Photochemistry of αα'-Disubstituted Azoalkanes. Part II.[1] Photolytic Dechlorination, Decomposition, and Oxidation of αα'-Dichloro- and αα'-Diacyloxy-azoalkanes

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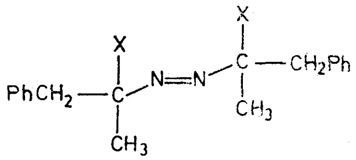
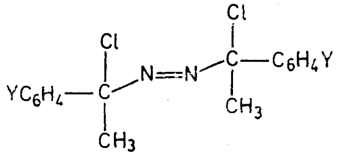
The photochemistry of a series of αα'-dichloro- (III) and αα'-diacyloxy-azoalkanes (IV) with α-phenyl groups has been studied. Irradiation of (III) yields both products of N_2 extrusion ($RN_2R \xrightarrow{h\nu} R\cdot + N_2 + R\cdot$) well known for unsubstituted azoalkanes and a new reaction leading to the loss of 2Cl· and formation of ketazines. In addition, the radical intermediates produced in both photoreactions are susceptible to oxidation. The dechlorination: N_2 extrusion ratio increases with increasing electron donor character of the substituted α-phenyl group. On the other hand irradiation of (IV) gives only N_2 extrusion. A sensitization and quantum yield study of αα'-dichloro- (I) and αα'-diacyloxy-azoalkanes (II) without α-phenyl substituents as well as of (III) and (IV) showed that the various photoreactions of this series proceed only with singlet sensitization. The photochemical mechanisms of these reactions are discussed.

IN Part I,[1] the newly discovered *meso* $\rightleftharpoons$ (±) photoisomerizations of αα'-disubstituted azoalkanes without α-phenyl substituents, $R^1R^2C(X)N{=}NC(X)R^1R^2$ (I; X = Cl) and (II; $X = O_2CR^3$), were reported. Despite the similarity of the photoreactions of (I) and (II), mechanistic studies indicate that while the photoisomerization of (I) is intramolecular, perhaps through a photoallylic rearrangement, the photoisomerization of (II) involves the formation of discrete $R^1R^2C{=}\overset{+}{N}{=}NC(O_2CR^3)R^1R^2$ and $R^3CO_2^-$ ions.

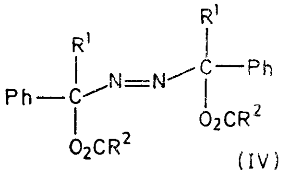


(I) X = Cl
(IIa) X = O2CMe
(IIb) X = O2CEt



(III)

a; Y = H
b; Y = *p* - CH3
c; Y = *p* - Cl
d; Y = *m* - Cl
e; Y = *p* - NO2



(IV)

a; R1 = R2 = Me
b; R1 = Et, R2 = Me
c; R1 = Me, R2 = Et

In this paper, results of a continuation of this study for series (III) and (IV) are given. New photodechlorination and photo-oxidation reactions were found for (III), while the exclusive symmetrical decomposition found for (IV) is reminiscent of the behaviour of unsubstituted azoalkanes. Also, the results of an extensive sensitization, quenching, and quantum yield study of the photoreactions of (I)—(IV) are reported.

Photochemistry of Series (III) *and* (IV).—In unsubstituted azoalkanes, the presence of α-phenyl groups does not affect the course of the photoreaction $RN{=}NR \xrightarrow{h\nu} R\cdot + N_2 + R\cdot$, though it permits triplet sensitization of the photodecomposition.[2] In αα'-disubstituted azoalkanes, the presence of α-phenyl groups entirely alters the photobehaviour of (III) and (IV) with regard to (I) and (II). Interestingly, as shown below, the diverse photoreactions of (I)—(IV) proceed only by direct irradiation or singlet sensitization.

Irradiation of incompletely degassed benzene solutions of (III) with a 450 W medium-pressure Hanovia lamp for 10 h leads to the formation of products (V)—(X). Similar irradiation in oxygen-saturated benzene results in the practical elimination of (VII)—(X), a reduction in the coupling product (VI), and the predominant formation of ketone (V). Quantitative analysis of the product mixture was carried out using n.m.r. spectroscopy. The α-chlorinated ketazines (VIII) and (IX) were prepared independently.[3] Chlorine addition to (VII) and (VIII) is successful and leads to the formation of the corresponding αα'-dichloroazoalkanes which are subject to hydrolytic decomposition,[4] while (IX), which is similar to α-bromoacetophenone azine,[5] does not add chlorine. Dichlorides (Xa and c) were identified by comparison with independently prepared samples.

It should be noted that the thermal decomposition of (IIIc) in benzene at room temperature leads to 70% ketone formation and only 30% formation of the coupling product (VIc) (probably the cage product). The ready oxidation of free radicals with α-chloro-substitution is illustrated by the conversion of tetrachloroethylene to Cl_3CCOCl by chlorination in the presence of oxygen.[6]

The addition of benzenethiol which is a very efficient

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[1] Part I, N. Levi and D. S. Malament, *Israel J. Chem.*, 1974, **12**, 925.

[2] P. S. Engel and C. Steel, *Accounts Chem. Res.*, 1973, **6**, 275.

