The Preparation and Photolysis of 3-Aryl-3*H*-Diazirines

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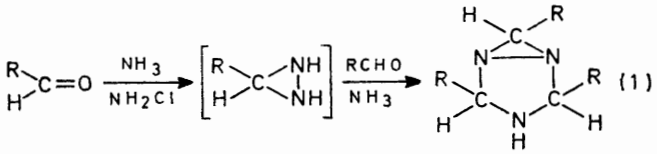
The preparation of a number of 3-aryl-3*H*-diazirines is reported. On irradiation, these materials undergo both photolytic fragmentation to the arylcarbene and photoisomerisation to the linear diazo-compound which is then itself photolysed. The existence of a second intermediate is also apparent from the spectral changes observed.

OUR interest in chemically stable precursors of non-rearranging carbenes for the photoaffinity labelling of biological receptor sites [1] has led us to explore synthetic routes to, and the photochemistry of, 3-aryl-3*H*-diazirines. Unlike the 3-aryl-3-halogenodiazirines, the 3*H*-compounds have not been well-studied and only one member of the series has been previously synthesised.[2] We report here a number of synthetic approaches to these compounds and evidence for two intermediates in the photochemical generation of carbenes from them. A preliminary account of some of this work has been published.[3]

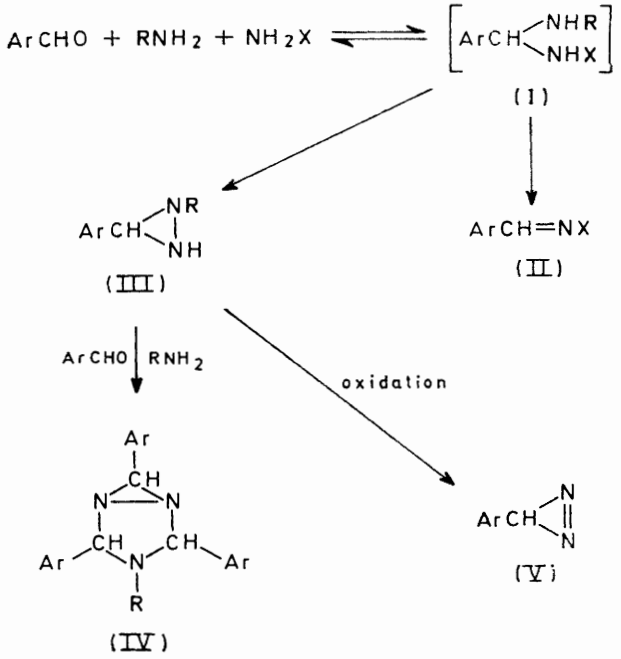
RESULTS AND DISCUSSION

Preparation of 3-*Aryl*-3H-*diazirines*.—Two general approaches to the 3*H*-diazirine skeleton have been reported. In the first, the reaction of aliphatic aldehydes with ammonia and chloramine results in the formation of 1,3,5-triazabicyclo[3.1.0]hexanes,[4] which arise from the condensation of first-formed diaziridine with excess of aldehyde and ammonia [reaction (1)].



Formation of the diazirine is achieved by partial acid hydrolysis of the bicyclic compound to the diaziridine which is trapped *in situ* by oxidation. Hydroxylamine-*O*-sulphonic acid can be used with advantage to replace the unstable chloramine.[5] The only reports of aromatic ketones or aldehydes being used with aminating agents and ammonia concern acetophenone [6] (from which the diaziridine is formed in very low yield) and benzaldehyde [7] (from which the triazabicyclohexane is produced in 30% yield).

In attempts to produce the triaryltriazabicyclohexanes from a variety of *p*-substituted benzaldehydes (H, *p*-Cl, *p*-CH_3, *p*-OCH_3) with an equimolar quantity of hydroxylamine-*O*-sulphonic acid in methanolic ammonia at or below 0°, only the ammonium salts of the corresponding *O*-sulphonyl-oximes were produced along with traces of the azines. These oximes are inert to further reaction with methanolic or liquid ammonia at temperatures at which any diaziridine formed could be stable. This behaviour is in contrast to the *O*-tosyl-oximes of perfluoroalkyl ketones which have been reported to react with ammonia to give diaziridines in high yield.[8] However, *O*-tosylbenzaldoxime was found not to react with ammonia to yield diaziridine, and the original chloramine method was investigated. When chloramine is used as the aminating reagent, ring closure of the *N*-chloro-*gem*-diamine [Scheme 1; (I)] becomes



SCHEME 1 Preparation of 3-aryl-3*H*-diazirines

competitive with elimination of amine [to (II)] and the resulting 3-aryl-3*H*-diaziridines (III) undergo further condensation with excess of aldehyde and ammonia to give 2,4,6-triaryl-1,3,5-triazabicyclo[3.1.0]hexanes (IV) (see Table 1).

The acid-catalysed partial cleavage of alkyltriazabicyclohexanes to diaziridines, followed by oxidation *in situ* with chromic acid, is a well established route to 3-alkyl-3*H*-diazirines.[4] Aryl substitution, however, renders opening of the *N*-protonated diaziridine ring

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[1] J. R. Knowles, *Accounts Chem. Res.*, 1972, **5**, 155.
[2] W. A. Graham, *J. Amer. Chem. Soc.*, 1966, **88**, 4677.
[3] R. A. G. Smith and J. R. Knowles, *J. Amer. Chem. Soc.*, 1973, **94**, 5072.
[4] E. Schmitz, *Chem. Ber.*, 1962, **95**, 795; E. Schmitz and R. Ohme, *Tetrahedron Letters*, 1961, 612.
[5] H. J. Abendroth, *Angew. Chem.*, 1961, **73**, 67.
[6] E. Schmitz and R. Ohme, *Chem. Ber.*, 1961, **94**, 2166.
[7] E. Schmitz, *Chem. Ber.*, 1962, **95**, 688.
[8] B. L. Dyatkin, K. N. Makarov, and T. L. Knunyants, *Tetrahedron*, 1971, **27**, 51.

competitive with the hydrolysis of the remainder of the triazabicyclohexane system, resulting in a low yield of diaziridine (Table 2) even if a large excess of dichromate with minimal amounts of acid are used.

TABLE 1

Reactions of aromatic aldehydes with aminating reagents and amines

Ar *	R *	X *	Product	Characterisation	Yield † (%)
a	H	OSO_3H	(IIa)	n.m.r., C. H, N, m.s.	41
b	H	OSO_3H	(IIb)	n.m.r., C, H, N, m.s.	37
c	H	OSO_3H	(IIc)	n.m.r., C, H, N, m.s.	35
d	H	OSO_3H	(IId)	n.m.r., C, H, N, S, Cl, m.s.	45
e	H	OSO_3H	(IIe)	n.m.r., C, H, N, S	26
a	H	Cl	(IVa)	n.m.r., C, H, N, i.r., m.s.	25
b	H	Cl	(IVb)	n.m.r., C, H, N, i.r., m.s.	28
c	H	Cl	(IVc)	n.m.r., C, H, N, i.r., m.s.	27
j	H	Cl	Isolation of nitrile	n.m.r., i.r.	
g	Bu^t	Cl	(IIg)	n.m.r., C, H, N, Cl, i.r., m.s.	
j	Bu^t	OSO_3H	(IIIj)	n.m.r., HI oxidation	
g	Bu^t	OSO_3H	Hydrazone	n.m.r., i.r.	
j	Allyl	OSO_3H	(IIIi)	n.m.r., HI oxidation	

* As in Scheme 1: a, phenyl; b, *p*-tolyl; c, *p*-methoxyphenyl; d, *p*-chlorophenyl; e, *p*-carboxyphenyl; f, *p*-carboxymethoxyphenyl; g, *p*-nitrophenyl; h, *m*-nitrophenyl; i, 4-pyridyl; j, 3-pyridyl. † Based on aldehyde.

