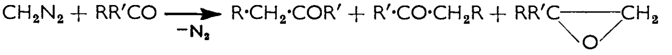
60. *The Reactions of Carbenes and Diazoalkanes with Ketones. Part II.*[1] *The Absorption Spectra of Diazoalkanes: the Photochemical Reaction between Diazomethane and Acetone in the Presence of Hydroxylic Compounds.*

By J. N. Bradley, G. W. Cowell, and A. Ledwith.

Photolysis of diazomethane in acetone containing hydroxylic compounds produces mainly ethyl methyl ketone and 2,2-dimethyloxiran by a reaction which does not involve singlet carbene. However, hydroxylic compounds do not affect the reaction of singlet carbene with alkanes and alkenes.

Absorption spectra for the lower diazoalkanes are reported.

Reaction of diazomethane with carbonyl compounds[1,2] leads mainly to the isomeric ketones (Ia and b) and the corresponding oxiran (epoxide) (II):



(Ia) (Ib) (II)

Usually the reaction is carried out in an inert solvent such as ether, and a suitable hydroxylic compound is added to accelerate the reaction.

In the case of acetone, R = R′ = Me, there is only one ketonic product, ethyl methyl ketone. Diazomethane reacts with acetone in the presence of alcohols to give this ketone and the corresponding oxiran (II; R = R′ = Me) in roughly equal amounts.[2] In the present work it is shown that there is no reaction between diazomethane and acetone in the dark unless hydroxylic compounds are present. When the reaction is carried out under irradiation with sunlight or ultraviolet light, both the nature and relative amounts of products depend critically upon the concentration of added catalyst and the temperature. Several different photochemical processes can occur in the reaction between diazomethane and acetone,[1] and the present investigation is concerned with a photochemical reaction in which diazomethane is the primary absorbing species but which does not appear to involve singlet carbene. The absorption spectra of the lower diazoalkanes in the presence of various solvents are also examined.

Experimental

Materials.—" AnalaR " ether and butan-1-ol were used without purification. Dimethyl sulphoxide was a purified sample provided by Mr. N. McFarlane. Isopentylamine, benzophenone, t-butyl alcohol, and 1,2-bis-2-methoxyethoxyethane were reagent-grade materials, used without purification. Cyclohexene was a commercial sample (B.D.H.), distilled before use through a short Vigreux column, a middle fraction, b. p. 82·5°, being used.

Acetone and cyclohexane were purified as described previously. Tetrahydronaphthalene, tetrahydrofuran, diethylene glycol dimethyl ether, and ethylbenzene were available as pure solvents from other work in this Department.

Method.—The preparation and photolysis of diazomethane solutions, and vapour-phase chromatography (v.p.c.) have been described.[1] V.p.c. analyses of products from cyclohexene were made on a di-n-decyl phthalate column.

Diazoethane and 1-diazopropane were obtained from the corresponding *N*-alkyl-*N*-nitrosourethanes essentially as described for diazomethane.[1]

Absorption Spectra.—These were measured on a Unicam S.P. 500 spectrophotometer. The cell used at −70° was a slight modification of that described by Passerini and Ross.[3]

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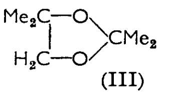
[1] Part I, Bradley and Ledwith, *J.*, 1963, 3840.

[2] Gutsche, " Organic Reactions," Wiley and Sons, New York, 1954, Vol. III, p. 364; Huisgen, *Angew. Chem.*, 1955, **67**, 439; Zollinger, " Azo and Diazo Chemistry," Interscience Publ., Inc., New York, 1961; Hancox, *R. Austral. Chem. Inst. J. and Proc.*, 1949, **16**, 282.

[3] Passerini and Ross, *J. Sci. Instr.*, 1953, **30**, 274.

RESULTS

It was shown in Part I that photolysis of diazomethane in acetone yields mainly ethyl methyl ketone (I; R = R′ = Me), 2,2-dimethyloxiran (II), and 2,2,4,4-tetramethyl-1,3-dioxolan (III). When the photolysis was carried out in the presence of certain additives, the ratios of these three products changed significantly, and in many cases the dioxolan derivative was not obtained, as shown in Table 1. Since the dioxolan (III) is thought to arise concurrently with singlet carbene attack on acetone[1] its formation was used as a guide to the extent of singlet carbene formation under the various conditions.* As a further test for singlet carbene, cyclohexane was added to several of the reaction mixtures. Singlet carbene reacts with cyclohexane to produce methylcyclohexane and thus the product ratio methylcyclohexane : ethyl methyl ketone could be used to estimate the extent of singlet carbene formation.



(III)

TABLE 1.

