Thermal and Photochemical Decomposition of Cycloalkanespirodiazirines

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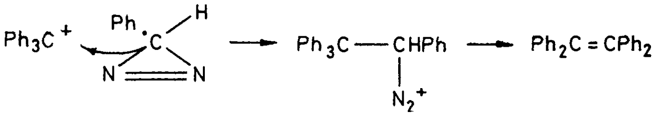
The decomposition of the cycloalkanespirodiazirines of ring size 5—8 have been investigated both thermally and photochemically. The thermal reactions are consistent with the formation of the corresponding cycloalkylidenes, which react intramolecularly to give cycloalkenes and bicycloalkanes. Photochemically the diazirine ring breaks down by competitive one- and two-bond rupture to give either the diazocycloalkane or the cycloalkylidene which then react further. In acetic acid the diazo-compounds may be trapped as the corresponding cycloalkyl acetates.

THE use of diazirines as sources of carbenes has been fairly well documented [1-3] since their first reported preparation.[4,5] Their relative ease of preparation coupled with their chemical stability allows a study of the formation of carbenes under a variety of conditions not readily accessible with other precursors. We report here on the thermal and photochemical formation of the polymethylene carbenes (VI; $n = 4$—7) under neutral and acidic conditions.

Although Schmitz [6] has recorded the reaction of diazirines with alkyl-lithiums and Grignard reagents, and their reduction by sodium amalgam, the most striking aspect of their chemistry, in strong contrast to that of their linear isomers, the diazomethanes, is their lack of reactivity towards most reagents. Schmitz [6] and Lau [7] have shown their remarkable insensitivity towards hydrochloric and phosphoric acids; the methods of preparation demonstrate their unreactivity towards acid dichromate and silver oxide.[6] The results of Church and Weiss [8] demonstrate their inertness towards acid chlorides, amines, and alkaline hypobromite. We have examined their reactivity towards a wide range of compounds. Cyclohexanespirodiazirine (III; $n = 5$) is recovered unchanged from treatment with electrophiles such as methyl iodide, peracetic acid, boron trifluoride–ether, tetracyanoethylene, and bromine. The only common acid that affects it is concentrated sulphuric acid, which causes instant decomposition to nitrogen and cyclohexene. It is not complexed by copper salts (which react with azo-compounds), nor by nickel(II) sulphate, nor by palladium(II) or platinum(IV) chlorides. It is also unaffected by nucleophiles such as triphenylphosphine and lithium dimethylamide. It is inert towards dienes, both electron rich, *e.g.* cyclopentadiene, and electron poor like 3,4-dicyano-2,5-diphenylcyclopentadienone, and also towards 1,3-dipoles like diazomethane and tetracyanoethylene oxide. We have, however, observed one example of electrophilic attack in which treatment of 3-phenyldiazirine with triphenylmethyl tetrafluoroborate gave a nearly quantitative yield of tetraphenylethylene [equation (1)]. The product is consistent with ring opening in the sense and with the polarity shown, which is the same as that of phenyldiazomethane. Similar polarisation has been invoked to explain the instability of 1-oxo- and 1-hydroxy-cyclohexane-2-spirodiazirine towards acid.[9] Monitoring reaction (1) by u.v. spectrometry gave no evidence for the formation of a 3-phenyldiazirinium cation, although



(1)

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[1] H. M. Frey, *Adv. Photochem.*, 1966, **4**, 225.

[2] R. W. Hoffmann, *Angew. Chem. Internat. Edn.*, 1971, **10**, 529.

[3] G. W. Griffin, *Angew. Chem. Internat. Edn.*, 1971, **10**, 537.

[4] S. R. Paulsen, *Angew. Chem.*, 1960, **72**, 781.

[5] E. Schmitz and R. Ohme, *Angew. Chem.*, 1961, **73**, 115.

[6] E. Schmitz, *Adv. Heterocyclic Chem.*, 1963, **2**, 83; *Angew. Chem. Internat. Edn.*, 1964, **3**, 333.

[7] A. Lau, *Spectrochim. Acta*, 1964, **20**, 97.

[8] R. F. R. Church and M. J. Weiss, *J. Org. Chem.*, 1970, **35**, 2465.

[9] E. Schmitz, A. Stark, and C. Hörig, *Chem. Ber.*, 1965, **98**, 2509; E. Schmitz, C. Hörig, and C. Gründemann, *ibid.*, 1967, **100**, 2093, 2101.

