Photolysis and Thermolysis of 3-n-Butyl-3-phenyldiazirine †

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The photochemical and thermal decompositions of 3-butyl-3-phenyldiazirine have been investigated in acetic acid and [$^2H_4$]acetic acid, and in other solvents with and without *m*-chloroperbenzoic acid. The results are consistent with the fact that the oxidation products are derived mainly from the reactions of 1-diazo-1-phenylpentane.

IN a previous paper,[1] we reported the results of thermal decomposition of 3-n-butyl-3-phenyldiazirine (1) in the presence of *m*-chloroperbenzoic acid (MCPBA). In the oxidation of (1) by MCPBA in chlorobenzene at 100 °C, the products were *cis*- and *trans*-1-phenylpent-1-ene oxide and valerophenone. The oxidation products and the information derived from kinetic studies indicate that the oxidation does not take place on the diazirine ring but rather on the decomposition products of the diazirine.

In order to gain more detailed information concerning the ring-opening process, we have investigated the thermal and photochemical decomposition of (1) in various solvents with and without MCPBA, and also in acetic and [$^2H_4$]acetic acid.

EXPERIMENTAL

Spectra were recorded using a Beckman model 4230 i.r. spectrophotometer, a Varian T-60 n.m.r. spectrometer, and a Unicam SP 800 u.v. spectrophotometer. G.l.c. analyses were carried out using a Perkin-Elmer model F-11 chromatograph equipped with a hydrogen flame ionization detector and fitted with a 12 ft column of 20% Carbowax on Chromosorb W. Radiation for the photolysis was provided by a Hanovia 450 W medium-pressure mercury lamp in a water-cooled quartz immersion well. This radiation was filtered by a Corning W5840 glass to allow transmission to the reaction mixture of wavelengths between 330 and 400 nm.

All products were identified by comparing their i.r., n.m.r., and u.v. spectra and g.l.c. retention time with those of authentic samples.

3-n-Butyl-3-phenyldiazirine and 1-diazo-1-phenylpentane were prepared by methods reported previously.[2]

Photolysis of 3-*n-Butyl*-3-*phenyldiazirine*.—(A) *In ether.* A solution of (1) (125 mg) and MCPBA (375 mg) in ether (30 ml) was irradiated in a Pyrex tube, thermostatted at 20 °C. The reaction was monitored by u.v. spectroscopy. Initially a red colour developed. After 50 minutes of irradiation, this colour and the diazirine absorption ($\lambda_{max.}$ 372 nm) had disappeared.

The mixture was diluted with ether (100 ml) and washed twice with saturated aqueous sodium hydrogencarbonate and then with water. The ether solution was separated and dried ($MgSO_4$). Removal of the solvent under reduced pressure yielded 105 mg of product. G.l.c. analysis of this product at 150 °C showed the presence of four components, *cis*-1-phenylpent-1-ene oxide (2.9%), *trans*-1-phenylpent-1-ene oxide (9.2%), valerophenone (80.3%), and acetophenone (7.5%).

(B) *In acetonitrile.* Photolysis of (1) and MCPBA in acetonitrile under conditions identical to those described in (A) was carried out. The products were *cis*-1-phenylpent-1-ene oxide (3.14%), *trans*-1-phenylpent-1-ene oxide (12.5%), valerophenone (81.6%), and acetophenone (2.6%).

(C) *In* NN-*dimethylformamide.* Photolysis of (1) and MCPBA in *NN*-dimethylformamide was carried out under similar conditions to those described above. The products were *cis*-1-phenylpent-1-ene oxide (5.5%), *trans*-1-phenylpent-1-ene oxide (23.1%), valerophenone (69.2%), and acetophenone (2.1%).

(D) *In* [$^2H_4$]*acetic acid.* A solution of (1) (175 mg) in CD_3COOD (4.5 ml) was irradiated for 5.5 h. The mixture was diluted with water (100 ml) and extracted with ether (2 × 50 ml). The combined ether extracts were washed with saturated aqueous sodium hydrogencarbonate (2 × 20 ml) and then with water (2 × 50 ml) and dried ($MgSO_4$). Removal of the solvent under reduced pressure yielded 150 mg of product.