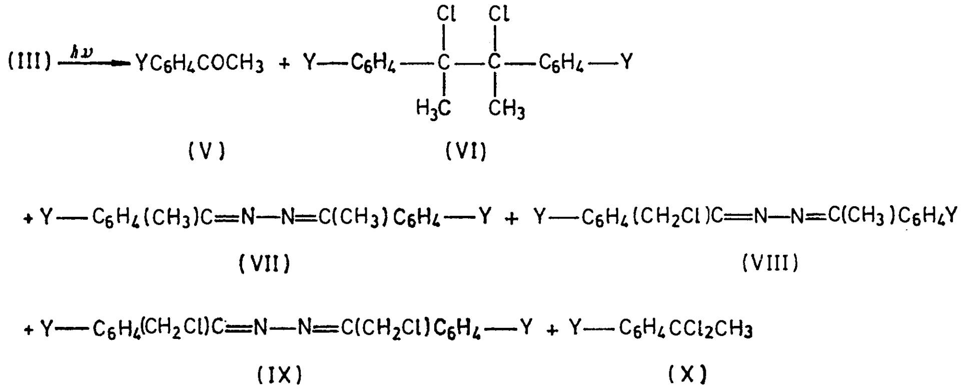
[3] D. S. Malament and J. M. McBride, *J. Amer. Chem. Soc.*, 1970, **92**, 4586.

[4] E. Benzing, *Annalen*, 1960, **631**, 10.

[5] D. S. Malament, unpublished work.

[6] C. Walling, ' Free Radicals in Solution,' Wiley, New York, 1968, p. 448.

radical scavenger[7] leads to a reduction in the yield of ketone (V), formation of the hydrogen-abstraction product $YC_6H_4CHClMe$, and formation of 27% coupling products (VI) upon irradiation at room temperature. Also, chlorinated ketazines (VIII) and (IX) are not produced in the presence of PhSH. Thus, it may be concluded that (VIII) and (IX) are products of the reaction of (VII) with Cl• and that PhSH acts as a scavenger of Cl•.



The mechanistic Schemes 1 and 2 may be used to explain formation of all the observed products. Products (V), (VI), and (VIII)—(X) are formed in Scheme 2 as products in reactions identical to (iv), (iii), (vii), (vii), and (viii) of Scheme 1, respectively.

TABLE 1

Direct irradiation products of (III) in benzene

	Azoalkanes irradiated				
Products (%)	(IIIa)	(IIIb)	(IIIc)	(IIId)	(IIIe)
Ketone (V)	10	10	9	5	10
Coupling products (VI)	24	10	33	49	90
Ketazines (VII)—(IX)	63	80	55	43	
Dichloride (X)	3		3	3	
Ratio (VII)—(IX) : (VI)	2.6	8.0	1.55	0.86	0.0

Scheme 2 allows the formation of a maximum of only 50% ketazines. Thus, this mechanism as a sole pathway is clearly excluded for (IIIa—c). Furthermore, according to Scheme 2, a significant amount of the $YC_6H_4\dot{C}$-(Cl)Me radicals should be formed not as members of a cage pair and thus the cage effect should be extremely low. The 27% cage effect which is consistent with the 30% thermal cage effect (room temperature, oxygen scavenger) indicates that most $YC_6H_4\dot{C}(Cl)Me$ radicals are formed as members of cage pairs, *i.e.* according to Scheme 1.

Further evidence against Scheme 2 and a carbene intermediate was found in the results of the irradiation of $Ph(CH_3)C{=}N_2$ and *p*-$ClC_6H_4(CH_3)C{=}N_2$ in toluene. *Ca.* 60% of the products formed are attributed to hydrogen abstraction by the carbene from toluene and subsequent radical coupling reactions with the general formula $PhCHRCH_3$ (the methyl groups in these products have characteristic n.m.r. absorption centred at τ 8.75). Similar irradiation of (IIIa and c) in toluene does not lead to the formation of such products thus indicating the absence of carbene intermediates.

It should be pointed out that the radical, PhMe$\overline{\mathrm{C{-}\dot{N}{-}N}}$-C(Cl)PhMe [radical (A)] proposed in Scheme 1 should not be scavenged by PhSH as the PhS• radical is known to be sufficiently reactive to abstract the α-hydrogen atom in PhMeCH-N=N-CHMePh.[8]

Upon irradiation of (IIIa and c) in non-aromatic hydrocarbons such as cyclohexane, cyclohexene, and *cis*-but-2-ene, ketazines were not formed though the yields of coupling product (VI) are the same as in benzene. The product mixtures were not fully characterized but the n.m.r. spectrum clearly showed that the major additional products arose by reaction with radicals derived from the solvent. Such radicals probably arise by hydrogen abstraction from the hydrocarbon solvents by chlorine atoms.

A clear correlation in degassed runs of the ratio of ketazines to coupling product (K : C ratio) with the electron-withdrawing nature of the phenyl substituent was found. This ratio is equivalent to the ratio of the rates of reactions (i) and (ii) in Scheme 1.

The correlation of the logarithm of the K : C ratio with the σ^+ scale[9] (ρ^+ −1.6) is similar to the substituent effects on the thermal decomposition rates of t-butyl arylperacetates (ρ^+ −1.1)[10] and undoubtedly is related to a greater charge separation in C–Cl cleavage than in C–N cleavage.

