The Thermal Decomposition of Diazirines: 3-(3-Methyldiazirin-3-yl)propan-1-ol and 3-(3-Methyldiazirin-3-yl)propanoic Acid

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The thermolyses of 3-(3-methyldiazirin-3-yl)propan-1-ol (**1**) and 3-(3-methyldiazirin-3-yl)propanoic acid (**2**) have been studied in solution over the temperature range 96–125 °C. The reactions are unimolecular and fit linear Arrhenius plots with

$$k(\mathbf{1}) = 10^{13.85 \pm 0.69}\exp[-31.80 \pm 1.21 \text{ kcal mol}^{-1}/RT]\text{s}^{-1}$$

$$\text{and } k(\mathbf{2}) = 10^{12.38 \pm 0.43}\exp[-29.26 \pm 0.75 \text{ kcal mol}^{-1}/RT]\text{s}^{-1}$$

The major products are the alkenes derived from the corresponding carbenes $Me\ddot{C}CH_2CH_2CH_2OH$ (**3**) and $Me\ddot{C}CH_2CH_2CO_2H$ (**4**). The new rate data, taken together with previous work, tend to confirm that diazirine thermolysis involves ring opening to a 'complex' followed either by nitrogen loss or by isomerization to a diazo compound. Whereas (**1**) gives no product of closure onto oxygen, the acid (**2**) affords about 5% γ-valerolactone.

The thermal decomposition of diazirines has been studied both in the gas phase and in solution. In general, the decompositions obey first-order kinetics even up to 90% conversion. Depending on the substituents, the formation of the corresponding diazomethane as an intermediate may or may not be observed.[1]

The major features of the decomposition are now clear. The diazirine eventually yields a carbene which subsequently reacts either inter-or intra-molecularly to give the observed products. It is also apparent that the process whereby the diazirine gets to the carbene is not a single step. All diazirine decompositions show very similar solvent effects and entropies of activation, pointing to a common rate-determining step regardless of the substituents present. A mechanism has been suggested in which a carbene–nitrogen complex is formed as the first intermediate.[2] This complex may, depending on the relative rates and stabilities of intermediates and products, collapse to a diazo compound and/or form a free carbene.

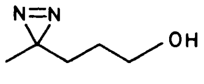
Specifically, there are two questions that still need to be answered in respect of diazirine decomposition. (*i*) Do all diazirines react by the same route? (*ii*) Do both thermal and photochemical decompositions go by way of the same intermediates?

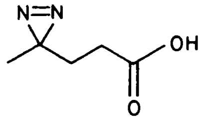
The thermal decompositions have been studied both in alcohol solution and in acetic acid, with results which have been helpful in delineating the mechanism.[3,4] However, no investigations have been carried out on diazirines which bear either an alcoholic group or a carboxylic acid as part of the molecule.

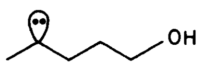
The decomposition of such compounds should give further insight into the nature of the ring rupture, and reported here are the results of such an investigation.

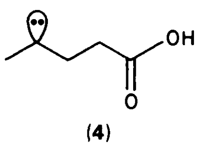
Results and Discussion

3-(3-Methyldiazirin-3-yl)propan-1-ol (**1**) was synthesized according to the method of Church and Weiss.[5] Reaction of 5-hydroxypentan-2-one with ammonia and hydroxylamine-*O*-sulphonic acid and subsequent *in situ* oxidation of the diaziridine formed by addition of iodine and triethylamine to the reaction mixture afforded (**1**) in 15% yield.


(**1**)


(**2**)


(**3**)


(**4**)

3-(3-Methyldiazirin-3-yl)propanoic (**2**) was obtained by the oxidation of (**1**) with chromic–acetic acid mixture. The thermal decomposition of (**1**) and (**2**) gave nitrogen and the alkenes shown in equations (1) and (2), respectively, as the major products. These alkenes can be rationalized as being derived from the carbenes (**3**) and (**4**) formed by loss of nitrogen from (**1**) and (**2**), followed by 1,2 hydrogen migration to the divalent carbon, either from the methyl group or from the adjacent methylene group.

$$(\mathbf{1}) \longrightarrow CH_3CH{=}CHCH_2CH_2OH + CH_2{=}CHCH_2CH_2CH_2OH \quad (1)$$

$$(\mathbf{2}) \longrightarrow CH_3CH{=}CHCH_2CO_2H + CH_2{=}CHCH_2CH_2CO_2H \quad (2)$$

In the present experiments, 1.3 × 10^{-2} mol dm^{-3} solutions of (**1**) and (**2**) were used in the kinetic measurements. The thermal decompositions were carried out over the temperature range 95–125 °C and were monitored by following the disappearance of the UV absorption of (**1**) and (**2**) at 365 nm and 363 nm, respectively. The decompositions were first order under the conditions employed; the rate coefficients were determined by standard methods and are given in Table 1. The first-order rate coefficients for the decomposition of (**1**) in iso-octane and (**2**) in

Table 1. First-order rate coefficients for the decomposition of diazirines (3) (iso-octane) and (2) (*p*-xylene).