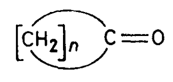
recent INDO calculations suggest that it should be both aromatic and stable.[10]

The conversion of the cycloalkanones (I; $n = 3$—7 and 11) into the corresponding diaziridines (II) was achieved by the method of Schmitz [11] using hydroxylamine-*O*-sulphonic acid (HOS) in methanolic ammonia. The yield of diaziridine was found to depend quite critically on the purity of HOS, which had to be $>90\%$, and preferably $>95\%$. Lower purities gave substantial amounts of oximes and azines as by-products. The yield of diaziridine varied in a predictable manner with ring size, if the formation of the ketimine is taken to be the rate-controlling step (Table 1). Attempted conversion of cyclodecanone into the diaziridine (II; $n = 9$) under a variety of conditions was unsuccessful, presumably because the formation of the intermediate (IV) is sterically unfavourable and the reagent reacts more rapidly with ammonia. The yield of diaziridine was also affected by the presence of water. It fell to only 25% for (II; $n = 4$) if all the reactants were thoroughly dry, and precautions taken to prevent entry of moisture. We ascribe this to an effect of general acid catalysis on the formation of ketimine, or of intermediate (IV; $n = 4$).

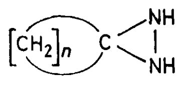
TABLE 1

Yield of diaziridine (II) as a function of ring size

Ring size ($n + 1$) in (I)	4	5	6	7	8	9	10	12
% yield of (II)	10	50	75	50	22	*ca.* 2	0	45



(I)



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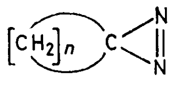

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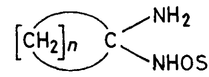

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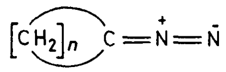

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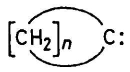

(VI)

The oxidation of the diaziridines into the diazirines (III) was carried out in a two phase (ether–water) system using silver oxide prepared *in situ*, in moderate to good yield.

Thermal decompositions of the diazirines were carried out at 160° in the liquid phase, either as pure liquids or as solutions in diglyme, without showing any appreciable difference in result, and the total yield of hydrocarbon products was *ca.* 90% in all cases. Photolyses also showed little variation over the solvent range neat liquid, n-hexane, diglyme, but the yield of hydrocarbon products did vary from 80 to 25% for the range (III; $n = 4$—7). The results of these decompositions (normalised to 100) are summarised in Table 2.

Analysis of the hydrocarbons was by g.l.c. using either 20% polypropylene glycol on Chromosorb P and/or 20% saturated silver nitrate in diethylene glycol on Chromosorb P. Identification was by dilution techniques using authentic samples, supplemented by trapping and spectroscopic investigation. While not exhaustive, in most cases it was ascertained that possible products which were not found could be detected by the analytical procedures used.

Examination of Table 2 shows that in all cases the preponderant reaction is that expected from a dialkylcarbene, *viz.* 1,2-hydrogen migration to form the cycloalkene, and that the results are in fairly close agreement with those obtained by toluene-*p*-sulphonylhydrazone decomposition under aprotic conditions,[12] and with the gas-phase results on (III; $n = 4$) [13] and (III; $n = 5$),[13,14] and the pyrolysis of (III; $n = 6$) in nitrobenzene.[15]

The photochemical reactions all show signs of a slight hot radical effect, which is most marked for the 1,2 carbon migration product (column 5). One would anticipate that this effect would diminish with increasing molecular size, as is observed in open chain compounds [16] but this appears to be offset by the change in strain involved in forming the products in the smaller rings.

Mechanism of Nitrogen Loss.—During the photolyses of the diazirines (III; $n = 6$ and 7) as neat liquid sit was noticed that the liquid developed a reddish colour which persisted for some time even if irradiation was stopped, which seemed indicative of the conversion of the cyclo to the linear diazo-compound [(III) $\longrightarrow$ (V); $n = 6$ and 7]. Confirmation of this was obtained by irradiating the diazirines between rock-salt discs and immediately measuring the i.r. spectrum. For the diazirines (III; $n = 5$—7), a band at 2 060 cm^{-1} developed, characteristic of aliphatic diazo-compounds.[17] For (III; $n = 5$), this band disappeared within a few minutes, but for (III; $n = 6$ and 7), a u.v. band at 480—490 nm could also be observed. In principle, this band can be used to estimate the conversion of (III) to (V) but the estimate

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[10] C. U. Pitman, A. Kress, T. B. Patterson, P. Walton, and L. D. Kispert, *J. Org. Chem.*, 1974, **39**, 373.

[11] E. Schmitz and R. Ohme, *Chem. Ber.*, 1961, **94**, 2166.