Photochemistry of $\alpha\alpha'$-Diacyloxyazoalkanes (IV).—The photochemistry of (IV) is identical with that of non-substituted azoalkanes such as azocumene. Irradiation in benzene leads to quantitative loss of N_2 and formation of the corresponding *meso* and (±) coupling products, (XI) in *ca.* 1 : 1 ratio. No oxidation of the intermediate

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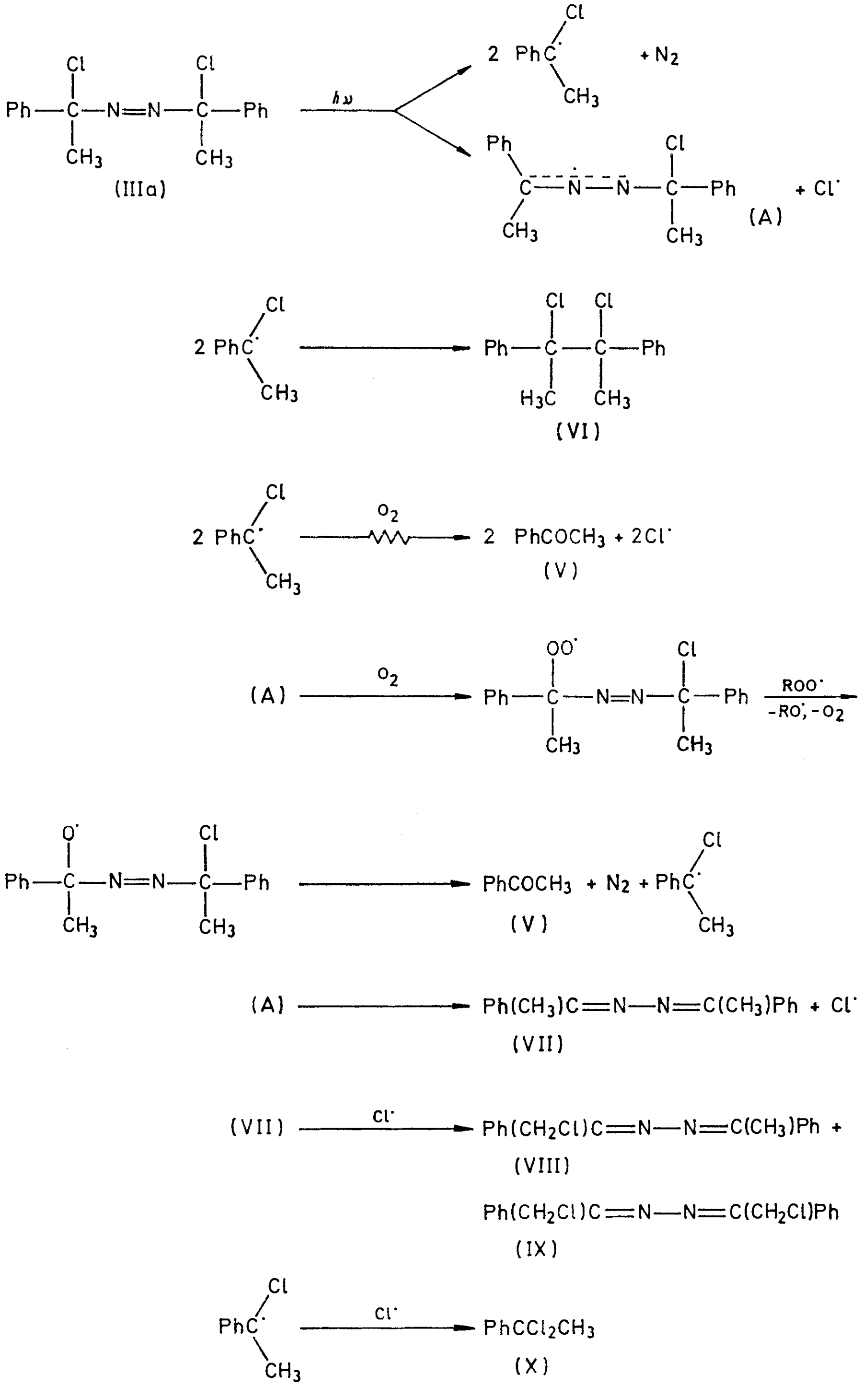
[7] Y. Schaafsma, A. F. Bickel, and E. C. Kooyman, *Rec. Trav. chim.*, 1957, **76**, 180.

[8] E. C. Kooyman, *Rec. Trav. chim.*, 1955, **74**, 117.

[9] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913.

[10] P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, 1960, **82**, 1756.

$Ph\dot{C}(O_2CR^2)R^1$ radical was found. The same reaction was found with methanol as solvent which indicates the lack of ionic intermediates.[1]



SCHEME 1 Competitive mechanism for (IIIa)

Considerable u.v. absorption was noted for the reaction solution and although no products other than the *meso* and (±) coupling products were found by n.m.r., it seems likely that some quinonoid addition product (XII), analogous to that found by Nelsen and Bartlett[11] for azocumene, is formed.

Sensitization, Quenching, and Quantum Yield Study of the Photoreactions of (I)—(IV).—The results of the quantum yields of direct and sensitized photolyses of

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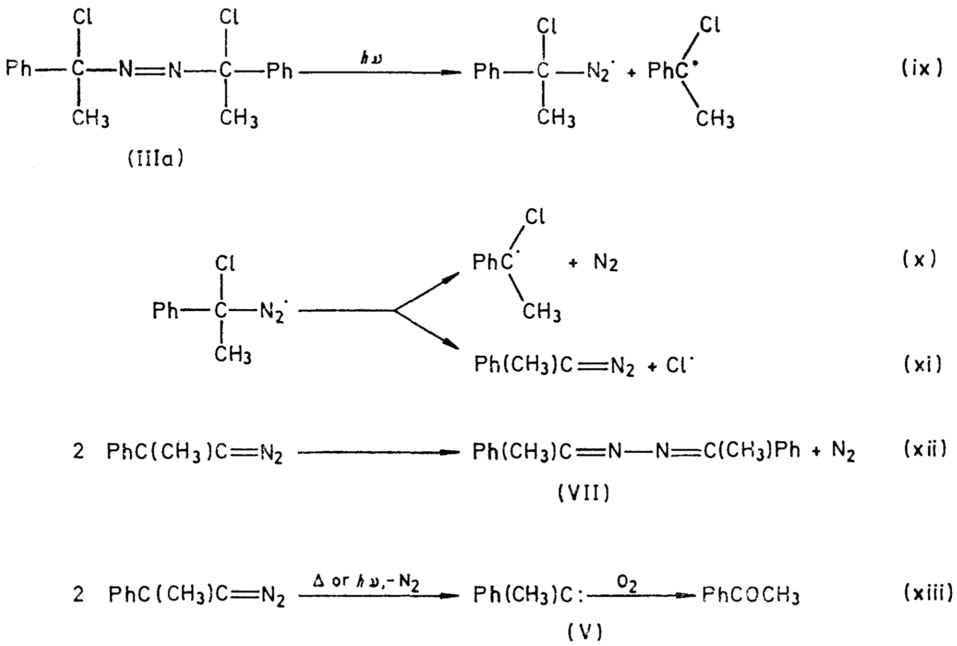
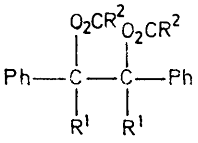
[11] S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1966, **88**, 143.