G.l.c. analysis of this product showed three components, *cis*-1-phenyl[1-^2H]pent-1-ene, *trans*-1-phenyl[1-^2H]pent-1-ene, and 1-phenyl[1-^2H]pentyl [$^2H_3$]acetate. Column chromatography on silica gel, eluting with CCl_4–$CHCl_3$ separated the total product into two fractions, a mixture of the isomeric olefins, δ ($CDCl_3$) 7.3 (s, 5 H), 6.35 (m, 1 H), 2.2 (m, 2 H), 1.5, (m, 2 H), and 0.95 (t, 3 H); *m/e* 147 ($M^{\cdot+}$), and the ester, $\nu_{max.}$ 1 745 cm^{-1}, δ 7.27 (s, 5 H), 1.83 (m, 2 H), 1.23 (m, 4 H), and 0.87 (t, 3 H).

Thermolysis of 3-*n-Butyl*-3-*phenyldiazirine*.—(A) *In* NN-*dimethylformamide.* A solution of (1) (37 mg) and MCPBA (112 mg) in *NN*-dimethylformamide (3 ml) was heated for 20 h at 150—154 °C. After cooling, the products were isolated by the method described in the photolysis procedure. The g.l.c. analysis of the total product showed three components, *cis*-1-phenylpent-1-ene oxide (8.4%), *trans*-1-phenylpent-1-ene oxide (40.1%), and valerophenone (51.4%).

(B) *In acetonitrile.* Thermolysis of (1) and MCPBA in acetonitrile was carried out at 80—82 °C under conditions identical to those described in (A). The products were *cis*-1-phenylpent-1-ene oxide (6%), *trans*-1-phenylpent-1-ene oxide (33%), and valerophenone (60.9%).

RESULTS AND DISCUSSION

Decomposition of (1) *in Acetic Acid*.—Both thermal and photochemical decomposition of (1) in acetic acid (and in CD_3COOD) produced *cis*-1-phenylpent-1-ene, *trans*-1-phenylpent-1-ene, and 1-phenylpentyl acetate [equations (1) and (2)]. The distribution of these products is given in Table 1.

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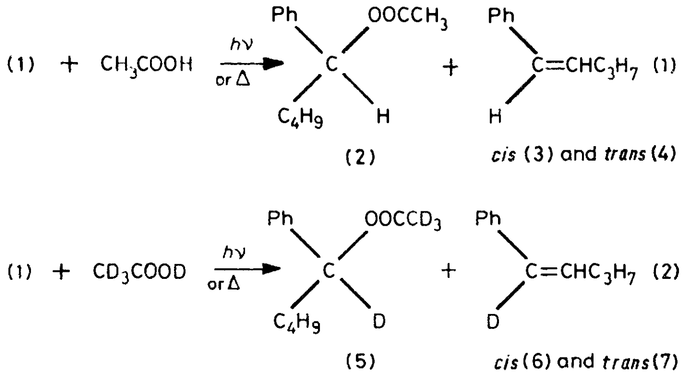
It can be seen from these data that both the identity and distribution of products from the thermolysis and photolysis experiments are nearly identical. This suggests that these reactions have a common intermediate, 1-diazo-1-phenylpentane. The agreement of these results indicates that, except for the mode of initiation and the character of the excited state initially formed, the reaction paths for thermolysis and photolysis are similar. The mechanism proposed for the photochemical decomposition of (1) in CD_3COOD is shown in Scheme 1.

Table 1

Percentage distribution of decomposition products

		Products					
Reaction	Solvent	(2)	(3)	(4)	(5)	(6)	(7)
$h\nu$	CH_3COOH	80.8	4.8	14.4			
Δ	CH_3COOH	84.0	3.8	12.2			
$h\nu$	CD_3COOD				80.7	4.0	15.2
Δ	CD_3COOD				84.7	4.0	11.3

Irradiation of (1) yields the electronically excited diazirine which, through one-bond cleavage (step a) gives the excited diazo-compound. This subsequently collapses to the ground state molecule which is stabilized by the presence of the phenyl substituent. Protonation of the diazo-compound yields the diazonium ion which gives rise to products (5)—(7) by the well known ground state reactions.