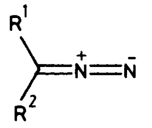
Diazirine (1)		Diazirine (2)	
T/°C	$k/10^{-5}$ s^{-1}	*T*/°C	$k/10^{-5}$ s^{-1}
96.5	0.960 ± 0.020	97.6	1.20 ± 0.16
101.5	1.59 ± 0.044	102.6	2.16 ± 0.13
104.9	2.42 ± 0.040	105.1	2.42 ± 0.06
109.5	4.62 ± 0.21	108.7	3.70 ± 0.03
114.8	6.85 ± 0.15	114.3	6.12 ± 0.17
118.4	12.7 ± 0.22	118.4	10.6 ± 0.15
124.8	18.6 ± 0.26	125.0	18.2 ± 0.60

p-xylene gave linear Arrhenius plots from which equations (3) and (4) were obtained by least-squares analysis.

$$k(1) = 10^{13.85 \pm 0.69}\exp[-31.80 \pm 1.21 \text{ kcal mol}^{-1}/RT]\text{s}^{-1} \quad (3)$$

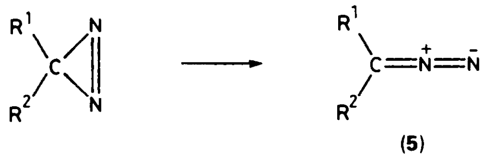
$$k(2) = 10^{12.38 \pm 0.43}\exp[-29.26 \pm 0.75 \text{ kcal mol}^{-1}/RT]\text{s}^{-1} \quad (4)$$

Irradiation of (1) at 350 nm for 20 min in methylene chloride produced an intense pink solution ($\bar{\nu}$ 2 040 cm^{-1}) indicating the presence of the diazo compound (5) However, the diazo intermediate is only moderately stable at room temperature and has a half-life of *ca.* 1–2 min. In an attempt to transform (1) into (5) thermally, (1) was heated in a sealed tube at 118 °C for 1.5 h. Approximately one half of the diazirine was decomposed, but no diazo compound (5) could be detected. Attempts to synthesize (5) by alternative routes have been unsuccessful. To confirm these observations, the first-order rate constants for the decomposition of (1) in *p*-xylene at 118.4 °C have been measured both by UV spectroscopy and also by nitrogen evolution. [The UV rate (k_{UV}) is a measure of the disappearance of diazirine (1); the nitrogen evolution rate (k_{N2} is the measure of the formation of the product N$_2$.] The experiments gave $k_{UV} = (9.53 \pm 0.28) \times 10^{-5}$ s^{-1} and ($k_{N2} = (9.40 \pm 0.10) \times 10^{-5}$ s^{-1}. The fact that k_{UV} and k_{N2} are identical within the error limits suggests that even if the diazo compound (5) is formed in the thermolysis of (1), it must immediately break down to the carbene and nitrogen at these temperatures. Under the same conditions as for (1), neither photolysis nor thermolysis of (2) produce any detectable diazo intermediate; however, the product studies discussed below indicate that some diazo compound must be formed in the photolysis and may also be produced in the thermolysis.



(5)

In addressing the first question posed above, it should be noted that the isomerization of diazirines to diazoalkanes, (Scheme 1) can occur either thermally, or photochemically.



Scheme 1.

Thus, when R^1 and R^2 are H$_2$C=CH,Me;[5] Ph,H;[6] Ph,Me[7] and Ph,Bu^n,[8] diazoalkanes intervene in both the thermal and photolytic decompositions. However, when R^1,R^2 are CF$_3$,Ph;[2] Me,CH$_2$CH$_2$CH$_2$OH; and –(CH$_2$)$_5$–, diazoalkanes only intervene detectably in the photolysis of the diazirines, not in their thermal decompositions. When R^1,R^2 are Et,Cl or Et,Br,[9] the diazo compounds are known to be unstable at −60 °C and have not been observed in the photolysis of the diazirines. When R^1,R^2 are Ph,Cl or Ph,Br, only traces of diazo compounds are found on photolysis, even in low-temperature matrix studies.[10] Finally, when R^1,R^2 are MeO,Cl or PhO,Cl, Sheridan[11] failed to detect even trace amounts of diazo compound, even in matrix photolysis. It is evident that a variety of diazo compounds with various degrees of stability can be generated in the decomposition of diazirines.