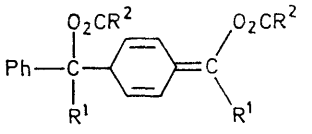


SCHEME 2 Carbene intermediate mechanism for (IIIa)

(I)—(IV) are given in Table 2. These data show that all the photoreactions observed proceed only upon direct irradiation or with singlet sensitization.



(XI)



(XII)

We recall our earlier work [1] demonstrating a *meso* $\rightleftharpoons$ (±) photointerconversion for (I). A typical photosubstitution of (II) is reaction (xiv).

$$(\text{IIb}) \underset{h\nu,\text{HO}_2\text{CEt}}{\overset{h\nu,\text{HOAc}}{\rightleftharpoons}} (\text{IIa}) \qquad (\text{xiv})$$

As in the case of other acyclic azoalkanes, u.v. absorption maxima in the vicinity of 360 nm with low extinction coefficients and no fluorescence or phosphorescence emission are found for (I)—(IV). Also, effective quenching of aromatic hydrocarbon fluorescence in benzene was observed for (I), $Me_2C(Cl)\text{-}N{=}N\text{-}C(Cl)Me_2$ (I′), (IIa), and $Me_2C(OAc)\text{-}N{=}N\text{-}C(OAc)Me_2$ (II′), as in the case of unsubstituted azoalkanes. Using triphenylene (singlet lifetime, 36.6×10^{-9} s) [12] in a Stern–Volmer study, the singlet quenching rates in benzene for all four disubstituted azoalkanes were $(4.0 \pm 0.2) \times 10^9$ l mol^{-1} s^{-1}. The maximum efficiency of sensitization is equal to $k_qc_q/(k_qc_q + 1/\tau)$ where k_q and c_q are the quenching rate and concentration of the quencher and τ is the lifetime of the excited sensitizer. For 0.020M-triphenylene and 0.20M-phenanthrene, the maximum singlet sensitization efficiencies are 0.75 and 0.82, respectively, while, for 0.25M-benzophenone, the maximum triplet sensitization efficiency is 0.80. The decreases in quantum yield in runs with triphenylene and phenanthrene compared with direct irradiation given in Table 2 correspond to maximum sensitization efficiency. Similar highly efficient singlet sensitization was observed by Engel and Bartlett [13] for the photodecomposition of unsubstituted azoalkanes.

Effective quenching of benzophenone triplet was found for these azoalkanes. In a semiquantitative experiment, relative quenching efficiencies of 3.0, 2.0, 1.6, and 1.0 were found for (I′), (I), (II′), and (IIa), respectively. This series in which triplet quenching efficiency appears to be related to steric hindrance is similar to results found for an analogous series of unsubstituted azoalkanes by Wamser.[14]

Despite effective triplet quenching, *no* discernible benzophenone triplet sensitized reaction was observed for (I)—(IV). The presence of triplet quenchers such as piperylene or O_2 had no effect on the quantum yields of the direct or singlet-sensitized photoreactions of (I) and (II).

Two further probes were made on the photosubstitution with diastereoisomerization of *meso*-(IIa). Irradiation of *meso*-(IIa) in benzene in the presence of CD_3CO_2D leads to introduction of the deuteriated acetyl group and *meso* $\rightleftharpoons$ (±) interconversion (in essence, this is a racemization process) with precipitation of (±)-(IIa). N.m.r. analysis of the precipitated product isolated after only *ca.* 10% reaction showed exactly 1 mol. equiv. of CD_3CO_2 incorporated per mol. equiv. of the (±)-product.

[12] I. Berlman, ' Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1965.

[13] P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1970, **92**, 5883.

[14] C. C. Wamser, *J. Amer. Chem. Soc.*, 1973, **95**, 2044.

This result is strong evidence that, under these conditions (*a*) there is no intramolecular photointerconversion and (*b*) that the substitution of each of the two α-positions requires a separate step.

Upon irradiation of 0.06M-(±)-(IIb) in benzene in the presence of 0.06—3.0M-acetic acid, it was found that the rates of attaining the photostationary state [100% (IIa) for 3.0M-AcOH to 50% (IIa)–50% (IIb) for 0.06M-AcOH] do not vary with AcOH concentration. This result indicates that the proposed intermediate ion pair, $R^1R^2C{=}\overset{+}{N}{=}N{-}C(O_2CR^3)R^1R^2 + R^3CO_2^-$ has a sufficient lifetime to allow at least 90% exchange of the $R^3CO_2^-$ anion with the carboxylic acid in the solvent at concentrations as low as 0.06M.

