

[10] C. Ouannès and T. Wilson, *J. Amer. Chem. Soc.*, 1968, **90**, 6527; C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. New York Acad. Sci.*, 1970, **171**, 139.

[11] D. Bethell, G. Stevens, and P. Tickle, *Chem. Comm.*, 1970, 792.

[12] *Cf.* D. Bethell and K. C. Brown, *J.C.S. Perkin II*, 1972, 895.

attack by singlet oxygen is indicated, and the transition states in the two solvents would seem to have rather similar polarities.

The examination of solvent effects on the reactions of singlet oxygen was extended to chloroform. Table 4 compares the β-values for 9,10-dimethylanthracene, 9-diazofluorene, and diazodiphenylmethane in acetonitrile, methanol, and chloroform. By combining the values of β with literature values[13,14] of the lifetime of singlet oxygen, τ (taken to be $1/k_q$), the absolute reactivity (k_A) of the acceptors in the three solvents can be derived. The largest variation in k_A, by a factor of 3.6, was observed for the standard singlet oxygen acceptor, 9,10-dimethylanthracene; for the diazoalkanes, the variation is substantially less.

TABLE 4

The influence of solvent on the reactivity of singlet oxygen acceptors

		Solvent		
		CH_3OH [a]	CH_3CN	$CHCl_3$
$10^6\tau/s$[12,13]		7	30	60
DMA	$10^3\beta/M$	2.96	0.195	0.181
		±0.60	±0.035	±0.068
	$10^{-9}\,k_A/l\ mol^{-1}\,s^{-1}$	0.048	0.171	0.092
DAF	$10^3\,\beta/M$	4.22	0.327	0.327
		±0.65	±0.060	±0.065
	$10^{-9}\,k_A/l\ mol^{-1}\,s^{-1}$	0.034	0.102	0.051
DDM	$10^3\,\beta/M$	0.208	0.029	0.020
		±0.039	±0.004 5	±0.004 0
	$10^{-9}\,k_A/l\ mol^{-1}\,s^{-1}$	0.69	1.16	0.83
$10^{-9}\,k_{diff}$ [b]$/l\ mol^{-1}\,s^{-1}$		12.1	19.2	12.2

[a] Because intercepts of plots of R^{-1} against $A^{-1}{}_{av}$ were small and subject to a large uncertainty, β values in MeOH are calculated assuming that the intercept is constant for all acceptors and equal to the average value obtained in determinations of β in CH_3CN and $CHCl_3$. Using observed β values in MeOH does not alter the pattern of results and conclusion. [b] Rate constant for diffusion, calculated from the expression,[15] $k_{diff} = 8RT/3\,000\eta$.

Labelling Experiments.—In order to trace the course of the reaction between diazo-compounds and singlet oxygen, in particular the production of nitrous oxide, photo-oxidation was carried out on 9-diazofluorene which had been labelled at its terminal nitrogen atom with ^{15}N. The labelled compound was prepared by treatment of fluorenone oxime with [^{15}N]chloramine generated from [^{15}N]ammonium chloride (85% enrichment) by treatment with sodium hypochlorite solution (Forster's method).[16] In our hands, the method did not yield enough 9-diazofluorene to permit recrystallisation, but a solution of sufficient concentration to allow examination of the exhaust gases from Methylene Blue sensitised photo-oxidation was obtained. The exhaust gases were passed through a trap cooled in pentane–liquid nitrogen (−131 °C) and the condensed material was analysed mass spectrometrically as before. The results were compared with those from mass spectrometric analysis of the condensate from photo-oxidation of 9-diazofluorene of normal isotopic composition prepared in a manner identical to that for the labelled diazo-compound (Table 5).

Peaks in the mass spectra at *m/e* 44 and 28 were ignored because of the presence of intense peaks in the background spectrum of the mass spectrometer; only the peaks at *m/e* 30 and 31 were considered. Unlabelled 9-diazofluorene gave rise to a condensate which produced peaks at *m/e ca.* 30 and 31 which were not derived from N_2O. These were taken as standards against which to estimate the intensity of the N_2O fragments so as to allow for differences in the amounts of diazo-compound decomposed in the two experiments. It can be seen in Table 5 that the effect of introducing ^{15}N at the terminal position of the diazoalkane is to diminish the intensity of the peak at *m/e* 29.999 and produce a new peak at 31.000, in keeping with the production from the labelled diazoalkane largely of $^{14}N^{15}NO$ (and hence $^{15}NO^+$ in the mass spectrometer) rather than $^{15}N^{14}NO$ (which should give only ^{14}NO). There seems to be no evidence for scrambling of the label during fragmentation of N_2O in the mass spectrometer.