Photolysis of diazomethane in acetone at 25°.*

	Product ratios			
	I/III		II/I	
Additive (vol. %)	Peak heights	Peak areas	Peak heights	Peak areas
None	2·3	3·1	1·0	0·4
H_2O 1%	0·6	0·8	2·5	1·0
Me_2SO 5%	2·4	2·9	1·6	—
$Bu^i\cdot CH_2\cdot NH_2$ 5%	1·0	2·1	2·0	0·9
$(MeO\cdot[CH_2]_2\cdot O\cdot CH_2)_2$ 10%	1·8	2·3	1·1	0·6
Et_2O 98%	2·1	2·2	oxide peak obscured by solvent	
Bu^tO 5%	1·8	2·2	1·1	0·4
,, 17%	0·5	0·8	1·7	0·8
Bu^nOH 5%	0·6	0·7	0·9	0·4
,, 50% †	0	0	3·6	1·5
Cyclohexane 50%	2·0 (14·7) ‡	2·5 (1·5) ‡	1·2	—
,, 50% †	2·7 (17·0) ‡	3·6 (1·2) ‡	1·1	—
Cyclohexane 25% + Bu^nOH 50%	0	0	2·7 (0·05) ‡	1·2
$COPh_2$ 30% §	0·4	0·6	0·8	—
,, 5% §	1·2	1·4	0·6	0·3
,, 5% §¶	1·1	1·4	1·0	0·5

* Product ratios were unaffected by variation in $[CH_2N_2]$ from 0·12M to 0·04M; reaction times were ~30 min. when the lamp was used and ~12 hr. for decomposition in sunlight. † Reaction in sunlight. ‡ Nos. in parentheses indicate product ratio, methylcyclohexane : COMeEt. § Wt./vol. ¶ At −78°.

TABLE 2.

Effect of butan-1-ol on photolysis of diazomethane in acetone ($[CH_2N_2]$ = 0·1M).

Bu^nOH (vol. %)	Temp.	Product ratios (areas) III/I	Product ratios (areas) II/I	Bu^nOH (vol. %)	Temp.	Product ratios (areas) III/I	Product ratios (areas) II/I
1	25°	2·1	0·4	5·0	−78°	1·3	0·6
2·5	,,	0·9	0·6 ‡	5·0	25 *	—	13·0
2·5	−78	1·56	0·7	17	25	0·1	1·5
5·0	25	0·7	0·4	33	,,	—	1·7
5·0	,,	0·8	0·8	33	,,	—	1·5
5·0	,,	0·5	0·5	50	25 †	—	1·4
5·0	−78	1·6	0·5	50	25 *	—	1·3
5·0	,,	1·6	0·5 §				

* In the dark. † 50 vol. % Bu^nOH; the dark reaction becomes significant and affects product ratios. ‡ Apparent activation energy 1·0 kcal. mole^{-1}. § Apparent activation energy (average) 1·4 kcal. mole^{-1}.

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* If the excited state of diazomethane has an appreciable lifetime, the conclusion from Part I[1] really implies that the dioxolan (III) and singlet carbene arise from the same precursor.

The reaction in the presence of butan-1-ol was studied in greater detail and the results are shown in Table 2.

Apparent activation energies for this photochemical reaction were calculated from relative rates at 25° and −80° as follows.

The dioxolan peak was used as a measure of the amount of ethyl methyl ketone produced by the singlet carbene reaction k_1, the excess of ethyl methyl ketone then giving the extent of the alternative reaction k_2. k_1 was assumed to have zero activation energy, so that the temperature-dependence of k_2/k_1 gave the apparent activation energies for formation of ethyl methyl ketone as noted in Table 2.

Kopecky, Hammond, and Leermakers [4] showed that photolysis of diazomethane in cyclohexene leads to norcarane and the various methylcyclohexenes. Similar results were obtained in the present work and it was also found that photolysis of diazomethane in cyclohexane containing butan-1-ol (up to 50 vol. %) did not alter the product ratios.

Absorption Spectra.—The absorption spectrum of diazomethane in solution in the wavelength region 3000—5000 Å shows four maxima. On change of the solvent in the sequence, hexane, cyclohexene, tetrahydronaphthalene, ethylbenzene, acetone, butan-1-ol, tetrahydrofuran, diethylene glycol dimethyl ether, the absorption maxima became progressively less distinct. Molecular extinction coefficients lie in the range 6·0—10·0 and $\lambda_{\max.}$ varies from 4150 to 4270 Å. At −70° the spectra are identical with those measured at room temperature, except for a slight enhancement of the long-wavelength peak (see Figures). With butan-1-ol as solvent the rapid decomposition of diazomethane precluded measurement of the absorption spectrum at room temperature.