TABLE 2

Direct and sensitized photoreactions of (I)—(IV)

Run	[Sensitizer]/ M	[Azoalkane]/ M	λ/nm	Light absorbed by azoalkane (%)	Quantum yield
(*a*) Photointerconversion of (±)- and *meso*-(I) in benzene					
Direct, degassed, and in the presence of O_2 and piperylene (1M)		0.033	366	100	0.1 ± 0.01
Triphenylene, degassed, in the presence of O_2 and piperylene (1M)	0.020	0.020	313	0.1	0.07 ± 0.01
Phenanthrene, degassed, in the presence of O_2 and piperylene (1M)	0.20	0.020	313	0.8	0.08 ± 0.01
Benzophenone, degassed	0.25	0.020	313	1.0	<0.01
(*b*) Photosubstitution of (IIb) in benzene with 3M-AcOH					
Direct, degassed, and in the presence of O_2 and piperylene (1M)		0.06	366	100	0.34 ± 0.04
Triphenylene, degassed, in the presence of O_2 and piperylene (1M)	0.020	0.016	313	0.1	0.20 ± 0.02
Phenanthrene, degassed, in the presence of O_2 and piperylene (1M)	0.20	0.016	313	0.6	0.24 ± 0.03
Benzophenone, degassed	0.25	0.016	313	0.8	<0.01
(*c*) Photoreaction of (IIIa) in benzene					
Direct, degassed and in the presence of piperylene (1M)		0.070	366	100	r [a]
Triphenylene, in the presence of O_2	0.020	0.020	313	0.1	r
Benzophenone, degassed	0.25	0.020	313	1.0	nr [b]
(*d*) Photodecomposition of (IVa) in benzene					
Direct, degassed		0.050	366	100	0.26 ± 0.03 [c]
Triphenylene, in the presence of O_2	0.020	0.020	313	0.1	r
Benzophenone, degassed	0.25	0.020	313	1.0	nr

[a] r, reaction proceeds but formation of coloured products prevents quantum yield determination. [b] nr, no reaction. [c] Understated value due to the formation of coloured products.

The Overall Photochemical Mechanism.—As shown by Engel and Bartlett,[13] most azoalkanes undergo photoreaction only with singlet sensitization though Engel[2] has also shown that some unsubstituted azoalkanes including those with α-phenyl groups undergo triplet photosensitized decomposition as well. In our study of the photoreactions of αα′-disubstituted azoalkanes, *only* singlet sensitization is effective *even* for α-phenyl substitution and that such triplet quenchers as piperylene, O_2, and bromobenzene have no effect on the reaction rate.

These results would seem to support the hypothesis that the photoreaction takes place directly from the excited singlet state. However, the gas-phase singlet lifetime for azoisopropane has been estimated at $<5 \times 10^{-11}$ s by Steel[15] and for azoisobutane, at $<7 \times 10^{-10}$ s by Calvert.[16] At the same time, Calvert[16] found from a study of the pressure dependence of the quantum yield of gas-phase photolysis of azoisobutane that the excited state in which the photoreaction occurs has a lifetime $>5 \times 10^{-10}$ s.

To reconcile these findings, Steel[15] has proposed that the photoreaction takes place from a $^3\pi\pi^*$ (T_2) state to which the excited $^1n\pi^*$ (S_1) state is demoted by intersystem crossing and to which it is impossible to arrive by triplet sensitization which gives only the lower energy $^3n\pi^*$ (T_1) state. The complete insensitivity of the proposed $^3\pi\pi^*$ state to standard triplet quenchers as well as the failure to observe any phosphorescence at 77 K for these compounds makes Steel's hypothesis somewhat suspect.

Another possibility for a general photochemical mechanism has been considered[2] in which there is a very fast *trans* $\rightleftharpoons$ *cis* interconversion of azoalkanes in the S_1 state followed by non-radiative decay to S_0. In

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[15] I. I. Abram, G. S. Milne, B. S. Salomon, and C. Steel, *J. Amer. Chem. Soc.*, 1969, **91**, 1220.

[16] S. S. Collier, D. H. Slater, and J. G. Calvert, *Photochem. and Photobiol.*, 1968, **7**, 737.

the gas phase, both vibrationally excited *cis*- and *trans*-azoalkanes may decompose before collisional deactivation. Increasing pressures would lead to reduced quantum yields as observed.[2]

In solution, for primary and secondary azoalkanes, the N_2 extrusion reactions is drastically reduced and *cis* $\rightleftharpoons$ *trans* isomerization becomes the predominant reaction.[2] Mill and Stringham [17] found that in solution tertiary *cis*-azoalkanes produced by the photoisomerization of the stable *trans*-forms decompose well below 0 °C and thus, it is not unreasonable to expect that not only C–N bond cleavage occurs for such *cis*-forms but, upon suitable substitution, 1,3-tautomerization, C–Cl bond cleavage, and ion-pair formation may also take place. All three of these latter three reaction variants involve the relief of strain of the *cis*-azoalkane and also may occur directly from S_1 or from T_2. Experimental distinction will be difficult.

In conclusion, although the precise photomechanism for the title compounds is unknown, the different photoreactions of (I)—(IV) are all subject to singlet sensitization and, as they are insensitive to triplet sensitization, clearly do not occur from the $^3n\pi^*$ (T_1) state.