[12] L. Friedman and H. Schechter, *J. Amer. Chem. Soc.*, 1960, **82**, 1002.

[13] H. M. Frey and A. W. Scaplehorn, *J. Chem. Soc. (A)*, 1966, 968.

[14] H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 1964, 4700.

[15] E. Schmitz, D. Habisch, and A. Stark, *Angew. Chem. Internat. Edn.*, 1963, **2**, 548.

[16] A. M. Mansoor and I. D. R. Stevens, *Tetrahedron Letters*, 1966, 1733.

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

depends on the value taken for the extinction coefficient of the band concerned, a matter which has been the subject of some doubt. However using the value given by Ledwith[17] of 6—10 leads to the conclusion that between 55 and 30% of the diazirine isomerises to diazo-compound.

Although Amrich and Bell[18] have suggested that in the gas-phase photolysis of diazirine itself, some 20% goes by isomerisation to diazomethane, the matrix isolation work of Moore and Pimentel[19] would seem to render their conclusions extremely dubious, particularly in view of the inability of the latter workers to detect any diazomethane when they photolysed diazirine in the gas phase with high pressures of added nitrogen and using filtered light. The only incontrovertible evidence for such an isomerisation has been the observation of the photointerconversion of diazirinylamides and diazo-amides,[20a] where the conversion of diaziridine to diazo-compound ranged from 15 to 30%. There is also very recent work on 3-aryldiazirines, where trapping by acetic acid suggests that about one half of the primary photoprocess is isomerisation to the 3-aryldiazomethane.[20b]

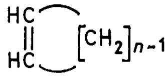
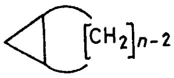
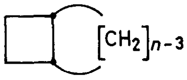
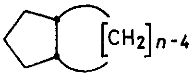
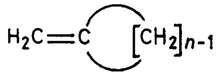
The conversion of (III) into (V) would account for the low yields of hydrocarbons observed from the photolyses of the diazirines, for diazo-compounds are known to react thermally to produce azines. Investigation showed that between 10 and 35% of azine was formed in the photolyses. This corresponds to the formation of diazo-compound to the extent of 20, 36, 59, and 70% respectively for the diazirines (III; $n = 4$—7), and should represent a minimum figure, for not all the diazo-compound will give azine. However, there is also the possibility that azine may arise from reaction of carbene with diazirine, as has been proposed by Padwa,[21] and hence these figures are open to some doubt.

In an attempt to improve the trapping of diazo-compound and gain more information concerning the ring-opening process, the diazirines were photolysed in acetic acid solution, and the products again analysed by g.l.c. Analyses were run separately to determine the amount of acetates produced and the hydrocarbon products. The results are recorded in Table 3. That the ratio of acetate to hydrocarbon products is not constant as ring size increases is not unexpected in view of the evidence from azine formation. However, a comparison of Table 3 with Table 2 shows that for the case of $n = 7$, there is a very marked change in the ratio of the various hydrocarbons produced, indicating that some proportion of the ion-pairs formed by protonation of the diazo-compound is going to hydrocarbon products. This could be anticipated on the basis of Cope's[22] work on the cyclo-octyl cation and also suggests that in the other cases too, some fraction of hydrocarbons arises *via* a carbonium ion path.

This was further investigated only for the case of (III; $n = 5$). Assuming that the mechanism shown in Scheme 1 is valid, then any alkene arising *via* diazo-compound and diazonium ion will contain a proton donated from the acid and hence can be detected if acetic [^{2}H]acid is used. Compound (III; $n = 5$) was photolysed in acetic [^{2}H]acid and the hydrocarbon product separated by preparative g.l.c. and analysed for deuterium content by ^{1}H n.m.r. spectrometry, using chloroform as internal proton standard. This showed that $33 \pm 2\%$ of the cyclohexene had one vinyl deuterium atom, and hence that 59% (39% acetate + 20% olefin) of the diazirine had decomposed by the path in Scheme 1. The remaining 41% of (III; $n = 5$) then afforded hydrocarbons by some other route, and two possibilities exist as shown in Scheme 2, direct partitioning of excited diazirine between formation of

TABLE 2

Hydrocarbon product composition from photolysis and pyrolysis of cycloalkanespirodiazirines (normalised to 100)

Ring size in (III) ($n + 1$)					
5 Δ[a]	100.0	0.0			0.0
hν[b]	99.6	0.3			0.1
6 Δ	100.0	0.0			0.0
hν	97.3	2.5	Trace		0.2
7 Δ	84.7	15.2	0.07		Trace
hν	82.8	15.1	1.75		0.3
8 Δ	47.0	9.0	0.0	44.0	Trace
hν	44.9	11.3	0.0	43.4	0.4
Diazocyclo-octane *hν*	65.3	5.4	0.0	29.3	
C_8 tosylH Δ[c]	45	9		46	

[a] Pyrolysis at 160°. [b] Photolysis at 0°, Pyrex filtered mercury arc. [c] Cyclo-octanone toluene-*p*-sulphonylhydrazone decomposition at 180°.[12]

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[18] M. J. Amrich and J. A. Bell, *J. Amer. Chem. Soc.*, 1964, **86**, 292.