TABLE 5

Mass spectrometric analysis of the condensate (−131 °C) from the exhaust gases from Methylene Blue sensitised photo-oxidation of 9-diazofluorene (FlN_2)

Labelled [a] $Fl^{14}N^{15}N$		Unlabelled $Fl^{14}N^{14}N$	
m/e [b]	Relative intensity [c]	*m/e* [b]	Relative intensity [c]
29.999	0.08	29.999	0.33
30.032	(1.00)	30.032	(1.00)
31.000	0.17	31.000	Not detected
31.018	(1.00)	31.018	(1.00)

[a] Not more than 85% enrichment. [b] $^{14}NO^+$ requires 29.998; ^{15}NO requires 30.995; $CH_4{}^{14}N^+$ requires 30.034; CH_3O^+ requires 31.018. [c] For each N_2O fragment, the intensity is given relative to the nearest background peak.

DISCUSSION

Mechanism of Methylene Blue sensitised Photo-oxidation.—The following evidence indicates that Methylene-Blue-sensitised photo-oxidation of diazodiphenylmethane and 9-diazofluorene takes place by the generation of singlet molecular oxygen which is subsequently partitioned between reaction with the diazo-compound and quenching.

(a) There is abundant evidence that irradiation of Methylene Blue in the presence of oxygen leads to the production of singlet oxygen.[6,9,13] DABCO is known to quench singlet oxygen efficiently and it has been found to suppress the photo-oxidation of the diazoalkanes.

(b) The dependence of the rate of disappearance of diazodiphenylmethane and 9-diazofluorene on the concentration of the diazo-compound is consistent with competition for a reactive intermediate between reaction with the diazo-compound and some other process such as quenching. The identity of the intercepts in Figure 1 for the two diazo-compounds and for 9,10-dimethylanthracene, a good acceptor for singlet oxygen, indicates that all three compounds react with the same intermediate. The quantum yield for formation of this intermediate (ϕ_0), determined approximately by us, is similar to literature estimates of the quantum yield for singlet oxygen formation sensitised by Methylene Blue.

(c) The reactivities of the diazoalkanes relative to that of 9,10-dimethylanthracene in thermal reactions with

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[13] R. W. Denny and A. Nickon, *Org. Reactions*, 1973, **20**, 174.

[14] P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, 1972, **94**, 1029, 7244; R. H. Young, A. Brewer, and R. A. Keller, *ibid.*, 1973, **95**, 375; see also C. A. Long and D. R. Kearns, *ibid.*, 1975, **97**, 2018.

[15] E. F. Caldin, 'Fast Reactions in Solution,' Blackwell Scientific Publications, Oxford, 1964, p. 10.

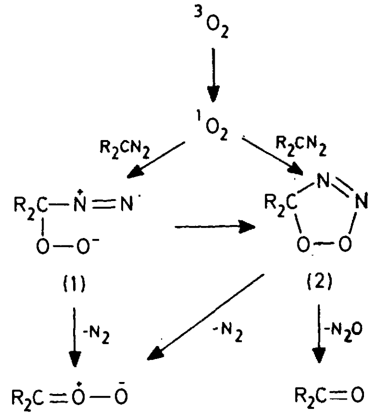
[16] (*a*) M. O. Forster, *J. Chem. Soc.*, 1915, **107**, 260; (*b*) J. Meinwald, *J. Amer. Chem. Soc.*, 1960, **82**, 2857.

triphenyl phosphite ozonide, a known source of singlet oxygen, are close enough to those determined in Methylene Blue sensitised photo-oxidation to indicate the involvement of singlet oxygen in the photochemical reactions.

(d) The observation that diazodiphenylmethane is more reactive than 9-diazofluorene and that the ρ value from relative reactivities of *para*-substituted diazodiphenylmethanes is negative in both acetonitrile and methanol confirm that photo-oxidation involves attack on the diazoalkane by an electrophile.