EXPERIMENTAL

Compounds.—The αα′-dichloro-azo-compounds (I), (I′), and (III) studied were prepared by our earlier procedure [3] which is a variation of the method of Goldschmidt and Acksteiner.[18] The αα′-diacyloxyazoalkanes (IIa and b), (II′), and (IVa—d) were prepared from the appropriate αα′-dichloroazoalkane by the procedure of Benzing.[19] The n.m.r. signals of the non-aromatic protons in 10% benzene solution, u.v. and m.p. data for compounds of types (I) and (II) have already been reported.[1] The slight differences in the n.m.r. spectral shifts of the *meso*- and (±)-isomers allowed the quantitative evaluation of the isomer ratios. The following data are for non-aromatic protons in 10% $DCCl_3$ solution (unless otherwise noted): *meso*-(IIIa), m.p. 109° (decomp.) [lit.,[18] 110° (decomp.)], τ 7.79 (6 H, s), $\lambda_{max.}$ (cyclohexane) 360 nm (ε 52); *meso*-(IIIb), m.p. 130° (decomp.) [lit.,[18] 130° (decomp.)], τ 7.67 (6 H, s) and 7.82 (6 H, s), $\lambda_{max.}$ (CH_2Cl_2) 360 nm (ε 45); *meso*-(IIIc), m.p. 121° (decomp.) [lit.,[18] 123° (decomp.)], τ 7.82 (6 H, s), $\lambda_{max.}$ (CH_2Cl_2) 353 nm (ε 57); meso-*αα′-dichloro-αα′-bis*-m-*chlorophenylazoethane meso*-(IIId), m.p. 100° (decomp.), τ 7.82 (6 H, s), $\lambda_{max.}$ (benzene) 355 nm (ε 46) (Found: C, 51.0; H, 3.7; N, 7.45; Cl, 37.85. $C_{16}H_{14}N_2Cl_4$ requires C, 51.05; H, 3.7; N, 7.45; Cl, 37.75%); *meso*-(IIIe), m.p. 120° (decomp.), τ 7.75 (6 H, s), no u.v. maximum at 360 nm (ε_{360} 500) in benzene (Chlorine addition to *p*-nitroacetophenone azine is relatively slow at −77 °C and was continued at this temperature for 60 min. The product could not be purified.); meso-*αα′-diacetoxy-αα′-diphenylazoethane meso*-(IVa), m.p. 105° (decomp.), τ 7.87 (6 H, s) and 8.17 (6 H, s), $\lambda_{max.}$ (CH_2Cl_2) 357 nm (ε 40) (Found: C, 67.7; H, 6.3; N, 7.9. $C_{20}H_{22}N_2O_4$ requires C, 67.8; H, 6.2; N, 7.9%); meso-*αα′-diacetoxy-αα′-diphenylazopropane meso*-(IVb), m.p. 70°, τ 7.65 (4 H, q, *J* 8 Hz), 8.17 (6 H, s), and 8.94 (6 H, t, *J* 8 Hz), $\lambda_{max.}$ (CH_2Cl_2) 352 nm (ε 40) (Found: C, 69.5; H, 6.75; N, 7.35. $C_{22}H_{26}N_2O_4$ requires C, 69.1; H, 6.8; N, 7.35%); *meso*-(IVc), m.p. 144° (decomp.) [lit.,[18] 146° (decomp.)], τ (benzene) 7.87 (4 H, q, *J* 8 Hz), 8.24 (6 H, s), and 9.17 (6 H, t, *J* 8 Hz), $\lambda_{max.}$ (CH_2Cl_2) 358 nm (ε 36).

All compounds were recrystallized from benzene.

Photolyses of Compounds (IIIa—e) *in Benzene*.—Preparative photolysis of (IIIa—e) was carried out using a 450 W medium-pressure Hanovia mercury arc lamp. After degassing and sealing *in vacuo*, ten ampoules (10 ml) each containing (III) (120 mg) in benzene (4 ml) were irradiated for 10 h. All the products except ketone (V) and dichloride (X) were crystalline. After evaporation of the benzene solvent and addition of light petroleum (b.p. 60—80°) to the crude product, the more crystalline coupling product (VI) [isomer (A)] generally precipitated out. Mixtures of both stereoisomers of (VI) could be obtained independently by thermal decomposition of (III) in refluxing benzene over 2 h and these isomers could be separated by recrystallization from benzene.

The physical characteristics of coupling products (VI) are given in Table 3.

TABLE 3

Physical characteristics of coupling products (VIa—e) obtained in photolyses of (IIIa—e) in benzene

Product	M.p. (°C)	Non-aromatic n.m.r. signals τ ($CDCl_3$)	$\nu_{max.}$/cm^{-1}
VIa(A)	163—165 (lit.,[18] 163—165)	7.87 (6 H, s)	
VIa(B)		7.74 (6 H, s)	
VIb(A)	173 (lit.,[18] 175)	7.67 (6 H, s) 7.90 (6 H, s)	
VIb(B)		7.67 (6 H, s) 7.80 (6 H, s)	
VIc(A)	189—192 (lit.,[18] 190)	7.90 (6 H, s) 7.74 (6 H, s)	
VId(A) *	178—180	7.94 (6 H, s)	1 570, 1 410, 1 180
VId(B)		7.77 (6 H, s)	
VIe(A) †	245—250	7.83 (6 H, s)	1 600, 1 350, 860
VIe(B)		7.64 (6 H, s)	

* Found: C, 55.1; H, 4.1; Cl, 40.7. $C_{16}H_{14}Cl_4$ requires C, 55.15; H, 4.0; Cl, 40.8%. † Found: C, 51.9; H, 3.9; N, 7.4; Cl, 19.3. $C_{16}H_{14}Cl_2N_2O_4$ requires C, 52.05; H, 3.8; N, 7.6; Cl, 19.2%.