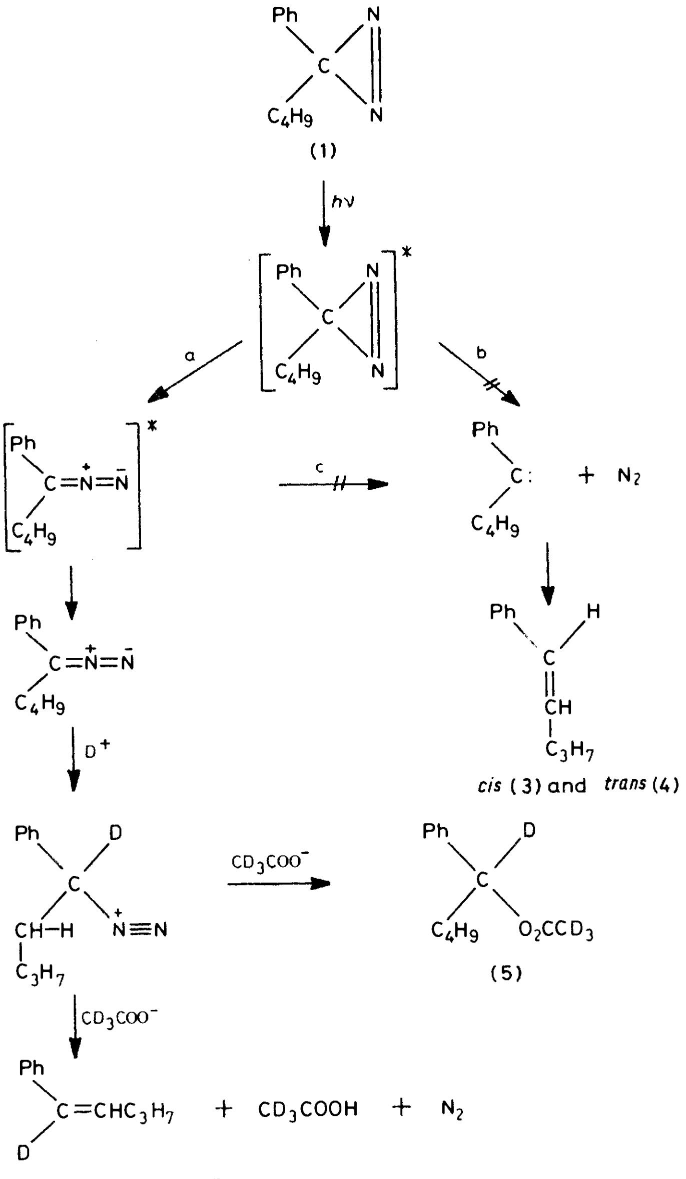
If steps b and c were significant, then the photolysis of (1) in CD_3COOD would give a mixture of deuteriated and non-deuteriated olefins. Careful analysis of n.m.r. spectra of the olefins formed reveals that only monodeuteriated olefins are produced. The deuterium atom must be incorporated from CD_3COOD as shown in Scheme 1. It is concluded that a carbene pathway is not important in the decomposition of (1) in acetic acid. The striking similarity of product distributions (Table 1) in thermal and photochemical decomposition argues that in both cases, the olefins are derived from the diazo-compound and not a carbene intermediate.