TABLE 2

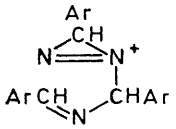
Oxidation of aryldiaziridines and triazabicyclohexanes

Starting material *	R *	Oxidant †	Product	Characterisation	Yield (%)
(IVa)	(H)	iii + iv	(Va)	n.m.r., u.v., i.r., m.s.	4
(IVa)	(H)	ii	(Va)	n.m.r., u.v., i.r.	48
(IIIa) ‡	H	i	(Va)	u.v.	1
(IIIb) ‡	H	i	(Vb)	n.m.r., u.v., i.r., m.s.	3·6
(IIIc) ‡	H	i	(Vc)	n.m.r., u.v., i.r.	1·9
(IIIf) ‡	H	i	(Vf)	n.m.r., u.v., i.r.	1·0
(IIIh) ‡	Bu^t	ii	(Vh)	n.m.r., u.v., i.r.	3·3
(IIIi) ‡	Bu^t	ii	(Vi)	n.m.r., u.v., i.r.	15
(IIIj) ‡	Bu^t	ii	(Vj)	n.m.r., u.v., i.r.	8·4

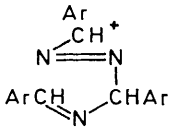
* As in Scheme 1 and Table 1. † i, HgO; ii, Bu^tOCl; iii, H^+; iv, $H_2Cr_2O_7$. ‡ Generated *in situ* from aldehyde.

Other oxidants that were tried in the hope of trapping the incipient diaziridine more effectively were H_2O_2–Cu^{2+} (*cf.* ref. 10), lead tetra-acetate, *N*-bromosuccinimide, and peracetic acid. Direct oxidative cleavage of the triphenyltriazabicyclohexane was achieved, however, with t-butyl hypochlorite in methanol at 0°, yielding 3-phenyl-3*H*-diazirine in 48% yield. Unfortunately, this appears not to be a general method since *para*-substituted arylbicyclohexanes (*e.g.* *p*-CH_3, *p*-OCH_3) give no diazirine with this reagent. The sensitivity of this reaction to the ring substituent can be attributed to the relative stabilities of the cations (VI) and (VII) formed by loss of chloride ion from N-3.

More success attended the oxidative trapping of the diaziridine on its way to the bicyclohexane, rather than as a product of acid-catalysed bicyclohexane hydrolysis.



(VI)



(VII)

Thus yellow mercuric oxide is sufficiently stable to ammonia and chloramine and yet adequately effective as an oxidant of diaziridine, to be added directly to the reaction mixture of arenecarbaldehyde–methanolic ammonia–chloramine. The yields of diazirine based on aldehyde are low, but the simplicity of the work-up procedure gives this reaction some synthetic utility. Oxidative trapping of the diaziridine in this way supports the view that the diaziridine ring is formed before a *sym*-hexahydrotriazine system.[9]

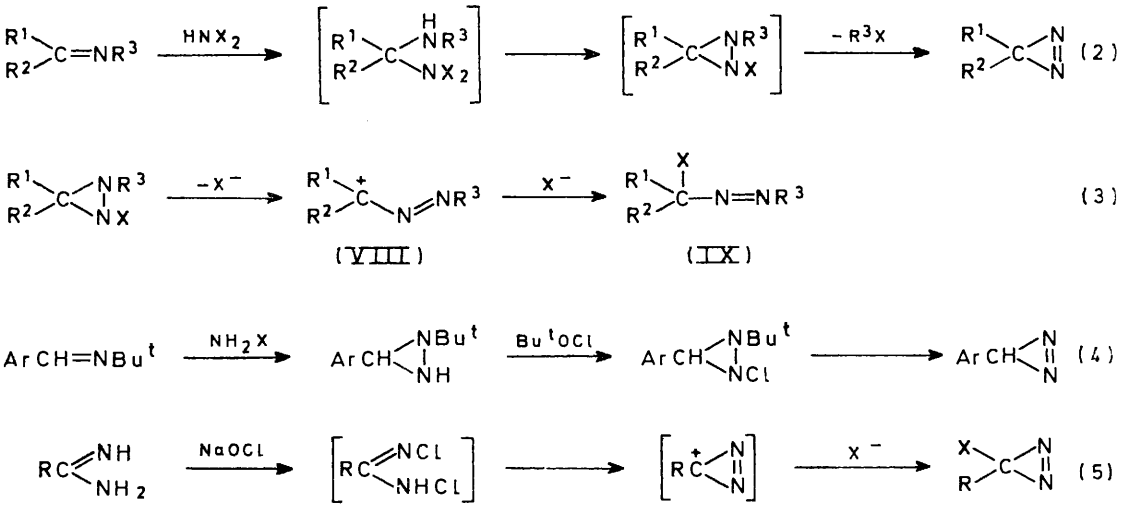
The second diazirine synthesis, due to Graham,[11] involves the reaction of an alkylimine with a dihalogenoamine, which is followed by the elimination of alkyl halide [reaction (2)]. Diazirine itself [reaction (2; $R^1 = R^2 = H$)] can be prepared by this reaction, difluoramine giving better yields than dichloramine. If R^1 or R^2 is electron-releasing, the stabilisation of the carbonium ion (VIII) leads to predominant formation of the azo-compound (IX) [reaction (3)].

3-(*p*-Nitrophenyl)-3*H*-diazirine was the only known example of a 3-aryl-3*H*-diazirine, and was prepared [2] by reaction (2), with difluoramine. Since difluoramine is a very hazardous and expensive reagent, dichloramine was used in the present work. No diazirine resulted from reactions in which dichloramine [generated from sodium hypochlorite and ammonia (*cf.* ref. 12) was extracted into an organic layer containing aryl-t-butylimine, and this approach was modified by preforming the 3-aryl-1-t-butyl-3*H*-diaziridine and following this by *N*-chlorination [reaction (4)]. 3-Aryl-1-t-butyl-3*H*-diaziridines are thermally unstable, and although the 3- and 4-pyridyl compounds were obtained in low yield from the corresponding aldehydes, extensive decomposition occurred during purification. From *p*-nitrobenzaldehyde t-butylimine and hydroxylamine-*O*-sulphonic acid, only the t-butylhydrazone of *p*-nitrobenzaldehyde resulted. Since the isolation of these t-butyldiaziridines proved impractical, it was decided to trap them by *N*-chlorination *in situ*. The putative diaziridines are generated by reaction of the t-butylimines with hydroxylamine-*O*-sulphonic acid in ethanol–water–base at 0°. After an appropriate time (commonly 2—3 h) t-butyl hypochlorite is added directly at −10—0°. Preparative t.l.c. suffices to purify the resulting diazirines from the complex mixture of products. 3-(3-Pyridyl)-3*H*-, 3-(4-pyridyl)-3*H*-, and 3-(*m*-nitrophenyl)-3*H*-diazirines were

[9] A. T. Nielsen, R. L. Atkins, D. W. Moore, D. Mallory, and J. M. Laberge, *Tetrahedron Letters*, 1973, 1167.
[10] S. Hünig, H.-R. Müller, and W. Thier, *Tetrahedron Letters*, 1961, 353.
[11] W. H. Graham, *J. Amer. Chem. Soc.*, 1962, **84**, 1063; W. H. Graham, *J. Amer. Chem. Soc.*, 1966, **88**, 4677.
[12] W. H. Graham, *J. Org. Chem.*, 1965, **30**, 2108.

prepared by this method in yields of 5—15%. Despite the complexity of the product mixture, the ease of isolation makes this a practicable route to electron-withdrawing 3-aryl-3*H*-diazirines.

To compare the photochemical behaviour of the 3*H*-diazirines with the more readily accessible 3-halogeno-diazirines (see below), some 3-aryl-3-halogenodiazirines were prepared. The method followed was that of halogenation of amidines in the presence of halide ion



first reported by Graham [13] [reaction (5)]. The 3-phenyl- and 3-*p*-methoxyphenyl-3-chloro-diazirine were prepared.