Ketazines (VII) were identified by comparison of their n.m.r. absorptions in benzene and $CDCl_3$ with those of authentic samples. Also, chlorine addition at −70° gave the starting αα′-dichloroazoalkanes (III) identified by n.m.r., N_2 evolution in methanol,[1,4] and comparison of the methanolysis products with those obtained from authentic (III) [non-aromatic n.m.r. signals (all for $CDCl_3$): (VIIa), τ 7.64 (6 H, s); (VIIb), τ 7.70 (6 H, s) and 7.64 (6 H, s); (VIIc), τ 7.67 (6 H, s); (VIId) τ 7.70 (6 H, s)].

Monomethyl-chlorinated ketazines (VIII) were identified by comparison of their n.m.r. absorptions with those of a chlorinated ketazine mixture prepared under conditions which give exclusively α-methyl chlorination.[3] Also chlorine addition at −70° leads to the disappearance of (VIII) and the appearance of products with slightly upfield

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[17] T. Mill and R. S. Stringham, *Tetrahedron Letters*, 1969, 1863.

[18] S. Goldschmidt and B. Acksteiner, *Annalen*, 1958, **618**, 173.

[19] E. Benzing, *Annalen*, 1960, **631**, 1.

n.m.r. signals. The new downfield signal assigned to the CH_2Cl group is an AB pattern as the CH_2Cl group is now adjacent to the asymmetric carbon. These chlorine addition products also decompose in methanol with nitrogen evolution [non-aromatic n.m.r. signals (all for $CDCl_3$): (VIIIa), τ 7.64 (3 H, s) and 5.34 (2 H, s); Cl_2 addition product of (VIIIa), τ 7.79 (3 H, s) and 5.57 (2 H, AB, *J* 12 Hz, $\Delta\nu$ 0.27 p.p.m.); (VIIIb), τ 7.70 (3 H, s), 7.64 (6 H, s), and 5.34 (2 H, s); Cl_2 addition product of (VIIb), τ 7.82 (3 H, s), 7.67 (6 H, s), and 5.57 (2 H, AB, *J* 12 Hz, $\Delta\nu$ 0.27 p.p.m.); (VIIIc), τ 7.64 (3 H, s) and 5.37 (2 H, s); Cl_2 addition product of (VIIIc), τ 7.79 (3 H, s) and 5.86 (2 H, AB, *J* 12 Hz, $\Delta\nu$ 0.23 p.p.m.); (VIIId), τ 7.67 (3 H, s) and 5.41 (2 H, s); Cl_2 addition product of (VIIId), τ 7.80 (3 H, s) and 5.64 (2 H, AB, *J* 12 Hz, $\Delta\nu$ 0.23 p.p.m.)].

Dimethyl-chlorinated ketazines (IX) were also identified by comparison with an independently prepared mixture of methyl-chlorinated ketazines. Ketazines (IX) do not add Cl_2 at $-70°$ in CH_2Cl_2 [non-aromatic n.m.r. signals (all for $CDCl_3$): (IXa), τ 5.31 (4 H, s); (IXb), τ 7.64 (6 H, s) and 5.27 (4 H, s); (IXc), τ 5.31 (4 H, s); (IXd), τ 5.37 (4 H, s)].

The ratio (VII) : (VIII) : (IX) in all cases was *ca.* 1 : 3 : 6. In all cases, the i.r. spectra of the product mixtures of the three ketazines show medium intensity bands at 1 610 cm^{-1} (lit.,[20] for ketazines, in general, 1 610 cm^{-1}).

Irradiation of 0.07M solutions of (IIIa and c—e) was carried out in the presence of 1M-PhSH for 10 h. The benzene solvent was then evaporated and the n.m.r. spectra of the product mixture taken in benzene and $CDCl_3$. Methylchlorinated ketazines (VIII) and (IX) were not present. *ca.* 1 : 1 mixtures of *meso*- and ($\pm$)-(VI) were obtained and the ratio of (VI) to $YC_6H_4CH(Cl)CH_3$ (hydrogen-abstraction product) was *ca.* 1 : 2.7 in all cases. In parallel thermal runs, 0.07M solutions of (IIIa and c—e) in the presence of 1M-PhSH were maintained at *ca.* 25° for 30 days. The ratio of the coupling products (VI) to ketone (V) + $YC_6H_4CHClMe$ was 1 : 2.6 (28% cage product).

Photolyses of $YC_6H_4(Me)C{=}N_2$ *in Benzene and Toluene.*—Diazo-compounds $YC_6H_4(Me)C{=}N_2$ (Y = H or *p*-Cl) were prepared by oxidation of the corresponding hydrazones with HgO.[20] Irradiation of 1M solutions of these compounds in benzene after degassing for 60 min led to the formation of mostly ketazine and ketone and <5% styrene. In the presence of O_2, ketone was the major product. Analogous irradiation of these diazo-compounds in toluene yields *ca.* 5% ketone (V), 35% ketazine (VII), and *ca.* 60% products giving a broad n.m.r. band centred at τ 8.75.

Irradiation of (IIIa *and* c) *in Toluene.*—Solutions of (IIIa and c) (0.07M) in degassed toluene were irradiated for 4 h. The products and product ratios were very similar to runs in benzene except that methyl-chlorinated ketazines (VIII) and (IX) were absent. Identification of ketazines (VIIa and c) was confirmed by conversion to the corresponding azo-dichloride and N_2 evolution from these azo-dichlorides in methanol. No signal in the n.m.r. spectrum for $CDCl_3$ solution at τ 8.75 was found.