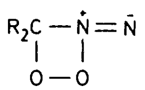
This evidence thus supplements that of Higley and Murray. Additional mechanistic conclusions can be drawn by combining this evidence with our other results. Thus, the reactivities of the diazoalkanes and dimethylanthracene are little affected by changes in the polarity or solvating power of the solvent; Hammett ρ values are small and negative in both acetonitrile and methanol. Moreover in the course of photo-oxidation, nitrous oxide is produced in which the oxygen atom is bonded to the nitrogen atom which was terminal in the diazo-compound.

Possible mechanisms are illustrated in the Scheme. One pathway involves attack by one of the oxygen atoms of singlet oxygen on the diazo-carbon atom to give the zwitterionic intermediate (1); the other takes place by 1,3-dipolar cycloaddition of the diazo-group and singlet oxygen yielding the dioxapyrazoline ring system (2), which could also result from the cyclisation of (1) as suggested by Higley and Murray.



SCHEME

An alternative mode of cycloaddition, the [2 + 2] process giving the intermediate heterocycle (3) is excluded by the labelling experiment, since terminally ^{15}N-labelled diazoalkane would yield $^{15}N^{14}NO$ and hence only $^{14}NO^+$ in its mass spectrum. This mode of cycloaddition has, however, been suggested in the reaction of singlet oxygen (from triphenyl phosphite ozonide) with diphenylketen,[17] an acceptor which is isoelectronic with diazodiphenylmethane. By analogy with the peroxylactone (dioxetanone) produced from diphenylketen, intermediate (3) might be expected to extrude nitrous oxide and produce benzophenone in its first excited triplet state. Diazodiphenylmethane was photo-oxidised in the presence of *trans*-stilbene, but no conversion into *cis*-stilbene was detected, indicating that triplet excited benzophenone was not appreciably formed.



(3)

The low sensitivity of the rate of reaction of singlet oxygen with diazoalkanes to changes in the solvent polarity is evidence against reaction by way of a transition state involving substantial change in charge separation compared with the reactants.[18] The formation of the zwitterionic intermediate (1) might be expected to take place by way of a transition state in which an increased charge separation had occurred. We conclude that this mechanism can be ruled out and that a concerted 1,3-dipolar cycloaddition is the preferred pathway. It should be borne in mind that, although most limiting structures for diazoalkanes are zwitterionic, the molecules themselves generally have rather low dipole moments;[19] for example, for diazodiphenylmethane, $\mu = 1.42$ D at 0° in carbon tetrachloride.[20] The decrease in charge distribution in the transition state leading to (2) the structure of which can be written without formal charges, is therefore likely to be small. 9,10-Addition of singlet oxygen to 9,10-dimethylanthracene is believed to be a concerted cycloaddition (*cf.* the Diels–Alder reaction) and this shows a similar solvent dependence of reaction rate to the diazoalkane reaction.

The ρ values of -0.63 and -0.49 from the correlation with σ of the reactivities of *para*-substituted diazodiphenylmethanes supports the view that the addition of singlet oxygen is concerted. A somewhat more negative value (-0.84) has been observed in the concerted addition of singlet oxygen to *para*-substituted 2-phenylfurans in methanol,[21] and the ene reaction of singlet oxygen with α,β,β-trimethylstyrenes gives a ρ value of -0.92 in the same solvent.[22] By contrast, for electrophilic attack on diazodiarylmethanes giving an open-chain zwitterion by proton transfer from toluene-*p*-sulphonic acid is slightly aqueous acetonitrile, ρ was -1.99 at 29 °C.[23] However, one must be cautious in interpreting these low ρ values for reactions involving singlet oxygen. As shown in Table 4, the rate of diffusion together of two reactants in the solvents used

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[17] L. J. Bollyky, *J. Amer. Chem. Soc.*, 1970, **92**, 3230; see also, W. Adam, G. A. Simpson, and F. Yany, *J. Phys. Chem.*, 1975, **78**, 2559.

[18] For a caveat, see, however, R. Gompper, *Angew. Chem. Internat. Edn.*, 1969, **8**, 312.