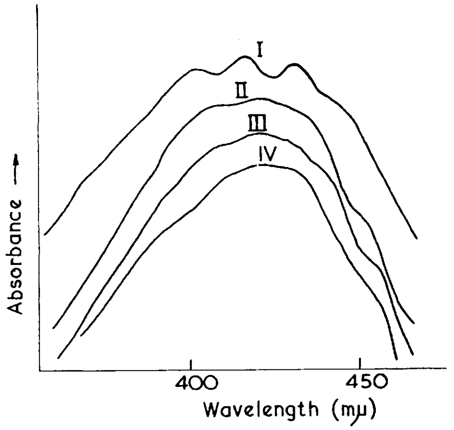

FIG. 1. Absorption spectra of diazomethane solutions at −70°.

Solvents: (I) hexane, (II) acetone, (III) tetrahydrofuran, (IV) butan-1-ol. The spectra were unaffected by changing [CH_2N_2] in the range 0·06—0·2M.

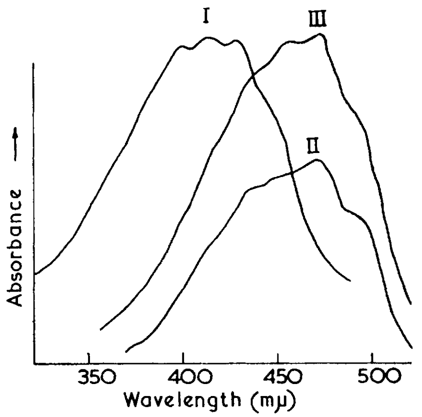

FIG. 2. Absorption spectra of (I) diazomethane, (II) diazoethane, and (III) 1-diazopropane in hexane at 20°.

Diazomethane and 1-diazopropane showed similar behaviour, but with a considerably more prominent long-wavelength band (see Fig. 2).

DISCUSSION

The results in Table 1 show that certain additives inhibit both the formation of the dioxolan and the singlet carbene reaction. The mechanism differs from that of the acetone-photosensitised decomposition [1] since the additives chosen were all transparent

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[4] Kopecky, Hammond, and Leermakers, *J. Amer. Chem. Soc.*, 1962, **84**, 1015.

in the wavelength region employed. The most obvious explanation is that the excited diazomethane molecule is prevented from decomposing to singlet carbene and from reacting to give the dioxolan by stabilisation of the excited state, by facilitation of an alternative route, *e.g.*, *via* a triplet species, or by a combination of the two.

Dimethyl sulphoxide, diethyl ether, 1,2-bis-2-'methoxyethoxyethane, and cyclohexane do not affect the course of the reaction, but the other additives display the following sequence of efficiencies: water > butan-1-ol > t-butyl alcohol > benzophenone ≈ isopentylamine. For the first three members of this sequence the relative efficiencies decrease approximately in the ratios 10 : 8 : 3. This shows that the hydroxyl group is particularly effective in inhibiting the carbene reaction and suggests that the additive may function by hydrogen bonding to diazomethane or acetone, since the sequence parallels the probable hydrogen bonding efficiency.

Additives such as butan-1-ol do not affect the reaction of diazomethane with cyclohexene to give products characteristic of C=C and C–H attack, that is, characteristic of singlet carbene formation, so that any interaction between the diazomethane and the butan-1-ol does not prevent eventual breakdown of the excited state of the diazomethane to singlet carbene. Another feature, illustrated in Table 2, is that the alcohol-catalysed reaction has a temperature coefficient of the order of 1 kcal. mole.$^{-1}$ An independent study of the dark reaction of diazomethane with acetone [5] shows an activation energy of ~15 kcal. mole^{-1} under corresponding conditions. The reaction depends on the butan-1-ol concentration, but it is difficult to specify a simple relation between rate and concentration because studies [5] on the dark reaction indicate that the ratio of epoxide to ketone in the products also depends on the butanol concentration. In none of these experiments is it possible to say whether the reactions are those of carbene or of diazomethane since there is no way of determining at what stage the nitrogen is lost. However, in all the experiments involving photolysis of diazomethane in the presence of both alcohols and acetone it is highly significant that products resulting from attack by carbene on either C–H or O–H bonds are formed, if at all, in negligible amounts, whereas alcohols alone are attacked by carbene. If carbene is directly involved it would imply a high degree of selectivity under these conditions. A more reasonable conclusion is that the presence of hydroxylic compounds provides a different mechanism for the reaction between excited diazomethane and acetone. It is noteworthy that recently Russell and Hendry [6] have shown aromatic solvents to have a marked effect on the products obtained in the photolytic reaction between diazomethane and benzene.

In Part I [1] it was shown that significant amounts of the dioxolan (III) were obtained when dilute solutions of diazomethane and acetone in diethyl ether were photolysed. This result suggests that two or more molecules of acetone form a complex with diazomethane, although the effect of acetone on the absorption spectrum of diazomethane indicates that such association must be quite weak.* We are indebted to a Referee for pointing out that the effect of alcohols in reducing the amount of dioxolan formed could be due simply to replacement of acetone by alcohol molecules in the association complex; but this would not explain the absence of singlet carbene reactions with cyclohexane or the observed temperature-dependence.