Properties of the 3-Aryldiazirines.—With the exception of the *p*-carboxymethoxyphenyl compound, all the aryldiazirines prepared were clear yellow oils, of limited stability in the pure state at or above room temperature. They can, however, be stored conveniently as dilute (<0·1M) solutions in inert solvents such as hexane, and are stable in this form for several months at −20°. The water-soluble diazirines (*p*-carboxymethoxyphenyl, and 3- and 4-pyridyl) were stable in aqueous solution for hours in 1M-acetic acid or 1M-NaOH: the half-life of the *p*-carboxymethoxyphenyl derivative in 0·1M-NaOH being *ca.* 30 h at 37°. 3-Phenyl-3*H*-diazirine does not react with cyclopentadiene at room temperature and is only slowly affected by dithionite, in contrast to linear azo-compounds. Unlike diazoalkanes and diazoketones, the decomposition of the aryldiazirines is not significantly catalysed by cupric ion. The position of the long-wavelength u.v. absorption band of the diazirines, characteristic of the azo-chromophore, depends on the substituents in the aromatic ring and there is a marked bathochromic shift of this band on protonation of the pyridine ring of the 3- and 4-pyridyl compounds. These observations suggest some interaction of the π-electron systems of the diazirine group and the aromatic ring.

The chemical stability of these diazirines contrasts markedly with the corresponding linear diazo-compound isomers, and augurs well for their use as reagents for the photolabelling of biological macromolecules.

Photolysis of 3-Aryl-3H-diazirines.—It is clearly important to understand, at least in outline, the processes consequent upon the irradiation of a potential photolabelling reagent. The ease of photolysis, the intermediacy of reactive species, and the selectivity of these species are all features that require evaluation.

On photolysis of diazirine itself, singlet methylene is produced,[14] and it has been proposed that at least 20% of the diazirine is photoisomerised to diazomethane *en route* to methylene.[15] In 3-alkyl-3*H*, 3,3-dialkyl, and other diazirines with α-hydrogen atoms, photolysis normally produces olefins,[16] presumably by rapid hydrogen migration following primary carbene formation. Small amounts of intramolecular carbene insertion products have also been observed. Cycloheptyl- and cyclo-octyldiazirines have been reported to photoisomerise to the diazo-compounds, photolysis in the presence of acetic acid yielding significant amounts of the cycloalkyl acetates.[17]

When 3-phenyl-3*H*-diazirine is irradiated in hexane solution, there is an immediate rapid rise in the u.v. absorbance at *ca.* 275, 362, (this latter being the diazirine $\lambda_{max.}$) and 480 nm, followed by a fall in intensity of all these bands (Figures 1 and 2). Successive spectra do not show isosbestic points. Provided that the concentration of absorbing species is sufficiently low that the absorption of the incident radiation by the solution does not significantly affect the radiation intensity over the bulk of the sample, the kinetics of the absorbance changes approximate to that expected for sequential first-order processes (Figure 2). Evidently the intermediate that accumulates early in the photolysis is also photolabile, although less so than the diazirine itself. The spectral changes are independent of diazirine con-

[13] W. H. Graham, *J. Amer. Chem. Soc.*, 1965, **87**, 4396.
[14] H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 1962, 79.
[15] M. J. Amrich and J. A. Bell, *J. Amer. Chem. Soc.*, 1964, **86**, 292.
[16] H. M. Frey, *Adv. Photochem.*, 1966, **4**, 225.
[17] G. F. Bradley, Ph.D. Thesis, University of Southampton, 1967 (quoted in W. Kirmse, 'Carbene Chemistry,' Academic Press, New York, 1971).

centration and of temperature (—60° and room temperature were studied). Other 3-aryl-3*H*-diazirines behave similarly, though the effect is smaller for (*e.g.*) the *p*-tolyl compound, and for the *p*-methoxyphenyl derivative no initial increase in absorbance is observed, though there are still marked deviations from first-order kinetics.

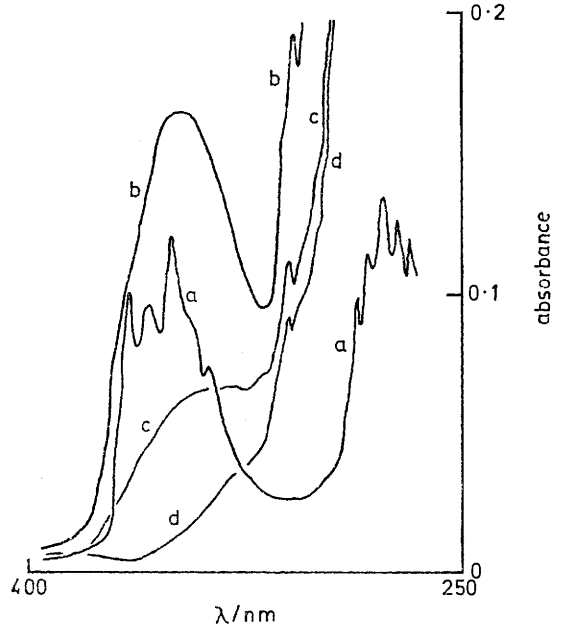


FIGURE 1 Successive u.v. spectra of 3-phenyl-3*H*-diazirine (0·374mM) in hexane on irradiation: a, initial spectrum; b—d, spectra after 1, 3, and 10 min respectively.

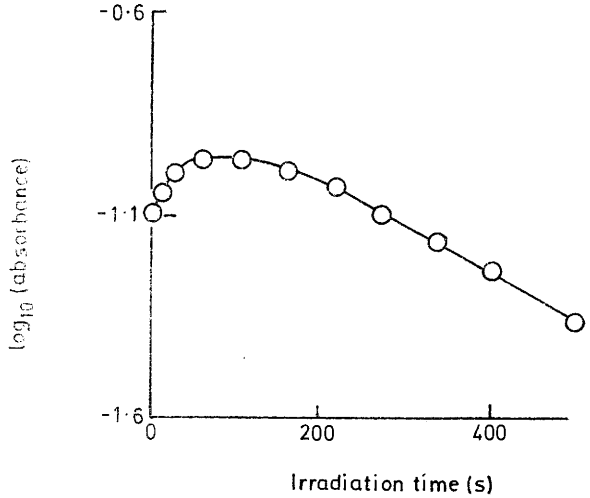


FIGURE 2 Time dependence of the absorbance at 362 nm for the irradiation of 3-phenyl-3*H*-diazirine (see Figure 1)

The new absorption bands that appear at *ca.* 275 and 480 nm correspond exactly to those reported for aryl diazo-compounds,[18] and two tests were applied to confirm the intermediacy of the linear diazo-compound in diazirine photolysis. First, in the presence of adequate acetic acid, diazo-compound should be destroyed faster than it is formed. For the 3-phenyl and 3-*p*-tolyl compounds it was found that at acetic acid concentrations of 0·1—0·5M, clean first-order kinetics were obeyed for the disappearance of the diazirine absorption band (Figure 3), and successive u.v. spectra showed isosbestic points. Secondly, when 3-*p*-tolyl-3*H*-diazirine was photolysed as a liquid film between sodium chloride discs or as a solution in carbon tetrachloride, the diazirine absorption at 1600 cm^{-1} disappeared concomitantly with the appearance and subsequent decay of the characteristic N=N stretching absorption of the diazo-compound at *ca.* 2000 cm^{-1}. These experiments confirm that the diazirines are at least partly photoisomerised to the linear diazo-compound during photolysis.