Table 2

Percentage product distribution as a function of acetic acid concentration

Moles of diazirine	Moles of acetic acid	Olefin (%)		Acetate (%)
		cis	*trans*	
1.1×10^{-3}	1.6×10^{-3}	4.5	18.4	77.1
1.1×10^{-3}	1.0×10^{-3}	4.4	19.2	76.3
1.1×10^{-3}	0.6×10^{-3}	3.7	19.3	76.9

In order to confirm this, thermal decomposition of (1) was carried out in various concentrations of acetic acid in acetonitrile. The results (Table 2) show that the olefin : acetate product ratio is insensitive to changes in acetic acid concentration. This indicates that these products are derived essentially as shown in Scheme 1, by reaction of the diazo-intermediate with acetic acid. If the carbene pathway were important, the olefin : acetate ratio should increase as the acetic acid concentration is decreased since the carbene may yield olefin by a simple



Scheme 1 Photochemical decomposition of (1) in CD_3COOD

intramolecular hydrogen transfer. The efficiency of such a reaction should be unaffected by the decrease in acetic acid concentration while acetate formation will be retarded under these conditions.

We therefore conclude that both thermal and photochemical decompositions proceed by one-bond rupture of the diazirine; the final products are formed by subsequent reaction of the diazo-compound produced from the diazirine. Experimental evidence indicates that reaction paths involving a carbene intermediate are inefficient in comparison with the diazo-route to products.

In view of the results of the experiments in acetic acid, we decided to carry out the photolysis of (1) in the presence of MCPBA in a variety of solvents. Solutions of (1) and MCPBA (diazirine : MCPBA 1 : 3) in diethyl ether, in acetonitrile, and in *NN*-dimethylformamide were prepared and irradiated (λ 330—400 nm) for 1—2 h. The products were *cis*- and *trans*-1-phenylpent-1-ene oxide, valerophenone, and acetophenone. The distribution of these products is given in Table 3 and the products are rationalized by the mechanism shown in Scheme 2.

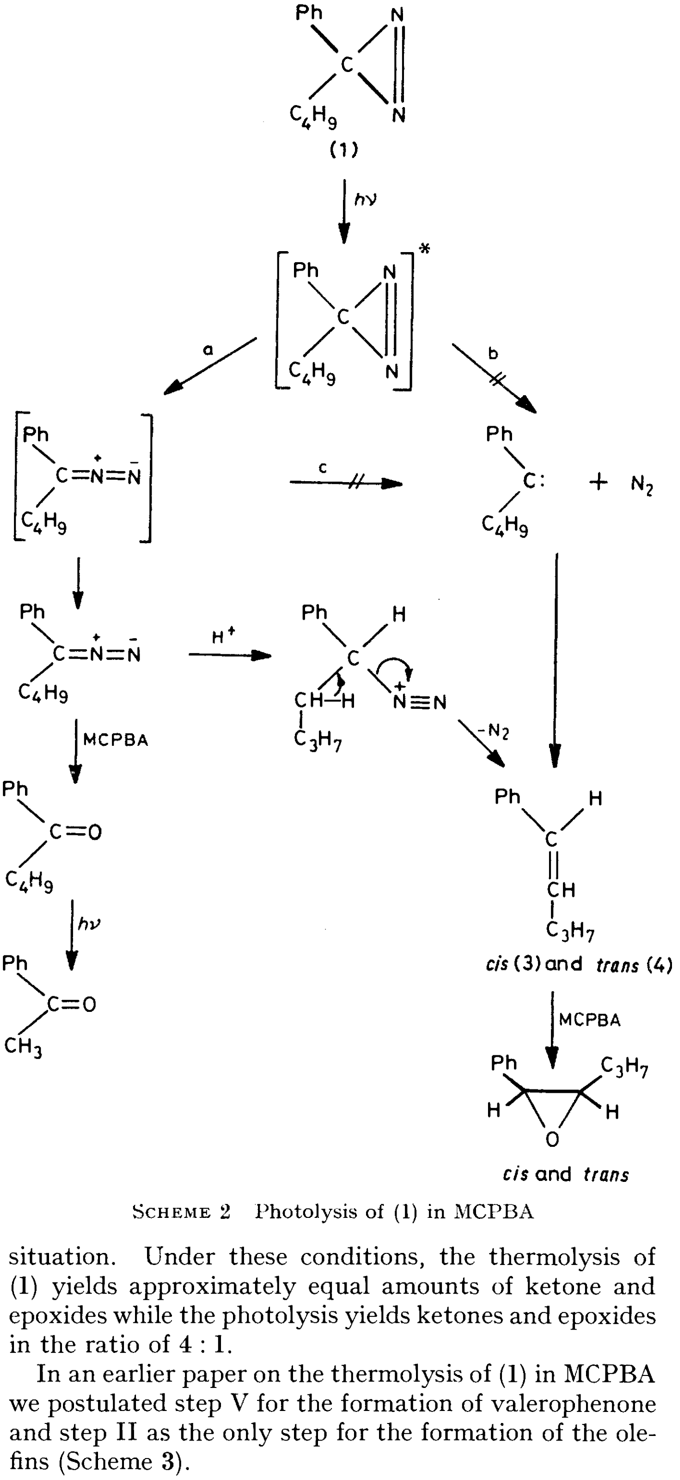
As discussed previously, 1-diazo-1-phenylpentane is oxidized by MCPBA to velerophenone which, under these conditions, undergoes a Norrish type II rearrangement to give acetophenone. The epoxides are the oxidation products of the corresponding olefins derived from the diazonium ion or *via* a carbene rearrangement. It will be seen later that the carbene routes, such as b and c, are not important in the photolysis. The results in Table 3 show the enhancement of epoxide formation when the solvent is changed from ether to *NN*-dimethylformamide. This is in accord with the proposed mechanism (Scheme 2), as the diazonium ion will be better stabilized by the more polar solvent.