[19] G. W. Cowell and A. Ledwith, *Quart. Rev.*, 1970, **24**, 119.

[20] N. V. Sidgwick, L. E. Sutton, and W. Thomas, *J. Chem. Soc.*, 1933, 406.

[21] R. H. Young, R. L. Martin, N. Chinh, C. Mallon, and R. H. Kayser, *Canad. J. Chem.*, 1972, **50**, 932.

[22] C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, 1971, **93**, 5162.

[23] D. Bethell and J. D. Callister, *J. Chem. Soc.*, 1963, 3808, 3806.

(k_{diff}) is 1—2 × 10^{10} l mol^{-1} s^{-1}, which is only about an order of magnitude greater than the rate constant for reaction of singlet oxygen with diazodiphenylmethane. Thus an early (*i.e.*, reactant-like) transition state might be expected and consequently a low ρ value independent of the detailed mechanism of reaction.[24] Nevertheless, taken in conjunction with the other evidence, such as the substantial difference in reactivity between diazodiphenylmethane and 9-diazofluorene, we believe that the small effect of changing the *p*-substituent to be indicative of a transition state with a charge separation little different from that of the reactants, namely, a cyclic transition state leading to the 1,3-dipolar cycloaddition products (2).

That (2) is indeed an intermediate follows from the labelling experiment. Decomposition should produce nitrous oxide in which oxygen is bonded to the labelled nitrogen. In the mass spectrum of the condensate from the exhaust gases, the NO^+ fragment should contain all the label and the $^{14}NO^+$ peak should be reduced in intensity to a level determined by the degree of enrichment of the diazoalkane. Our observations are consistent with these predictions, and we conclude that the N_2O produced in the photo-oxidation of 9-diazofluorene arises from an intermediate of type (2). We stress that this experiment does not prove that the only mechanism of decomposition of the diazoalkane is *via* (2); that conclusion is suggested by the kinetic results. Indeed, as indicated earlier, the formation of the ketone is not quantitative in methanol; at least two other products are detectable by t.l.c., and u.v. spectrophotometry.

The present results provide a satisfying explanation of observations [25] on the ozonolysis of diazoalkanes giving the corresponding carbonyl compound, provided that it is assumed that the initial ozone–diazoalkane adduct breaks down to liberate nitrogen and one molecule of singlet oxygen. From the present results it would be predicted that diazodiphenylmethane, because of its high reactivity, would trap this singlet oxygen efficiently, leading to a 2 : 1 overall stoicheiometry. Reaction with 9-diazofluorene would compete less effectively with quenching of singlet oxygen and give a lower diazoalkane : ozone ratio. Further, for a given diazoalkane, the stoicheiometry would be higher in solvents such as chlorinated methanes than in methanol because of the lower value of k_q. Such predictions are borne out in practice, and indeed the formation of nitrous oxide in diazoalkane oxidation by the decomposition of (2) was first proposed in the ozonolysis.

Orbital Symmetry Considerations.—If it is accepted that all the reaction of singlet oxygen with diaryldiazoalkanes takes place by way of (2), then we are dealing with a conventional 1,3-dipolar cycloaddition. Kearns [26] has shown how correlation diagrams for the concerted cycloaddition of singlet oxygen to dienes are to be constructed, and his diagrams can be readily modified for the addition to a 1,3-dipole. The modification suggests that the 1,3-dipolar cycloaddition should be more exothermic than the addition to the diene, leading to an earlier transition state.

For present purposes, however, it is more convenient to discuss the reaction in frontier molecular orbital terms.[27] Figure 2 shows the frontier orbitals calculated by the CNDO/2 method for 9-diazofluorene; both are π-type orbitals perpendicular to the molecular plane (*cf.* diazomethane.)[28] Also shown are the HOMO and LUMO of $^1\Delta_g$ oxygen which have the same symmetry but are orthogonal. It can be seen that concerted suprafacial cycloaddition is allowed in two modes: (i) by using the diazoalkane HOMO and oxygen LUMO in either a 1,2(*N*,*N*)- or a 1,3-sense, and (ii) in a 1,2(*C*,*N* or *N*,*N*)-sense using the diazoalkane LUMO and singlet oxygen HOMO. From the magnitudes of the coefficients, the favoured pathways should be 1,3-cycloaddition in mode (i) and 1,2(*N*,*N*)-cycloaddition in mode (ii). The observation in the labelling experiment clearly indicates that mode (i) is the preferred pathway, *i.e.* the diazoalkane HOMO and singlet oxygen LUMO are the interacting orbitals. Singlet oxygen thus behaves like an electron-deficient alkene [30] or a carbene.