Two questions now arise: can diazirine be formed photochemically from diazo-compound in significant

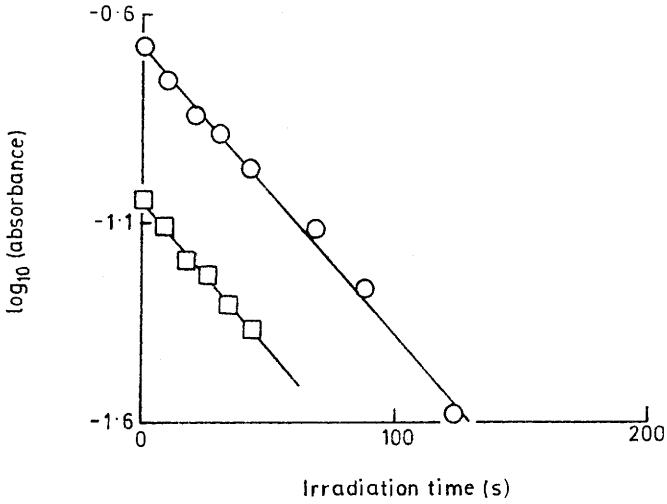


FIGURE 3 Time dependence of the absorbance at the diazirine $\lambda_{max.}$ during the photolysis of 3-phenyl-3*H*-diazirine (□) (362 nm; 0·304mM in hexane containing 0·1M-acetic acid); and of 3-(*p*-tolyl)-3*H*-diazirine (○) (368 nm; 0·69mM in hexane containing 0·5M-acetic acid)

amounts, and does the diazirine also eliminate N_2 directly to the arylcarbene? On irradiation of phenyldiazomethane under conditions similar to those used for the diazirine photolysis, no diazirine absorption could be detected in the u.v. If a photochemical equilibrium is set up between diazirine and diazo-compound, it is clearly (as expected) in favour of the diazo-compound. To investigate whether the diazirine fragments directly, the products from irradiating the diazirine in hexane containing varying amounts of acetic acid, were investigated. The products are almost exclusively the corresponding benzyl acetate, and a mixture of arylheptanes. The ratio of benzyl acetate (from the reaction of diazo-compound with acetic acid) to arylheptane (from carbene insertion into solvent) is shown in Figure 4. The product ratios were obtained from n.m.r. of the crude photolysis reaction mixture after concentration. Confirmation of the presence of the

[18] G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, 1964, **86**, 4042.

benzyl acetates and arylheptanes was provided by mass spectrometry and i.r. spectroscopy. It is apparent from

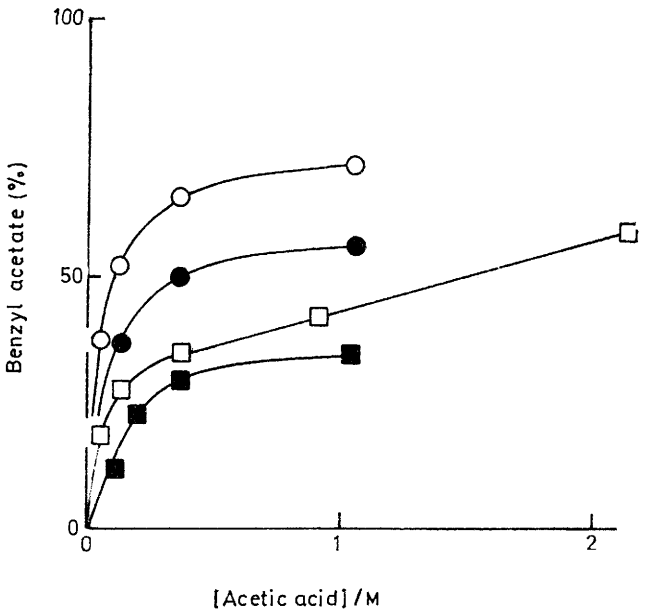


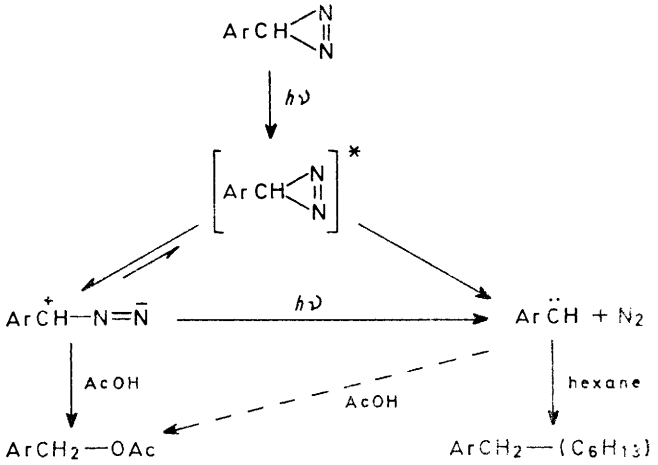
FIGURE 4 Variation in product composition with added acetic acid, for the photolysis of various 3-aryl-3*H*-diazirines in hexane: phenyl, □; *p*-tolyl, ●; *p*-methoxyphenyl, ○; 4-pyridyl, ■

Figure 4 that up to *ca.* 0·2M acid the proportion of benzyl acetate increases rapidly with increasing acid concentration, indicating that low acid concentrations are insufficient to convert diazo-compound to acetate (by protonation and nitrogen loss) before it is itself photolysed. The observation of plateaux in the curves indicates an upper limit for conversion of diazirine to acetate *via* diazo-compound and suggests that above *ca.* 0·5M-acetic acid, the acetate : heptane ratio represents the true partition ratio of diazirine that photoisomerises to diazo-compound and diazirine that photolyses directly. The plateaux of Figure 4 are not flat (as is shown for the unsubstituted compound) and this is presumably due to the direct insertion of arylcarbene into the O–H bond of acetic acid. This implies some electrophilic selectivity of the arylcarbene favouring O–H insertion, since even at 2M-acetic acid, the molar ratio of C–H to O–H bonds is *ca.* 50 : 1. From these results we may conclude that the diazirine does indeed fragment to arylcarbene directly, the direct fragmentation being about as probable as the photoisomerisation process (Scheme 2).

It can also be seen from Figure 4 that the photoisomerisation competes more effectively if electron-releasing substituents are present, and it is likely that the transition state for the diazirine–diazo-compound conversion has some dipolar character [reaction (6)].

The photolytic pathway derived so far (Scheme 2) is, however, inadequate to explain the following. If solutions of 3-phenyl-3*H*-diazirine in hexane are irradiated briefly until the maximal increase in absorbance at 275, 362, and 480 nm has occurred, and then acetic acid is added in the dark to destroy all the phenyldiazomethane, the resulting spectrum shows that the bands at 275 and 480 nm have disappeared, but there is no change in the increased absorbance at 362 nm. Another intermediate, in addition to phenyldiazomethane, is therefore implicated. Since no anomalies are seen in the photolysis of diazirines in the presence of acid, this second intermediate must be photochemically connected to an acid-labile substance, presumably the diazo-compound.

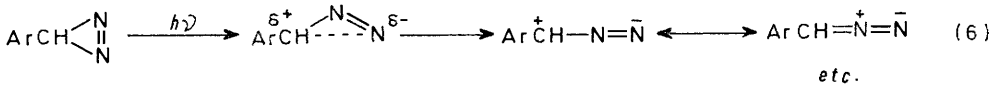
By using relatively large amounts of diazirine at low concentration, this second intermediate could be generated in small though significant quantity. Analysis by t.l.c. showed a component that migrates very close to the unchanged diazirine. This component had the following properties: $\lambda_{max.}$ (n-hexane) 233 and 355 nm (no fine structure); $\nu_{max.}$ 1604 cm^{-1} (? N=N); τ 2·8 and 3·1 (4H, m), 4·2br (1H, s), and 7·1 (1H, s). On irradiation it appears from the changes in the u.v. that this



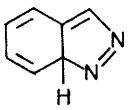
SCHEME 2 Simplified scheme for the photolysis of 3-aryl-3*H*-diazirines

material can be converted photochemically to the diazo-compound, since an acid-sensitive absorption band at 273 nm appears at early stages of the photolysis (Figure 5).

This second intermediate has spectroscopic properties consistent with its being an azo-compound, and since it is generated from 3-phenyl-3*H*-diazirine and undergoes apparent photolysis to phenyldiazomethane structure (X), 7a*H*-indazole, is tentatively assigned to it. No examples of 7a*H*-indazoles are known, though these species have been suggested as intermediates in the



pyrolytic generation of carbenes from 1*H*-indazoles.[19] Despite the high reactivity expected of such a structure,



(X)

the number of plausible alternatives is limited. Benzonitrile imine ($PhC\equiv\overset{+}{N}-\bar{N}H$) ⟷ ($Ph\bar{C}=\overset{+}{N}=NH$) [20] is a very reactive 1,3-dipole that has defied isolation and does not give rise to carbene insertion products. 2-*H*- and 3a-*H*-Indazoles should be as prone to rearrangement as 7a*H*-indazole, and are not compatible with the n.m.r.