Unlike the photolysis of (1) in acetic acid, photolysis in the presence of MCPBA gives a negligible amount of ester, in this case benzoate. This result is attributed to increased steric hindrance. The bulky *p*-chlorobenzoate anion might be expected to experience greater difficulty than the acetate ion in its approach to the diazonium ion.

In order to estimate the importance of pathways b and c in our scheme, the *cis* : *trans* ratio of epoxides, formed in the presence of MCPBA, and of olefins, isolated in the absence of MCPBA, were obtained for both thermolysis and photolysis of (1). The results are given in Table 4. When MCPBA is present, the *cis* : *trans* ratio (of epoxides) is *ca.* 1 : 4 and is nearly insensitive to the mode of initiation, suggesting that the epoxides are derived from a common intermediate such as 1-diazo-1-phenylpentane. Hence the contribution from the carbene pathways b and c are insignificant.

However, when MCPBA is absent, the *cis* : *trans* ratio (of olefins) in thermolysis is quite different from that of photolysis. In thermolysis, the average value (in four solvents) of the ratio is 1 : 6.6, while in photolysis, the average value (in three solvents) is 1 : 2.8. This difference is consistent with the postulate of a ' hot ' carbene intermediate[3] in the photolysis of (1) in ether, *NN*-dimethylformamide, and acetonitrile.

The products of both thermolysis and photolysis of (1) in the presence of MCPBA may be grouped as ketones and epoxides. A comparison of the distribution of products between these two groups from thermolysis with that from photolysis indicates an anomalous situation. Under these conditions, the thermolysis of (1) yields approximately equal amounts of ketone and epoxides while the photolysis yields ketones and epoxides in the ratio of 4 : 1.



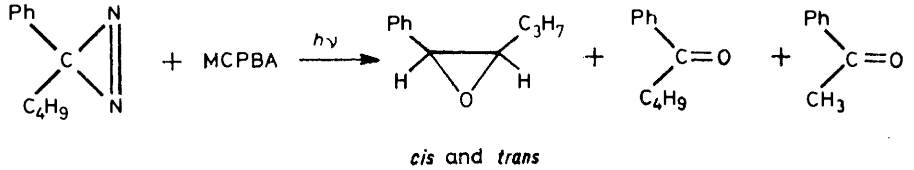
SCHEME 2 Photolysis of (1) in MCPBA

In an earlier paper on the thermolysis of (1) in MCPBA we postulated step V for the formation of valerophenone and step II as the only step for the formation of the olefins (Scheme 3).