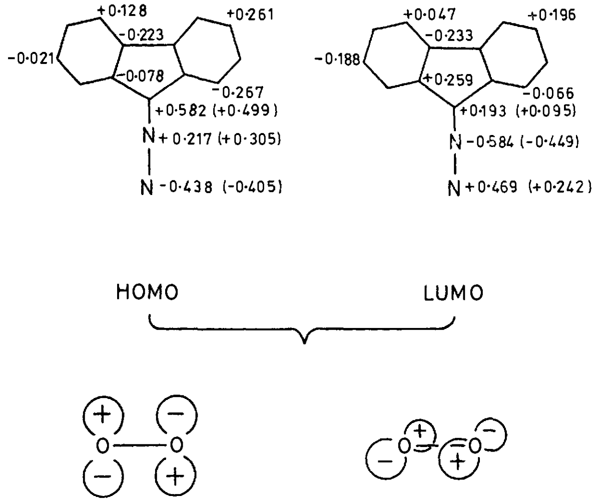

FIGURE 2 Frontier orbital coefficients for 9-diazofluorene and frontier orbital symmetries for singlet oxygen. Assumed geometry: 9-diazofluorene, N–N 1.13 Å, C–N 1.34 Å; 2,2′-biphenyleneketen, C=O 1.16 Å, C=C 1.33 Å. The remainder of both molecules was taken to be identical with fluorene.[29] Corresponding coefficients for 2,2′-biphenyleneketen in parentheses

It is worth noting that a similar treatment of the

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[24] *Cf.* D. Bethell and P. N. Clare, *J.C.S. Perkin II*, 1972, 1464.

[25] A. M. Reader, P. S. Bailey, and H. M. White, *J. Org. Chem.*, 1965, **30**, 784; A. M. Reader and P. S. Bailey, *Chem. and Ind.*, 1961, 1063.

[26] D. R. Kearns, *J. Amer. Chem. Soc.*, 1969, **91**, 6554.

[27] K. N. Houk, *J. Amer. Chem. Soc.*, 1972, **94**, 8953; K. N. Houk, J. Sims, R. E. Duke, R. W. Strozier, and J. K. George, *ibid.*, 1973, **95**, 7287; K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, p. 7301; K. N. Houk, *Accounts Chem. Res.*, 1975, **8**, 361; J. Bastide, N. El Ghandour, and O. Henri-Rousseau, *Bull. Soc. chim. France*, 1973, 2290; J. Bastide and O. Henri-Rousseau, *ibid.*, p. 2294.

[28] W. L. Jorgensen and L. Salem, 'The Organic Chemist's Book of Orbitals,' Academic Press, New York, 1973, p. 126.

[29] D. M. Burns and J. Iball, *Proc. Roy. Soc.*, 1955, *Ser. A*, **227**, 200.

[30] R. Sustmann, *Tetrahedron Letters*, 1971, 2717.

(concerted) addition of singlet oxygen to biphenyleneketen, which is isoelectronic with 9-diazofluorene, leads to similar conclusions, although there are minor differences in coefficients. 1,2-Cycloaddition to the carbon–carbon double bond is predicted to be less likely than 1,3-cycloaddition in mode (i) and would presumably involve a $({}_\pi2_s + {}_\pi2_a)$-type pathway. The observed reaction of singlet oxygen with diphenylketen gives benzophenone and carbon dioxide *via* a peroxylactone, the 1,2-cycloaddition product; the 1,3-cycloaddition on the other hand would lead to an intermediate cyclic dioxacarbene. Nevertheless, this difference in behaviour between the isoelectronic singlet oxygen acceptors merits further investigation.