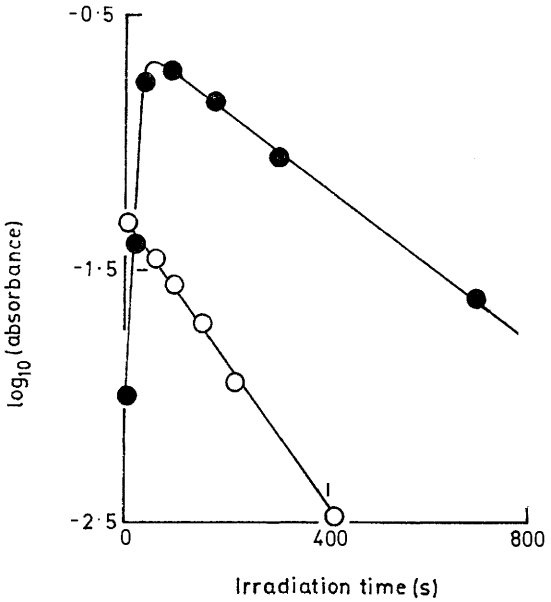


FIGURE 5 Time dependence of the absorbance at 273 (●) and at 360 nm (○) of the photolysis of the second intermediate (X) (see text) (*ca.* 1mM) in hexane containing no (●) or 0·2M-acetic acid (○)

data. Polymerisation products would not be expected to show the observed photolysis behaviour. Where this second intermediate lies in Scheme 2 is not clear, but the ultimate formation of arylcarbenes in high chemical yield from the photolysis of 3-aryl-3*H*-diazirines is without doubt.

In contrast to the photochemical behaviour of the 3-aryl-3*H*-diazirines described, the analogous 3-aryl-3-halogenodiazirines show no spectral peculiarities on irradiation. Acetic acid is without effect, and first-order decay of the u.v. absorption bands with clean isosbestic points are observed. This suggests that for the 3-halogeno-compounds either no photoisomerisation occurs (as has been implicitly assumed in previous studies of these compounds) or that the α-halogenodiazo-compounds decompose very rapidly. Chlorodiazomethane is known to be thermally most unstable.[21] Very recently, Liu and Chen [22] have reported the thermolysis of some 3-aryl-3-chlorodiazirines in cyclohexene. Their conclusions concerning the mode of breakdown of aryldiazirines are in broad agreement with the photochemical results presented here.

Recent work on the mechanism of photoaffinity labelling has emphasised the importance of generating a reaction intermediate whose lifetime is less than the molecule's residence time within its receptor site.[23] It is likely that the shorter life-times and more indiscriminate reactivity of arylcarbenes may make them more suitable intermediates for such experiments than the arylnitrenes used in earlier work from this laboratory.[24] Furthermore, bonds formed in labelled material by arylcarbenes are not likely to be labile, as are some that may be formed in nitrene insertion reactions. The aryldiazirine–arylcarbene system should also score over the α-ketodiazo-compound–α-ketocarbene conversion used by a number of investigators,[25] both in respect of the lesser chemical reactivity of the diazirine precursor and of the absence of wasteful molecular rearrangement (to keten) which α-ketocarbenes undergo.

EXPERIMENTAL

^1H N.m.r. spectra were obtained on a Perkin-Elmer R14 100 MHz spectrometer at ambient probe temperature with tetramethylsilane as internal reference and CCl_4 or [$^2H_6$]-dimethyl sulphoxide (DMSO) as solvent. Mass spectra were measured on an A.E.I. MS9 spectrometer. Analytical and preparative t.l.c. was carried out on silica gel plates using the following solvent systems: (*a*) light petroleum–acetone 4 : 1 (v/v); (*b*) light petroleum–chloroform 1 : 1 (v/v); (*c*) light petroleum–acetone 2 : 1 (v/v); (*d*) n-hexane; (*e*) n-hexane–acetone 2 : 1 (v/v); (*f*) n-hexane–chloroform 1 : 1 (v/v); (*g*) benzene–glacial acetic acid 6 : 1 (v/v); (*h*) n-hexane–acetone 10 : 7 (v/v); (*i*) chloroform; (*j*) light petroleum–acetone 5 : 1 (v/v); (*k*) benzene–glacial acetic acid 10 : 1 (v/v); (*l*) light petroleum–acetone 17 : 13 (v/v).

N-Benzylidenehydroxylamine-O-sulphonic Acid Ammonium Salt (IIa; X = OSO_3H).—Benzaldehyde (21·2 g) was dissolved in ammonia-saturated methanol (500 ml) and cooled to −70°. Hydroxylamine-*O*-sulphonic acid (22·6 g) was added over 30 min and the mixture allowed to warm to room temperature over 4 h. The material was then evaporated to dryness, washed with ether, and recrystallised from ethanol–methanol 4 : 1 (v/v) to give *crystals* (17·8 g), m.p. 156°, τ (DMSO) 1·73 (1H, s, CH=N), 2·33 (2H, m, aromatic), 2·55 (3H, m, aromatic), and 2·88br (s, exchangeable NH), *m/e* 103, $\lambda_{max.}$ (ethanol) 206 (ε 19,000), 250 (19,400),

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277 (2400), and 288 (1400) nm, $\nu_{max.}$ (mull) 3250 cm^{-1} (NH) (Found: C, 37·3; H, 4·7; N, 13·0. $C_7H_{10}N_2O_4S$ requires C, 38·5; H, 4·6; N, 12·8%), approximate *M* (osmometry) 191. The material liberated iodine from HI solutions and, on heating alone to 120°, decomposed rapidly to benzonitrile (i.r.).

N-p-*Methylbenzylidenehydroxylamine*-O-*sulphonic Acid Ammonium Salt* (IIb; X = OSO_3H).—This compound was prepared analogously to the unsubstituted material, yellow *platelets*, m.p. 154°, τ (DMSO) 1·75 (1H, s, CH=N), 2·36 (2H, d, 2- and 6-H), 2·70 (2H, d, 3- and 5-H), 3·00br (s, exchangeable NH), and 7·67 (3H, s, CH_3), *m/e* 117, $\lambda_{max.}$ (EtOH) 211 (ε 27,600), 253 (26,400), 284 (12,600), 293 (9400), and 306 (600) nm, $\nu_{max.}$ (mull) 3200 cm^{-1} (NH) (Found: C, 42·8; H, 5·5; N, 12·3. $C_8H_{12}N_2O_4S$ requires C, 41·4; H, 5·2; N, 12·1%). In a separate experiment the crude reaction mixture was poured into water, and the mixture extracted with chloroform. The combined extracts were dried (Na_2SO_4), evaporated to dryness, and the resulting solid recrystallised from methanol to give *p*-tolualdehyde azine as yellow plates, m.p. 160° (lit.,[26] 157°) (Found: C, 81·2; H, 6·8; N, 11·7. Calc. for $C_{16}H_{16}N_2$: C, 81·4; H, 6·8; N, 11·9%).

N-p-*Methoxybenzylidenehydroxylamine*-O-*sulphonic Acid Ammonium Salt* (IIc; X = OSO_3H).—This compound was prepared analogously, yellow *crystals*, m.p. 128—129° (decomp.), τ (DMSO) 1·82 (1H, s, CH=N), 2·39 (2H, d, 2- and 6-H), 2·93br (s, exchangeable NH), and 3·00 (2H, d, 3- and 5-H), methyl resonance obscured by DMSO, *m/e* 133, $\lambda_{max.}$ (ethanol) 205 (ε 24,200), 215 (24,000), 270 (29,600), 291 (14,000), and 300 (10,000) nm, $\nu_{max.}$ (mull) 3250 cm^{-1} (NH) (Found: C, 40·0; H, 5·0; N, 11·2. $C_8H_{12}N_2O_5S$ requires C, 38·8; H, 4·8; N, 11·3%).