[19] C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, 1964, **41**, 3504.

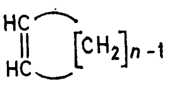
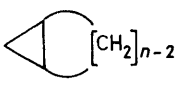
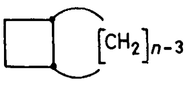
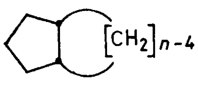
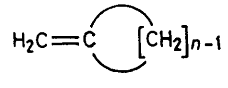
[20] (*a*) R. A. Franich, G. Lowe, and J. Parker, *J.C.S. Perkin I*, 1972, 2034; (*b*) R. A. G. Smith and J. R. Knowles, *J.C.S. Perkin II*, 1975, 686.

[21] A. Padwa and D. Eastman, *J. Org. Chem.*, 1969, **34**, 2728.

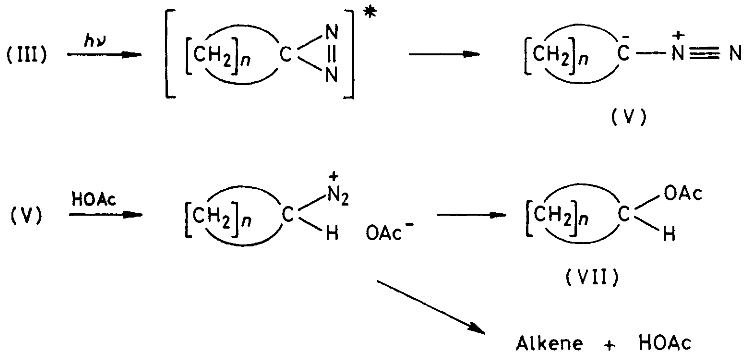
[22] A. C. Cope, M. Brown, and G. L. Woo, *J. Amer. Chem. Soc.*, 1965, **87**, 3107.

Table 3

Products from photolysis of cycloalkanespirodiazirines in acetic acid solution

Ring size in (III) ($n + 1$)	Acetate (VII) (%)	Hydro-carbon (%)	Hydrocarbon composition (% of hydrocarbon fraction)				
							
5	39.9	60.1	99.6	0.3			0.1
6	39.0	61.0	97.2	2.55			0.25
7	33.9	66.1	83.4	14.7	1.7		0.4
8	31.5	68.5	62.9	14.1	0	22.6	0.4
6 (pyrolysis)	23.0	77.0	100	0			0

excited diazo-compound and formation of carbene, or partitioning of excited diazo-compound between decomposition and collisional deactivation. The only piece of evidence we have which has a bearing on this is the direct photolysis of diazocyclo-octane, in which the product composition (penultimate line, Table 2) is sufficiently different from that for the diazirine (III; $n = 7$) to suggest that we are observing direct partitioning of the diazirine (steps a and b of Scheme 2). We therefore conclude that photolytic opening of the diazirine ring occurs by two competing routes, one in which only one C–N bond is broken and which gives diazo-compound and the other which gives carbene and nitrogen.



Scheme 1

If one makes the assumption that for (III; $n = 7$) the carbene gives equal amounts of cyclo-octene and bicyclo[3.3.0]octane (as in toluene-*p*-sulphonylhydrazone decomposition,[12] Table 2) and uses this to partition the hydrocarbon fraction from the photolysis in acetic acid, then one calculates that 61% of the diazirine (III; $n = 7$) is converted to diazo-compound. This is sufficiently close to the value found for (III; $n = 5$), to suggest that the competing paths a and b (Scheme 2) account for 60 and 40% respectively for all cases.

Thermal decomposition of (III; $n = 5$) in acetic acid was briefly investigated and showed that 23% cyclohexyl acetate and 77% cyclohexene were formed. While by no means conclusive, this is most easily accommodated by assuming a mechanism similar to that of Scheme 2, with a different partition ratio for the two paths.