It is clear from our present experiments that steps III and IV are also possible routes for the formation of the olefins in the thermolysis of (1) in MCPBA. It is not feasible to distinguish the exact percentage contribution from II—IV.

TABLE 3

Percentage distribution of photolysis products in various solvents



t/min	Solvent	Epoxide		Valerophenone	Acetophenone
		cis	*trans*		
50	Et$_2$O	2.9	9.2	80.3	7.5
120	CH$_3$CN	3.14	12.5	81.6	2.6
100	DMF	5.5	23.1	69.2	2.1

Diazirine: MCPBA 1 : 3.

In summary, the photochemical decomposition of (1) proceeds *via* a one-bond breaking process to give the diazo-intermediate. In the thermolysis of (1), the major pathway is also the isomerization to the diazo-compound, and the direct two-bond rupture to give a carbene intermediate is considered to be only a minor process. The problem is that the contribution of the latter process is difficult to assess by conventional experiments since solvent dependence provides further complications.

In the liquid phase photolysis of cycloalkanespirodiazirine,[4] Stevens and his co-workers provided evidence for the formation of diazocycloalkane in the initial phase of the reaction. The photolysis of pentamethylenediazirine in acetic acid and acetic [^{2}H]acid respectively suggested that, in the photolysis of a diazirine, competitive one- and two-bond ruptures of the diazirine ring are possible. As well, in the thermal decomposition of 3-chloro-3-methoxydiazirine, a direct two-bond cleavage to nitrogen and chloromethoxycarbene is proposed.[5] In the photolysis of 3-aryl-3*H*-diazirines,[6] Smith and Knowles reported that the photolytic fragmentation to the arylcarbene and the photoisomerization to the linear diazo-compound are both possible. The experimental results of Liu and Toriyama[7] on the thermal unimolecular isomerization of 3-methyl-3-vinyldiazirine are consistent with a one-bond rupture mechanism.

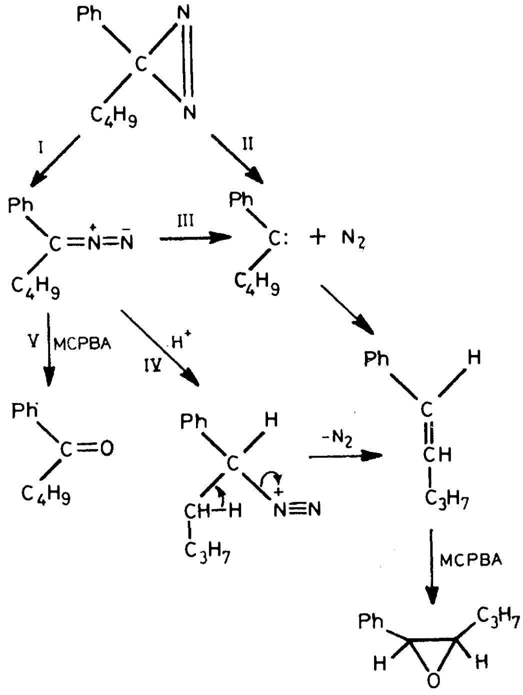
TABLE 4

Product ratios for photolysis and thermolysis of (1)

Solvent	*cis* : *trans* Epoxide ratio	*cis* : *trans* Olefin ratio
Photolysis		
Et$_2$O	1 : 3.5 *	1 : 2
DMF	1 : 4.2 *	1 : 3
CH$_3$CN	1 : 4.3 *	1 : 3.2
Thermolysis		
PhCl		1 : 5
DMF	1 : 4.1 *	1 : 6.1
CH$_3$CN	1 : 4.3 *	1 : 7.5
DMSO		1 : 7.8

* In MCPBA.

Evidence available in the literature appears to indicate that both sequential 'one-bond' and simultaneous 'two-bond' rupture of the C–N bonds are possible decomposition modes. The relative importance of these two elementary processes depends upon the substituents on the diazirine ring.



SCHEME 3 Thermolysis of (1) in MCPBA

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