N-p-*Chlorobenzylidenehydroxylamine*-O-*sulphonic Acid Ammonium Salt* (IId; X = OSO_3H).—This compound was prepared analogously, *plates*, m.p. 170°, τ (DMSO) 1·70 (1H, s, CH=N), 2·28 (2H, d, 2- and 6-H), 2·49 (2H, d, 3- and 5-H), and 3·00br (s, exchangeable NH), *m/e* 135, $\lambda_{max.}$ (ethanol) 206 (ε 25,000), 217 (18,000), 260 (28,400), 284 (4800), and 294 (2800) nm, $\nu_{max.}$ (mull) 3240 cm^{-1} (Found: C, 33·0; H, 3·4; N, 11·9; Cl, 13·7; S, 12·8. $C_7H_9ClN_2O_4S$ requires C, 33·2; H, 3·6; N, 11·1; Cl, 14·0; S, 12·7%).

p-*Hydroxysulphonyloxyiminotoluic Acid Monoammonium Salt* (IIe; X = OSO_3H).—The reaction mixture from *p*-formylbenzoic acid (5 g), methanolic ammonia (330 ml), and hydroxylamine-*O*-sulphonic acid (5·6 g) was evaporated to dryness, suspended in 1N-H_2SO_4 (30 ml), filtered, and dried. The product was dissolved in hot ethanol–methanol 1 : 1 (v/v), the solution was filtered, and the filtrate partially evaporated. The resulting *precipitate* was filtered and dried (2·2 g), m.p. 220°, τ (DMSO) 2·63 (1H, s, CH=N), 2·96 (2H, d, *J* 7 Hz, 2- and 6-H), 3·18 (2H, d, *J* 7 Hz, 3- and 5-H), and 3·7—4·1br (envelope, exchangeable NH and CO_2H), $\lambda_{max.}$ (ethanol) 204, 265, and 298 nm, $\nu_{max.}$ (mull) 3240 and 1700 cm^{-1} (Found: C, 36·5; H, 3·5; N, 10·4; S, 12·6. $C_8H_{16}O_6N_2S$ requires C, 36·7; H, 3·8; N, 10·7; S, 12·2%).

1,3,5-*Triphenyl*-2,4,6-*triazabicyclo*[3.1.0]*hexane* (IVa).—This compound was prepared as described by Schmitz.[7]

1,3,5-*Tri*-(p-*tolyl*)-2,4,6-*triazabicyclo*[3.1.0]*hexane* (IVb).—Chloramine was prepared by cautious addition of t-butyl hypochlorite (6 ml) to methanolic ammonia (100 ml) at −60°. *p*-Tolualdehyde (10 g) was added and the stirred solution allowed to warm to 4° overnight. A solid (2·26 g) was precipitated, and this was recrystallised from ethanol–methanol and light petroleum–ethanol to give needles, m.p. 175°, R_F 0·7 [system (*j*)], oxidising to HI, τ (DMSO) 2·4—2·9 (12H, m, aromatic), 4·47 (1H, t, *J* 5 Hz, s on addition of ^2H_2O,CH), 5·13 (1H, t, *J* 5 Hz, s on addition of ^2H_2O,CH), 5·64 (1H, m, exchangeable NH), 6·41 (1H, s, CH), and 7·70 (9H, s, CH_3), *m/e* 236, 208, 192, 149, 145, and 119, $\lambda_{max.}$ (ethanol) 205, 214, 222, 264, and 272 nm (Found: C, 80·8; H, 7·1; N, 11·7. $C_{24}H_{25}N_3$ requires C, 81·1; H, 7·1; N, 11·8%).

1,3,5-*Tris*-(p-*methoxyphenyl*)-2,4,6-*triazabicyclo*[3.1.0]-*hexane* (IVc).—Chloramine was prepared from t-butyl hypochlorite (10 ml) and methanolic ammonia (150 ml) at −60°. *p*-Anisaldehyde (8·35 g) was added, and the mixture allowed to warm to room temperature over 48 h. A white solid (2·36 g) precipitated and was recrystallised from ethanol to give material *A* (the triazabicyclohexane), m.p. 120—122°, and a yellow solid *B*, m.p. 169°, R_F [system (*b*)] 0·09 (*A*), 0·46 (*B*). *A*: τ (DMSO) 2·3—3·1 (12H, m, aromatic), 4·37 (1H, s, CH), 4·77 (1H, s, CH), 6·15 (9H, s, OCH_3), and 6·79 (1H, s, CH), *m/e* 268, 254, 241, 225, and 134, $\nu_{max.}$ 3306 and 3290 cm^{-1} (Found: C, 69·1; H, 6·2; N, 10·4. $C_{24}H_{25}N_3O_3$ requires C, 69·7; H, 6·1; N, 10·2%). *B*: τ (DMSO) 1·38 (1H, s, CH=N), 2·20 (2H, d, *J* 9 Hz, 2- and 6-H), 3·04 (2H, d, *J* 9 Hz, 3- and 5-H), and 6·12 (3H, s, OCH_3), *m/e* 268, 240, 225, 161, and 134. The spectral properties of *B* are consistent with those of the azine (lit.,[27] m.p. 168°).

Reaction of Pyridine-3-*carbaldehyde with Chloramine and Ammonia.*—Pyridine-3-carbaldehyde (15 g) was added to chloramine [from methanolic ammonia (250 ml) and t-butyl hypochlorite (15 ml)] at −60°. The mixture was allowed to warm to −20° and maintained at this temperature for 16 h. After warming to room temperature, the mixture was concentrated by rotary evaporation. T.l.c. [system (*a*)] showed components with R_F 0·00, 0·06, 0·16, 0·20, 0·43 (aldehyde), and 0·60, of which the first and third showed HI oxidising power which was lost on standing at room temperature. Components with R_F 0·60 (*A*) and 0·2 (*B*) were isolated by preparative t.l.c. [system (*a*)]. *A*: τ (DMSO) 1·21 (1H, s, 2-H), 1·31 (1H, d, *J* 6 Hz, 6-H), 2·14 (1H, d, *J* 9 Hz, 4-H), and 2·70 (1H, m, 5-H), $\nu_{max.}$ (CCl_4) 2240 cm^{-1}, m.p. 46°. *A* is pyridine-3-carbonitrile (lit.,[28] m.p. 48—49°). *B*: τ (DMSO) 0·95 (1H, s, CH=N), 1·20 (1H, s, 2-H), 1·28 (1H, d, *J* 7 Hz, 6-H), 1·71 (1H, d, *J* 9 Hz, 4-H), and 2·46 (1H, m, 5-H), *m/e* 210 (M^+, 100%), 182, 163, 156, 132, 120, and 105, m.p. 133—136°. *B* is pyridine-3-carbaldehyde azine (lit.,[29] m.p. 148°).

Reaction of p-*Nitrobenzaldehyde t-Butylimine with Chloramine.*—*p*-Nitrobenzaldehyde was condensed with t-butylamine using azeotropic removal of water with benzene, m.p. (from hexane) 75°. Imine (3·09 g) in methanol (25 ml) was added to a chloramine solution [from methanolic ammonia (60 ml) and t-butyl hypochlorite (15 ml)] at −40° and allowed to warm to room temperature. The resulting precipitate was recrystallised from ethanol to give pale yellow plates (1·76 g), τ 1·1 (1H, s, CH=N) and 1·7—2·14 (4H, q, aromatic), $\lambda_{max.}$ (EtOH) 281 (ε 20,000) nm, no NH i.r. band, *m/e* 184/186, 154/156, 149, and 119 {Found: C, 45·0; H, 3·0; N, 14·9; Cl, 18·8. $C_7H_5ClN_2O_2$ requires [for (IIg)] C, 45·5; H, 2·7; N, 15·2; Cl, 19·3%}.

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Reaction of p-*Nitrobenzaldehyde t-Butylimine with Hydroxylamine-O-sulphonic Acid.*—Hydroxylamine-*O*-sulphonic acid (2·5 g) in methanol (10 ml) was added to *p*-nitrobenzaldehyde t-butylimine (3·9 g) in methanol (80 ml) at −60°. The solution was allowed to warm to room temperature and stirred over 18 h. Evaporation of the filtered solution and recrystallisation of the residue from hexane gave an almost white solid, m.p. 130°, τ 1·60 (1H, s, CH=N), 1·70 (2H, d, *J* 9 Hz, aromatic), 2·10 (2H, d, *J* 9 Hz, aromatic), 2·30br (s, NH), and 8·74 (9H, s, t-butyl), $\nu_{max.}$ 1627 cm^{-1}, not oxidising to HI. This is believed to be the t-butylhydrazone of *p*-nitrobenzaldehyde.