The thermal unimolecular decomposition of diazirines has been the object of several investigations. The earlier ones tended to favour a mechanism involving direct conversion to carbene and nitrogen,[14, 23-25] while the later ones have favoured one where the bond breaking is stepwise.[26-29] The very small $\Delta S^\ddagger$ (0.5—3 cal mol^{-1} K^{-1}) show that the transition state has no additional free rotations, but gives no indication of the path beyond it. Because $F_2C{:}N{\cdot}N{:}CF_2$ is formed in the decomposition of difluorodiazirine, Mitsch[27] has postulated the transient intermediacy of difluorodiazomethane, but recognised that the azine may be formed by direct attack of $:CF_2$ on the diazirine. The most convincing argument in favour of a stepwise process has been put forward by Liu,[29] from a comparison between the solvent effects on the rate of isomerisation of 3-methyl-3-vinyldiazirine to 3-methylpyrazole and those on the

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[23] H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 1962, 3865.

[24] M. R. Bridge, H. M. Frey, and M. T. H. Liu, *J. Chem. Soc.* (*A*), 1969, 91.

[25] H. M. Frey and M. T. H. Liu, *J. Chem. Soc.* (*A*), 1970, 1916.

[26] G. A. Bottomley and G. L. Nyberg, *Austral. J. Chem.*, 1964, **17**, 406.

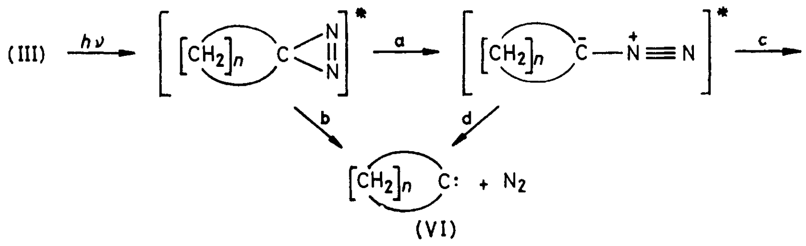
[27] E. W. Neuvar and R. A. Mitsch, *J. Phys. Chem.*, 1967, **71**, 1229.

[28] M. T. H. Liu and K. Toriyama, *J. Phys. Chem.*, 1973, **76**, 797; *Canad. J. Chem.*, 1972, **50**, 3009; M. T. H. Liu and D. H. T. Chien, *J.C.S. Perkin II*, 1974, 937.

[29] M. T. H. Liu and K. Toriyama, *Canad. J. Chem.*, 1973, **51**, 2393.

rate of decomposition of 3-chloro-3-phenyldiazirine.[28] The close similarity of solvent effects for the two reactions, as well as of their entropies of activation, argues for closely similar transition states, and because the isomerisation can only proceed by a one-bond cleavage, then nitrogen loss must be a two-step one.

Liu has also discussed the polarity of the transition state,[28,29] but appears to be labouring under the misapprehension that $>\dot{C}-N=\dot{N}$ and $>\overset{+}{C}-N=\overset{-}{N}$ represent different species. While he has interpreted his substituent effects in terms of a diradical-like transition state, the fact that the thermal stability of diazirines is decreased both by electron-withdrawing,[9,10] and by electron-donating-substituents,[28-30] argues more strongly in favour of a variably polar transition state. This would also accord better with the chemical reactivity.



Scheme 2

Our analysis of the mechanism of nitrogen loss still leaves one unanswered (and unanswerable?) problem, which is to what extent does the intermediate carbene react with acetic acid to give cycloalkyl acetate? Attempts to trap secondary alkylcarbenes with olefins have so far all been unsuccessful,[31] and this has been ascribed to the unequal competition of inter- and intramolecular reactions. Thus it would seem probable that this possibility can be discounted. However, by using diazirine as a source of methylene, it has been shown that in the gas phase methylene reacts with acetic acid to insert into the O–H bond 30 times more rapidly than into the C–H bond,[32] suggesting that the problem may indeed be a real one.

EXPERIMENTAL

Instruments.—I.r. and u.v. spectra were taken on Unicam SP 200 and SP 800 spectrometers. ^{1}H N.m.r. spectra were recorded using a Varian A60, with tetramethylsilane as internal reference. Analytical g.l.c. was done on a Perkin-Elmer F11 equipped with a flame ionisation detector and using nitrogen as carrier. Peak areas were integrated using a Disc Series 200 ball and disc integrator. In so far as possible calibration factors were determined using mixtures of known composition and ethylbenzene as an internal standard. Columns used were 0.125 in stainless steel packed with 20% polypropylene glycol on 60—80 mesh Chromosorb P (4 m), 20% saturated silver nitrate in diethylene glycol on Chromosorb P (2 m), and 15% silicone oil on Chromosorb P (1.5 m). Small scale preparative, and some analytical studies were done using 0.25 in columns in a Perkin-Elmer model 452 instrument. Identification was by retention time and addition of authentic samples, coupled with trapping and spectroscopic investigation.