Absorption Spectra.—The spectral investigation confirms that of Adamson and Kenner,[7] indicating the possibility of two distinct electron transitions. For diazomethane, the present work shows that the major band is centred around 4200 Å and has at least three peaks due to vibrational fine structure, while the weaker long-wavelength absorption occurs around 4525 Å. The suggestion that two electron transitions are involved is

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* Detailed studies [5] of the dark reaction between diazomethane and acetone in the presence of butan-1-ol shows that some association between acetone and diazomethane is kinetically important.

[5] Bradley, Cowell, and Ledwith, unpublished work.

[6] Russell and Hendry, *J. Org. Chem.*, **1963**, **28**, 1933.

[7] Adamson and Kenner, *J.*, **1937**, 1551.

supported by the general shape of the absorption curves for the three diazoalkanes considered, and also from the effect of different solvents on the position of the two bands.

The gas-phase spectrum of diazomethane [8] showed diffuse fine structure from 4710 to 4250 Å, beyond which a continuum was obtained. The latter was attributed to the immediate dissociation of diazomethane into carbene and nitrogen. Further work [9] suggested weak fine structure from 4300 to 3200 Å but provided no evidence for fine structure in the region reported earlier,[8] and this seems to invalidate the conclusion then made. The gas-phase spectrum reported by Brinton and Vollman [9] shows fine structure which, apart from a slight wavelength shift, is surprisingly similar to that reported here for solutions in hexane. The fact that this fine structure is observed clearly in the solution spectra, where the solvent would be expected to reduce it considerably, indicates that the upper electronic state is binding and consequently may have an appreciable lifetime. The significance of this observation is that photolytic reactions of diazomethane in solution cannot be assumed to involve carbene without further justification.

Diazomethane is isoelectronic with nitrous oxide and hydrazoic acid, and the electronic structures of these two molecules have been discussed by Walsh [10] and Closson and Gray,[11] respectively. Diazomethane can be treated in a similar manner and the electronic structure likely to be involved in visible absorption can be written (with the previous nomenclature [11]):

$$ {}^{b}\pi_u^{2}(x)\pi_g^{2}(x)\pi_u^{2}(y) \quad {}^{1}A_1 $$

($n \longrightarrow \pi^*$ transitions are considered unlikely because of the absence of the expected [12] solvent shifts: see also refs. 10 and 11).

The excited states produced by single electron transitions can then be written:

$$ \begin{array}{ll} {}^{b}\pi_u^{2}(x)\pi_g^{1}(x)\pi_u^{*1}(x)\pi_u^{2}(y) & {}^{1}A_1{}' \\ {}^{b}\pi_u^{2}(x)\pi_g^{1}(x)\pi_u^{2}(y)\pi_u^{*1}(y) & {}^{1}A_2\ ({}^{3}A_2) \\ {}^{b}\pi_u^{2}(x)\pi_g^{2}(x)\pi_u^{1}(y)\pi_u^{*1}(y) & {}^{1}A_1{}'' \end{array} $$

The transition ${}^{1}A_1 \longrightarrow {}^{1}A_2$ will occur at the longest wavelength and will be forbidden, this is identified with the peak at 4520 Å; transition ${}^{1}A_1 \longrightarrow {}^{1}A_1{}''$ ($\pi \longrightarrow \pi^*$) is the highest-energy transition and is believed to represent the strong absorption which occurs below 3000 Å; the main visible peak at 4200 Å is then allocated to the transition ${}^{1}A_1 \longrightarrow {}^{1}A_1{}'$. Although not forbidden, the transition probability of this band will be considerably reduced by the different electron densities on the central nitrogen atom in the two states.[10,11]

It is worth noting that the upper states ${}^{1}A_1{}'$ and ${}^{1}A_2$ are likely to be bent and hence formed with appreciable vibrational energy. The main absorption at 4200 Å could also be ascribed to the ${}^{1}A_1 \longrightarrow {}^{1}A_2$ transition but it then becomes difficult to explain the long-wavelength peak which is even more prominent for the higher diazoalkanes.[1] However, the assignment of the bands does not affect the conclusions regarding the bonding nature of the excited state.

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[8] Kirkbride and Norrish, *J.*, 1933, 119.

[9] Brinton and Vollman, *J. Chem. Phys.*, 1951, 1394.

[10] Walsh, *J.*, 1953, 2260.

[11] Closson and Gray, *J. Amer. Chem. Soc.*, 1963, **85**, 290.

[12] Jaffé and Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley and Sons, New York, 1962, p. 186.