Reaction of Pyridine-3-carbaldehyde t-Butylimine with Hydroxylamine-O-sulphonic Acid.—Pyridine-3-carbaldehyde (4·25 g) was refluxed for 8 h with t-butylamine (15 ml) in ethanol (10 ml) and benzene (40 ml). Solvents and excess of t-butylamine were removed by rotary evaporation and the resulting oil dissolved in ethanol (50 ml), water (50 ml), and t-butylamine (10 ml). Hydroxylamine-*O*-sulphonic acid (8·0 g) was added over 15 min and the temperature rose to 45°. The mixture was cooled, filtered, and the filtrate concentrated by rotary evaporation. A tenth of this mixture was purified by t.l.c. [system (*c*)] to give a yellow oil (0·14 g; R_F 0·3) oxidising to HI. This substance rapidly decomposed on standing and was re-purified [t.l.c. system (*c*)] to give 43 mg of a mixture of pyridine-3-carbaldehyde (n.m.r., i.r.) and an oxidising oil (IIIj), τ (DMSO) 1·44 (1H, s, 2-H), 1·56 (1H, d, *J* 6 Hz, 6-H), 2·40 (1H, m, 4-H), 2·87 (1H, m, 5-H), 6·53 (1H, d, *J* 7 Hz, diaziridine CH), and 8·95 (9H, s, t-butyl).

Reaction of Pyridine-4-carbaldehyde Allylimine with Hydroxylamine-O-sulphonic Acid.—Pyridine-4-carbaldehyde (5·35 g) was refluxed with allylamine (5·6 g), in benzene (40 ml), and ethanol (10 ml) for 3 h. The solvents were then removed by evaporation, and the residue fractionally distilled to give pyridine-4-carbaldehyde allylimine as a yellow oil, b.p. 88—90° at 1 mmHg. Allylamine (11·4 g), ethanol (30 ml), and water (10 ml) were cooled to −5° and hydroxylamine-*O*-sulphonic acid (2·26 g) added. To this mixture the imine (1·46 g) in ethanol (10 ml) was added slowly, the temperature being maintained below 5°. After stirring at 0° for 4 h, ethanol was removed by evaporation. The residue showed an oxidising component, R_F 0·28 [system (*c*)]. A portion of the mixture was purified using the same t.l.c. system, and resulted in the isolation of a yellow oil (40 mg), τ (DMSO) 1·50 (2H, d, *J* 5 Hz, 2- and 6-H), 2·62 (1H, d, *J* 6 Hz, NH), 2·80 (2H, d, *J* 5 Hz, 3-H), 4·15 (1H, octet, allyl CH), 4·80 (2H, m, allyl CH_2), and 6·80 (3H, superimposed d, CH_2 and diaziridine CH).

3-*Phenyl*-3H-*diazirine* (Va).—1,3,5-Triphenyl-2,4,6-triazabicyclo[3.1.0]hexane (IVa) (15·65 g) was dissolved in acetone (250 ml) and added dropwise at 0° to a mixture of sodium dichromate (26·2 g), acetone (125 ml), water (125 ml), and concentrated H_2SO_4 (1 ml). After stirring in the dark at 4° for 12 h, the mixture was poured into a solution of sodium metabisulphite (400 g) in water (3 l) and the suspension extracted into n-hexane (6 × 50 ml). The combined extracts were dried (Na_2SO_4), concentrated by evaporation below 20°, and purified by t.l.c. [system (*a*)]. The component of R_F 0·9 was eluted with ether and the solvent evaporated to leave a yellow oil (0·14 g), τ (DMSO) 2·95 (3H, irregular t, aryl), 3·32 (2H, irregular d, aryl), and 8·24 (1H, s, diazirine 3-H), $\lambda_{max.}$ (hexane) 253 (ε 294), 259 (314), 265 (371), 272 (274), 276 (220), 344 (179), 354 (230), 362 (299), 373 (230), 382 (245) nm, fine structure was less apparent in ether solution, $\nu_{max.}$ (film) 1580 (N=N) and 987 cm^{-1}, *m/e* 90 ($M^+ - N_2$).

Very much better yields were obtained by oxidising the 1,3,5-triphenyl-2,4,6-triazabicyclo[3.1.0]hexane (IVa) with t-butyl hypochlorite. Triazabicyclohexane (4 g) was suspended in methanol (30 ml) at 0° and t-butyl hypochlorite (2 ml) in t-butanol (5 ml) added dropwise over 10 min. After stirring at 5° for 1 h, the mixture was poured into sodium metabisulphite solution [50 g in water (500 ml)] and extracted into n-hexane (4 × 20 ml). T.l.c. [system (*a*)] showed mainly (Va) (yield based on $E_{362\ nm}$, 0·72 g).

Surprisingly, reaction of 1,3,5-tri-(*p*-tolyl)-2,4,6-triazabicyclo[3.1.0]hexane (IVb) with t-butyl hypochlorite, did not yield the tolyldiazirine (Vb), but largely α-chloro-*p*-tolualdehyde *p*-methylbenzylidenehydrazone.

Oxidative trapping of 3-phenyl-3*H*-diaziridine could be achieved with yellow mercuric oxide. Benzaldehyde (20 g) was added to a solution of chloramine prepared from methanolic ammonia (150 ml) and t-butyl hypochlorite (25 ml) in t-butanol (25 ml), at −60°. The mixture was allowed to warm to room temperature over 4 h. Yellow mercuric oxide (20 g) was added and the mixture stirred, more oxidant being added after 12 (5 g) and 30 h (10 g). The mixture was filtered, concentrated, and added to a solution of sodium metabisulphite (150 g) in water (1·5 l). Extraction into cyclohexane (2 × 50 ml) and purification of the extracts by t.l.c. [system (*a*)] gave a low yield of material identical (t.l.c. and u.v.) with (Va).

3-(p-*Tolyl*)-3H-*diazirine* (Vb).—*p*-Tolualdehyde (12 g) was added to a solution of chloramine prepared from methanolic ammonia (200 ml) and t-butyl hypochlorite (30 ml) at −40° and the mixture allowed to warm to room temperature over 2 h. Yellow mercuric oxide (20 g) was added and stirring continued at 4° in the dark. After 12 h, more oxidant (20 g) was added. After 8 h at 4°, the mixture was filtered, the filtrate concentrated by evaporation, and poured into ice–water (1 l). The product was extracted into n-hexane (3 × 50 ml). Concentrated extracts were purified by t.l.c. [system (*d*)] to give the diazirine as a yellow oil (0·45 g), τ (DMSO) 2·97 (2H, d, *J* 8 Hz, aromatic), 3·18 (2H, d, *J* 8 Hz, aromatic), 7·68 (3H, s, CH_3), and 8·12 (1H, s, diazirine 3-H), $\lambda_{max.}$ (hexane) 272 (ε 319), 281 (297), 350 (183), 368 (311), 380 (232), 389 (253) nm, *m/e* 104, $\nu_{max.}$ ($CHCl_3$) 1620 and 1600 cm^{-1}.

3-(p-*Methoxyphenyl*)-3H-*diazirine* (Vc).—*p*-Anisaldehyde (20 g) was added to a solution of chloramine prepared from methanolic ammonia (250 ml) and t-butyl hypochlorite (45 ml) at −60°, and the mixture allowed to warm to room temperature over 8 h. The solution was filtered, concentrated by evaporation and yellow mercuric oxide (10 g) added. The mixture was stirred at room temperature for 4 h, methanolic ammonia added (50 ml) and stirring continued for a further 4 days. Concentrated HCl (5 ml) was added to the wine red solution and the material poured into a solution of sodium metabisulphite (100 g) in water (2 l). Extraction into n-hexane (200 ml), drying (Na_2SO_4), and preparative t.l.c. of extracts gave the diazirine as a yellow-green oil (0·32 g), R_F 0·5 [system (*a*)], τ (DMSO) 3·20 (4H, s, aromatic), 6·18 (3H, s, OCH_3), and 8·06 (1H, s, diazirine 3-H), $\lambda_{max.}$ (hexane) 359 (ε 193), 378 (290), 390 (207), 399 (207), $\nu_{max.}$ ($CHCl_3$) 1615 and 1610 cm^{-1}.