Preparations.—Cyclobutanone was prepared by the method of Machinskaya.[33] It had b.p. 98—102°, $\nu_{max.}$ 1 780 cm^{-1}, τ 7.0 (4 H, t) and 8.0 (2 H, dt).[34] Hydroxylamine-*O*-sulphonic acid was prepared by the method of Matsuguna.[35] Only acid of purity >90% was used for diaziridine preparations. t-Butyl hypochlorite was prepared by the method of Teeter and Bell.[36] Diazocyclooctane was prepared by the method of Heyns.[37] The method used for the preparation of diaziridines was essentially that of Schmitz and Ohme.[11] The procedure given for cyclopentanespirodiaziridine is typical.

Cyclopentanespirodiaziridine. Cyclopentanone (0.20 mol) in methanol (20 ml) was cooled to −30°. Liquid ammonia (*ca.* 75 ml) was added with mechanical stirring and the temperature then lowered to −60 to −70°. After 1 h, HOS (0.206 mol) was added in small portions, with vigorous stirring, over 4 h, while the temperature was maintained below −60°. After allowing the mixture to warm up overnight and the ammonia to evaporate, the solid residue was extracted with ether (4 × 50 ml). The extract was dried and the ether distilled off at atmospheric pressure. The residual oil was dissolved in water (35 ml), extracted with two small portions of ether, and the aqueous layer saturated with potassium hydroxide. Extraction with ether (4 × 25 ml), drying and removal of the ether gave the crystalline diaziridine (9.75 g, 50%). Table 4 records the data for the compounds prepared.

Oxidation of diaziridines to diazirines. An aqueous solution of diaziridine (65 mmol in 15 ml) was added dropwise with stirring to a mixture of silver oxide [prepared from silver nitrate (197 mmol) and potassium hydroxide (214 mmol) in water (75 ml)] and ether (75 ml), over a period of 10 min. After a further 5 min the mixture was filtered, and the ether separated, dried, and distilled off. The residual diazirine was then distilled at reduced pressure. Table 5 records the data for the compounds prepared. All

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[30] N. P. Smith, Ph.D. Thesis, University of Southampton, 1973.

[31] M. Jones and R. A. Moss, 'Carbenes,' Wiley, New York, 1973, Vol. I, p. 20.

[32] I. D. R. Stevens and M. A. Voisey, unpublished observations.

[33] I. V. Machinskaya, G. P. Smirnova, and V. A. Barklash, *Zhur. obschei Khim.*, 1961, **31**, 2563.

[34] C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, 1960, **82**, 4067.

[35] H. J. Matsuguna and L. F. Audrieth, *Inorg. Synth.*, 1957, **5**, 122.

[36] H. M. Teeter and E. W. Bell, *Org. Synth.*, 1963, Coll. Vol. IV, 125.

[37] K. Heyns and A. Heins, *Annalen*, 1957, **604**, 133.

the diazirines showed typical u.v. absorption spectra from 300—375 nm,[14,23] and the longest wavelength peak (in cyclohexane) is given in Table 6.

1,3,5-*Triphenyldiaziridino*[a]-1,2,4-*triazolidine*.[38] Methanol (250 ml) was saturated with ammonia at 5°, and then cooled to −40°. t-Butyl hypochlorite (30 ml) in t-butyl alcohol (30 ml) was added dropwise with stirring during 45 min. Benzaldehyde (36.1 g) was then added dropwise during 10 min, while the temperature was kept at −10 to −15°. After a further 20 min, the solution was allowed to warm to room temperature overnight. The white crystals were filtered off and recrystallised from ethanol (yield 4.72 g, 19%), m.p. 160—162° (lit.,[38] 160—162°), τ 2.59 (15 H, m, phenyl), 4.34 and 4.73 (1 H, s, 1- and 3-H), and 6.76 (1 H, s, 5-H).

TABLE 4

Physical constants for cycloalkanespirodiaziridines

Ring size of cycloalkane	M.p. (°C)	Found (%)			Formula	Calculated (%)		
		C	H	N		C	H	N
5	74.5—75.5	61.4	10.6	27.6	$C_5H_{10}N_2$	61.2	10.2	28.6
6	105—106 [a]	64.1	10.8	24.1	$C_6H_{12}N_2$	64.3	10.7	25.0
7	43—45.5	66.5	11.0	22.1	$C_7H_{14}N_2$	66.7	11.1	22.2
8	26—27.5	68.6	11.4	19.0	$C_8H_{16}N_2$	68.6	11.4	2.0

[a] Lit.,[11] 103—106°.