Irradiation of (IIIa, c, *and* d) *in Cyclohexane and Cyclohexene.*—Solutions of (IIIa, c, and d) (0.07M) in degassed cyclohexane and cyclohexene were irradiated for 10 h. The n.m.r. spectrum in $CDCl_3$ after solvent evaporation indicated formation of ketone (V), coupling product (VI), no ketazines (VII)—(IX), and extensive products of solvent-derived radicals (broad n.m.r. band at τ 9). In runs in cyclohexene, a broad band at τ 4.4 corresponding to cyclohexene olefin protons was found.

Photolyses of (IVa—c).—Solutions of (IVa—c) (0.1M) in benzene and methanol were irradiated for 60 min. Rapid gas evolution was noted. The n.m.r. spectra in benzene and $CDCl_3$ taken after solvent evaporation are identical to those obtained for the product of thermal decomposition of these compounds in refluxing benzene over 3 h. In the case of (IVa), the more crystalline coupling product (A) was isolated by recrystallization form EtOH from both the photo- and pyro- lytic runs.

Coupling Products (XIa—c).—*αα'-Diacetoxy-αα'-dimethylbibenzyl* (XIaA) had m.p. 215—217°, τ ($CDCl_3$) 7.90 (6 H, s) and 8.11 (6 H, s), $\nu_{max.}$ ($CHCl_3$) 1 100, 1 370, and 1 720 cm^{-1} (Found: C, 73.6; H, 6.8. $C_{20}H_{22}O_4$ requires C, 73.6; H, 6.75%). Compound (XIaB) had τ ($CDCl_3$) 7.90 (6 H, s) and 7.97 (6 H, s). Compound (XIbA) had τ (benzene) 8.01 (4 H, q, *J* 8 Hz), 8.07 (6 H, s), and 9.11 (4 H, t, *J* 8 Hz). Isomer (XIbB) had τ (benzene) 8.00 (6 H, s), 8.01 (4 H, q, *J* 8 Hz), and 9.11 (6 H, t, *J* 8 Hz). Compounds (XIcA and B) had τ (benzene) 7.52 (4 H, m), 8.09 (6 H, s), 8.14 (6 H, s), and 9.11 (6 H, m).

Luminescence Emission and Quenching.—Fluorescence and phosphorescence studies of (I), (I'), and (IIa)—(IVa) were conducted on an Aminco-Bowman spectrofluorimeter. Attempts to observe fluorescence for these compounds in benzene and cyclohexane at concentrations of 0.02—0.03M with excitation at 366 nm were not successful. Similarly, no phosphorescence was observed for 0.05—0.10M solutions in glassy 2 : 1 methylcyclohexane–2-methylpentane at 77 K after four cycles of freeze–thaw degassing in sealed quartz ampoules.

Benzene solutions containing 0, 8×10^{-3}, 1.2×10^{-2}, and 2.0×10^{-2}M-(Ia), -(I'), -(IIa), -(II'), and -(IVa) and 1.0×10^{-4}M-triphenylene, m.p. 198° (Fluka), were irradiated at 313 nm in quartz tubes and the fluorescence emission intensities (*I*) at 353 nm were observed. The values for the concentration of ($\pm$)-(I) ($\times 10^3$M) and I_0/I are: 0, 1; 8, 2.1; 12, 2.6; 16, 3.1; 20, 4.7. The values for the other azoalkanes studied were within 5% of these values. Stern–Volmer treatment of these data give a quenching rate for these compounds of 4.0×10^9 l mol^{-1} s^{-1}.

A semiquantitative phosphorescence quenching experiment was performed for (I), (I'), (IIa), and (II') (0.02M) solutions in glassy 2:1 methylcyclohexane–2-methylpentane in the presence of 0.1M-benzophenone at -77 K without degassing with excitation at 313 nm and measurement of the benzophenone phosphorescence intensity at 445 nm. Reproducibility was $\pm 20\%$.

Quantum Yield Studies.—The quantum yields listed in Table 2 were obtained in direct and comparative determinations. The quantum yields of the photoracemization of 0.020M-($\pm$)-(I) in benzene in the presence of 0.20M-phenanthrene (no trace of anthracene seen in u.v. spectrum) and the photoconversion of 0.060M-($\pm$)-(IIb) to (IIa) in benzene in the presence of 3.0M-AcOH and of ($\pm$)-(IIb) in benzene in the presence of 1.0M-AcOH–0.20M-phenanthrene were determined using a medium pressure, 125 W Philips mercury lamp at 366 (for direct runs) and 313 nm (for sensitized runs) equipped with a self-regulating power supply with measured output from 6.5×10^{-8} to 2.5×10^{-7} einstein min^{-1} in 1×1 cm square quartz cells. The quantum output of the lamp was monitored by ferrioxalate

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[20] L. I. Smith and K. L. Howard, *Org. Synth.*, 1955, Coll. Vol. III, p. 351.

actinometry by the method of Hatchard and Parker [21] and found to vary over the course of a run by $<5\%$.

All other quantum yields were measured by comparison employing a 450 W medium pressure Hanovia mercury arc lamp equipped with appropriate filters and located in a merry-go-round device.

The quantum yields for the photoracemization of (I) and photosubstitution of (IIb) are based on the fact that the absorption of the stereoisomeric azoalkane products are identical to those of the starting materials and thus, the fraction of light absorbed by the product is equal to the overall conversion to product. Therefore, at constant light input, the photoreaction rate should observe a first-order kinetic equation.

The quantum yield for the decomposition of (IVa) in methanol (0.26 ± 0.3) found for direct irradiation was calculated on the assumption of the usual zero-order photokinetics by following the diminution of the u.v. maximum of the starting material at 366 nm.

Quantum yields for the photoreactions of (III) could not be obtained due to the appearance of highly coloured ketazine products.

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[21] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*,**235**, 518.