p-(*Carboxymethoxyphenyl*)-3H-*diazirine* (Vf).—*p*-Formylphenoxyacetic acid (14 g) was added to a solution of chloramine prepared from methanolic ammonia (600 ml), t-butyl hypochlorite (120 ml), and t-butyl alcohol (45 ml)

at −40°. The mixture was stirred at −20° for 1 h and yellow mercuric oxide added. The mixture was cautiously allowed to warm to 0°, stirred at this temperature for 3 h and then at 4° for 45 h in the dark. The material was filtered under suction into ice (1 kg) and then added to 4N-HCl (8 l) containing NaCl (500 g) at 0°. Extraction into ether (6 × 500 ml) was carried out until the absorbance at 380 nm in both ether and aqueous layers was negligible. The combined extracts were dried at 4° (Na_2SO_4) and evaporated to a yellow solid. Two thirds of this solid was dissolved in ethanol and immediately purified by t.l.c. [system (*g*)] (R_F 0·59). Extraction into methanol, evaporation, and trituration with ether and hexane gave a yellow precipitate. The remaining third was purified directly using t.l.c. [system (*h*)], eluting with tetrahydrofuran, and triturating with hexane (total yield 0·16 g), τ (CD_3OD) 3·14 (4H, s, aromatic), 5·36 (2H, s, CH_2, visible only in the presence of CF_3CO_2H), and 7·90 (1H, s, diazirine 3-H), $\lambda_{max.}$ (Tris–HCl buffer, 0·1M, pH 7·9) 269 (ε 1607), 277 (1450), and 378 (300), $\nu_{max.}$ (mull) 1663 (CO_2H), 1615, and 1610 (C=C and N=N) cm^{-1}.

3-(m-*Nitrophenyl*)-3H-*diazirine* (Vh).—*m*-Nitrobenzaldehyde (1·5 g) was dissolved in t-butylamine (20 ml), benzene (10 ml) was added, and the mixture allowed to stand for 1 h at room temperature. Solvents were removed by evaporation, and the residual oil was dissolved in ethanol (10 ml) containing triethylamine (5 ml). Hydroxylamine-*O*-sulphonic acid (2 g) was added in small amounts with stirring at 0°. Stirring was continued at 0° for 3 h and t-butyl hypochlorite (2 ml) then added dropwise. After stirring at 0° for 30 min, the mixture was poured into water (300 ml) containing sodium metabisulphite (30 g), and then extracted into methylene chloride (2 × 30 ml). The extracts were dried (Na_2SO_4), concentrated, and purified by t.l.c. systems (*e*) (diazirine R_F 0·52) and (*f*) (R_F 0·6) to give the diazirine as a yellow oil (55 mg), τ (DMSO) 1·86 (1H, d, *J* 8 Hz, aromatic), 2·19 (1H, s, aromatic), 2·52 (1H, t, *J* 8 Hz, aromatic), 2·97 (1H, d, *J* 8 Hz, aromatic), and 7·82 (1H, s, diazirine 3-H), $\lambda_{max.}$ (hexane) 301 (ε 1200), 334 (462), 352 (589), 362 (462), 372 (420) nm, $\nu_{max.}$ ($CHCl_3$) 1625 (C=C), 1586 (N=N), and 1358 (NO_2) cm^{-1}.

3-(4-*Pyridyl*)-3H-*diazirine* (Vi).—Pyridine-4-carbaldehyde (4·28 g) and t-butylamine (10 ml) were mixed at room temperature, allowed to stand for 24 h, and excess of amine removed by evaporation. The resulting oil was dissolved in water (25 ml) and methanol (15 ml) and hydrated sodium carbonate (28 g) added. Hydroxylamine-*O*-sulphonic acid (5·6 g) was added over 20 min at 0°. After 3 h, t-butyl hypochlorite (3 ml) in t-butyl alcohol (4·5 ml) was added dropwise at 0°. The solution was stirred for 2 h and poured into saturated brine (400 ml) and extracted into chloroform (4 × 30 ml). The extracts were dried (Na_2SO_4), concentrated by evaporation, and purified by t.l.c. systems (*h*) (diazirine R_F 0·7), (*c*) (R_F 0·8), and (*i*) (R_F 0·25) to give a yellow oil (0·395 g), τ (DMSO) 1·38 (2H, d, *J* 5 Hz, 2- and 6-H), 3·26 (2H, d, *J* 5 Hz, 3-H), and 7·99 (1H, s, diazirine 3-H), $\lambda_{max.}$ (hexane) 330 (ε 107), 345 (191), 355 (167), and 364 (164) nm, $\lambda_{max.}$ (hexane–0·1M-acetic acid) 331 nm, $\nu_{max.}$ (film) 1610 (C=C) and 1590 (N=N) cm^{-1}.

3-(3-*Pyridyl*)-3H-*diazirine* (Vj).—Pyridine 3-carbaldehyde (4·28 g) was dissolved in t-butylamine (7·5 ml) and allowed to stand for 16 h. Addition of benzene (20 ml) followed by evaporation gave a yellow oil which was dissolved in ethanol (25 ml), triethylamine (10 ml), and water (10 ml), and cooled to −10°. Hydroxylamine-*O*-sulphonic acid (6 g) was added over 15 min with vigorous stirring. The temperature rose to 0°, and stirring was continued at this temperature for 2 h. t-Butyl hypochlorite (6 ml) was added slowly and the yellow solution stirred at 4° for 16 h. The product was concentrated by evaporation, filtered, and a fifth of the filtrate was purified by t.l.c. [system (*l*)] (R_F 0·65) to give a yellow oil (90 mg), τ (DMSO) 1·53 (1H, d, *J* 5 Hz, 6-H), 1·66 (1H, s, 2-H), 2·85 (1H, m, 5-H), 3·04 (1H, m, 4-H), and 7·98 (1H, s, diazirine 3-H), $\lambda_{max.}$ (hexane) 356 (ε 275), 366 (197), and 377 (191) nm, $\nu_{max.}$ (film) 1622 (C=N) and 1590 (N=N) cm^{-1}.

Photolysis Experiments.—Spectroscopic investigations of diazirine photolysis were carried out with solutions of diazirines (0·4—3mM) in n-hexane, in stoppered quartz cuvettes (3 ml) using a medium pressure Hanovia mercury vapour u.v. lamp in a Pyrex cooling jacket. For the determination of product ratios in diazirine photolysis in the presence of acetic acid, diazirine (*ca.* 10mM) in hexane containing acetic acid at varying concentrations (greater than the diazirine concentration) was photolysed in closed glass vials (10 ml) under nitrogen, 5 cm from the source of the lamp, at 25° for 90 min. The solutions were washed with water (2 × 15 ml) and 2M-sodium carbonate (2 × 15 ml), dried (Na_2SO_4), and evaporated to oils. The residues were dissolved in CCl_4 and n.m.r. spectra showed that at least 90% of the material could be assigned to benzyl acetate and the arylheptanes. Mass and i.r. spectra were obtained for some of these mixtures (Table 3).

TABLE 3

Mass and i.r. spectral data for diazirine photolysis mixtures

Diazirine	*m/e* acetate (M^+)	$\nu_{max.}$ (cm^{-1}) acetate *	*m/e* heptanes	$\nu_{max.}$ (cm^{-1}) heptanes †
3-Phenyl-3*H*		1747		2920
3-(*p*-Tolyl)-3H	164	1740	190	2950
3-(*p*-Methoxyphenyl)-3*H*		1738		2940
3-(4-Pyridyl)-3*H*	151	1740	177	2900

* In CCl_4, C=O stretch. † In CCl_4, C–H stretch.

Isolation of the Second Intermediate.—3-Phenyl-3*H*-diazirine (63 mg) was dissolved in nitrogen-purged hexane (200 ml) and irradiated in a cylinder (250 ml) fitted with an aluminium foil reflector and mounted 8 cm from the lamp source. After 3 min, the irradiation was stopped and glacial acetic acid (1·2 ml) added. The mixture was stirred for 10 min, washed with 1N-NaOH (100 ml) and then dried (Na_2SO_4). Concentration of the solution was followed by t.l.c. [system (*d*)], and gave the second intermediate (R_F 0·6), after extraction into ether and evaporation, as a brown oil (20 mg).

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