3-*Phenyldiazirine*. Potassium dichromate (15 mmol) in 2N-sulphuric acid (60 ml) was added to the triazolidine (15.1 mmol) in 2N-sulphuric acid (100 ml). The reaction flask was heated to 45—50°, and the pressure within the flask reduced to *ca.* 50 mmHg. A slow stream of nitrogen was passed through the reaction mixture and the distillate collected in a trap at −78° during 30 min. The distillate (20 ml) was extracted with ether (2 × 15 ml), and the ether was shaken with sodium hydrogen sulphite solution, washed, and dried. Removal of the ether followed by fractional distillation of the residual liquid (3 ml) at reduced pressure gave 3-phenyldiazirine (0.18 g, 45%) as a liquid, $\nu_{max.}$ 1 625, 1 607, 1 582, 1 550, and 982 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 331 (ε 112), 348.5 (215), 359.5 (280), 365.5 (360), 378 (255), and 386.8 nm (281); τ 2.78 (3 H, m, *m*- and *p*-H), 3.07 (2 H, m, *o*-H), and 8.08 (1 H, s, 3-H). This diazirine is thermally much less stable than the others and could not be microanalysed. Yields varied from 45 to 80%.

TABLE 5

Physical constants for cycloalkanespirodiazirines

Ring size of cycloalkane	Yield (%)	B.p. (°C) [p/mmHg]	$\nu_{max.}$/cm^{-1}	Found (%)			Formula	Calculated (%)		
				C	H	N		C	H	N
5	40—65	58 [240]	1 590, 1 545, 958	62.4	8.4	29.0	$C_5H_8N_2$	62.5	8.3	29.2
6	75—85	56 [85] [a]	1 595, 1 570, 912	65.1	8.9		$C_6H_{10}N_2$	65.5	9.1	
7	60—70	77 [30] [b]	1 595, 1 587, 1 520, 855	67.4	9.9	22.9	$C_7H_{12}N_2$	67.7	9.7	22.6
8	80	67 [16] M.p. 16—17°	1 592, 1 540, 840	69.4	10.2	20.2	$C_8H_{14}N_2$	69.6	10.2	20.3
12	20	M.p. 45	1 585							

[a] Lit.,[14] b.p. 64° at 100 mmHg. [b] Lit.,[15] b.p. 41° at 12 mmHg.

Triphenylmethyl tetrafluoroborate was prepared by the method of Dauben.[39]

Photolyses and Thermolyses.—A conventional high vacuum system was used, with Viton A diaphragm valves to minimise absorption of starting materials or products. Gas-phase pyrolyses and photolyses were carried out in Pyrex gas pipettes of 150—200 ml volume. Liquid phase reactions were carried out in gas pipettes of 5—10 ml volume, and for photolyses only the volume of liquid was exposed to the light source. Liquid samples were thoroughly degassed by several freeze–evacuate–thaw cycles, and then the space over filled to atmospheric pressure with dry, oxygen free, nitrogen before being decomposed.

Photolyses were carried out using a 125 W, Pyrex filtered, medium pressure mercury arc, and were at room temperature for gas samples and at 0° for liquid samples. No variation of product composition with time of irradiation was detected and most reactions were therefore carried to near completion, 3—6 h.

Pyrolyses were carried out in a refluxing vapour bath at 160° for 1 h. The products were stable to these reaction conditions.

Photolyses in Acetic Acid.—The diazirine (0.5 ml) and acetic acid (1 ml) were transferred into a photolysis vessel and degassed. The system was sealed (Viton A valve) and irradiated at 20° for 6 h. After cooling to 5°, and addition of internal standard, samples were withdrawn using a microlitre syringe and analysed by g.l.c.

Cyclohexanespirodiazirine (0.5 ml) and acetic $[^2H]$acid (1 ml; 94% $^2H_1$) were irradiated as above. Cyclohexene was separated by preparative g.l.c. (4 m × 0.25 in; 20% PPG; 50°). The trapped cyclohexene (102 mg) was added to chloroform (170 mg) and made up to 3 ml with carbon tetrachloride. The ^{1}H n.m.r. spectrum was recorded and the peaks for $CHCl_3$, the vinyl protons and the methylene protons integrated several times. The averaged ratios were $CHCl_3$, 10.9; vinyl, 16.1; methylene, 77.3_6. The

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[38] E. Schmitz and R. Ohme, *Chem. Ber.*, 1962, **95**, 688.