Direct Photo-oxidation of Diazoalkanes.—Our evidence on direct irradiation of diazodiphenylmethane in the presence of oxygen indicates that photolysis to the carbene is the major reaction path. The accompanying photo-oxidation of 9,10-dimethylanthracene and its quenching by DABCO suggest, however, that some singlet oxygen is generated in the system. If this is indeed so, then, using the reactivities of diazodiphenylmethane and 9,10-dimethylanthracene obtained from the Methylene Blue sensitised photo-oxidation, it can be calculated that only *ca.* 10% of the diazoalkane consumed should have reacted with singlet oxygen. This may explain our failure conclusively to detect this reaction through its suppression by DABCO; more detailed investigation would be necessary.

EXPERIMENTAL

Materials.—The diazoalkanes were prepared and purified as described in previous papers. Methylene Blue was a commercial sample used without further purification. Acetonitrile was dried by using phosphorus pentaoxide and methanol by using magnesium methoxide prior to fractionation. Chloroform was of analytical reagent grade and contained 2% ethanol.

Photolyses.—All photolyses were conducted at room temperature. Arrangements for the rate studies and quantum-yield determinations were as previously described.[24] A 50 W quartz–iodine lamp from which the 650 nm radiation was selected by using an interference filter (Spindler and Hoyer, Göttingen) was used in the Methylene Blue sensitised photo-oxidations. The same source provided the 545 nm radiation for direct photolysis; the 311 nm radiation was selected from the output of a 250 W medium pressure mercury arc.

Potassium reineckate was used for actinometry at 650 nm.[8] Although reproducibility between replicate determinations was relatively poor (standard deviation ±20% of the mean intensity), the measurements showed no trend over the period of the study, indicating substantial constancy of the intensity of the light reaching the reaction mixture.

The progress of photolyses was monitored by u.v. spectrophotometry at 300 (diazodiphenylmethane), 348 (9-diazofluorene), or 376 nm (9,10-dimethylanthracene). Samples of the reaction mixtures were diluted with the appropriate solvent containining Methylene Blue, the diluent also being used as the reference solution. Corrections for thermal decomposition were applied in some cases by using changes in the absorbance of a portion of the reaction mixture maintained under conditions identical with those of the photolysed solution but kept in the dark. Because of the sensitivity of reaction mixtures to even short exposure to daylight, all operations were conducted in a dark room equipped with a safelight incorporating a Wratten OB filter.

Product Studies.—Products from photolyses in the very dilute solutions used were identified by their t.l.c. behaviour and by u.v. spectroscopy. Comparisons were made with authentic specimens of the likely products, benzophenone, substituted benzophenones, fluorenone, and the corresponding azines, and 9,10-dimethylanthracene 9,10-*endo*-peroxide.

In order to investigate gaseous products of the reaction, the exhaust gases were passed first through a trap held at −95 °C (liquid nitrogen–toluene), which was intended to remove solvent, and then through a trap maintained at −131° (liquid nitrogen–pentane) in order to retain any nitrous oxide (m.p. −102.3°). At the end of the photolysis, the trap was sealed off by taps, allowed to warm to room temperature, and transferred to the mass spectrometer (MS 902) to which it was attached through the cold inlet system. Mass spectra recorded on samples of the gas showed the presence of N_2O and residual acetonitrile solvent. Accurate masses were obtained from the spectra by interpolation.

Preparation of ^{15}N-*Labelled 9-Diazofluorene*.—A slightly modified version of Meinwald's procedure[16b] was used. [^{15}N]Ammonium chloride (1 g; 85% enriched) and fluorenone oxime (1 g) were mixed with water (40 ml) and light petroleum (b.p. 40—60°; 60 ml) together with sodium hydroxide (3 pellets). The mixture was stirred magnetically in a cold water-bath, and aqueous sodium hypochlorite solution (*ca.* 1M; 10 ml) was added dropwise during 45 min. When all the hypochlorite had been added, stirring was continued for a further 5 min, and the pink organic layer was separated. Further 9-diazofluorene was extracted by using a second portion of light petroleum (60 ml) and stirring for another 10 min. A second treatment of the aqueous layer with sodium hypochlorite (5 ml) and extraction with light petroleum gave yet more product. The extracts were combined, dried, and the solvent removed at low temperature. The residue was insufficient to permit crystallisation and was taken up immediately in acetonitrile (14.5 ml) containing Methylene Blue.

For comparison, a sample of unlabelled 9-diazofluorene was prepared under identical conditions.

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