[39] H. J. Dauben, L. R. Honnen, and K. M. Harman, *J. Org. Chem.*, 1960, **25**, 1442.

concentration of $CHCl_3$ is 0.474M, of cyclohexene 0.415M, which should give a vinyl integration value of 19.0_8. Hence [^{2}H]cyclohexene = 2(19.08 − 16.1)/19.08 = 31.2%. The ratio of vinyl to methylene hydrogen atoms gives a value of 33.2% for [^{2}H]cyclohexene, in good agreement with the above value considering that the errors are certainly greater. Correction for the incomplete deuteriation of the acetic acid gives a value of 33% [1-^{2}H]cyclohexene, with an estimated error of ±2. The figure of 33% is likely to be slightly low, for the acid decomposition of secondary diazoalkanes goes by an $A–S_E2$ mechanism, and they exhibit isotope effects (k_{D_2O}/k_{H_2O}) from 0.6 to 0.4.[40] Correction for this leads to values from 34 to 36%.

TABLE 6

U.v. and 60 MHz ^{1}H n.m.r. spectra of cycloalkane spirodiazirines

Ring size of cycloalkane	$\lambda_{max.}(C_6H_{12})$/ nm ($\varepsilon$)		τ ($CDCl_3$)	
			α-CH_2	Other CH_2
4	358	155		
5	366.3	150	8.72 (4 H, m)	8.14 (4 H, m)
6	369.7	153	8.86 (4 H, narrow m)	8.37 (6 H, m)
7	369.7	108	8.81br (4 H, m)	8.35 (8 H, narrow m)
8	371	52	8.76 (4 H, narrow m)	8.44 (10 H, m)
12	350	60		

Photoisomerisation of Cyclo-octanespirodiazirine.—Cyclo-octanespirodiazirine (5.57 mg) in cyclohexane (5 ml) was irradiated with a 125 W medium pressure mercury arc using a filter which transmitted from 310 to 430 nm (maximum transmittance at 370 nm). The sample was contained in a stoppered 10 mm Suprasil u.v. cell, and the visible spectrum was monitored every 60 s. After 120 s a new absorption at 495 nm was detectable, its intensity reached a maximum after 660 s, and decreased only slightly up to 1 260 s. The bands due to diazirine decreased steadily throughout the whole time. At 660 s the observed absorbances were:

Diazirine bands	361 nm	355 nm	Diazo band	495 nm
Absorbance	0.158	0.176		0.017
ε	63.5	70.3		6—10
Hence concentration (mmol l^{-1})	2.52	2.51		2.98—1.79

The decrease in diazirine concentration = 8.07 − 2.52 = 5.55 mmol l^{-1}. Thus the percentage conversion into diazo-compound is 53.6—32.2.

Reaction of 3-Phenyldiazirine with Triphenylmethyl Tetrafluoroborate.—3-Phenyldiazirine (0.52 mmol) in acetonitrile (0.5 ml) was added dropwise to a solution of triphenylmethyltetrafluoroborate (0.49 mmol) in acetonitrile (1 ml) at room temperature. Over a period of 20 min the solution changed from orange to dark red, crystals began to form and gas to be evolved. Two 0.1 ml portions were withdrawn during the reaction. After 6 h, the light orange solution (1.3 ml) was filtered and tetraphenylethylene (85.2 mg, 0.257 mmol), m.p. 224.5—226°, $\lambda_{max.}$ 312.5 nm (log ε 4.15) isolated [lit.,[41] m.p. 223—224°, $\lambda_{max.}$ 313 nm (ε 4.15)].[42] The filtrate and the aliquot portions were subjected to aqueous work-up, and an impure solid (largely triphenylmethanol) (45 mg) was isolated. The yield of $Ph_2C{:}CPh_2$ is 57% based on diazirine, and 89% based on Ph_3C^+ converted. U.v.–visible spectra run on the portions withdrawn showed no evidence for any species other than the two reactants.

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[40] R. A. More O'Ferrall, *Adv. Phys. Org. Chem.*, 1967, **5**, 331; H. Dahn and G. Diderich, *Helv. Chim. Acta*, 1971, **54**, 1950.

[41] R. E. Buckles and G. M. Matlack, *Org. Synth.*, 1963, Coll. Vol. IV, 914.

[42] G. Kortum and G. Dreesen, *Chem. Ber.*, 1951, **84**, 182.