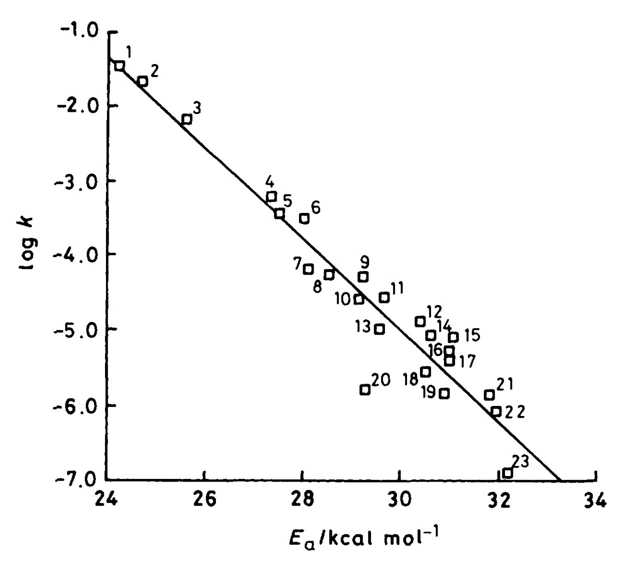


Figure 1. Plot of log *k* (80 °C) *vs.* activation energy (see Table 2 for legend).

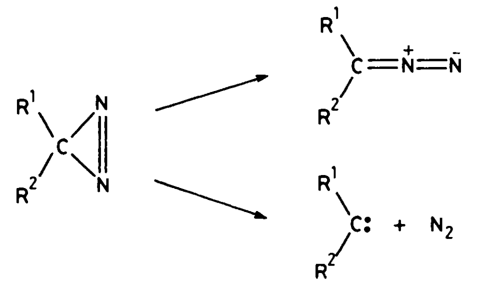
All the kinetic studies on the thermolysis of diazirines have demonstrated that the entropy of activation for decomposition indicates a relatively tight transition state with no additional free rotations. More importantly, these *A* factors show a remarkable constancy for all types of substituents, despite the large change in rate and hence free-energy of activation brought about by the substituent. The first-order rate constants at 80 °C and the activation energies for diazirines (1) and (2) together with 21 other diazirines are listed in Table 2. These data were chosen to include decomposition both in the gas phase and in solution. The rate constants in Table 2 cover a range of five orders of magnitude from the least reactive diazirine (R^1 = R^2 = F) to the most reactive diazirine (R^1,R^2 = MeO,Cl). Figure 1 shows a plot of log *k vs.* E_a for these 20 diazirines with correlation coefficient >0.96.

A linear correlation of this type is remarkable, and possible only if the *A* factors (and hence entropies of activation) in all the decompositions are similar. Such is the characteristic of all diazirine decompositions. If the mechanism for the thermal decomposition of diazirines consists of two competitive paths (Scheme 2), this would require that the substituents exert an exactly parallel influence on the *A* factor for the two transition states while at the same time having a remarkably different influence on the stability of the products and the ratio of the two paths. This suggests that not only do all diazirines follow a single path but also that the rate- and product-determining steps are different.

While a single path involving the opening of the ring to give the diazo compound, followed by nitrogen loss, could account for many of the thermal decompositions—with the diazo

Table 2. Activation energies and first-order rate coefficients (at 80 °C) for the decomposition of diazirines.

Entry	R^1	R^2	Conditions	k/s^{-1}	E_a/kcal mol^{-1}	Ref.
1	MeO	Cl	MeOH	3.27×10^{-2}	24.19	12
2	1-Methyl-2-oxoindoline-3-spiro-3′-diazirine		c-C_6H_{12}	2.13×10^{-2}	24.62	13
3	H_2C=CH	Me	EtOH	6.31×10^{-3}	25.60	6
4	Ph	Br	c-C_6H_{10}	5.71×10^{-4}	27.36	16
5	c-C_3H_5	Cl	c-C_6H_{10}	3.68×10^{-4}	27.49	15
6	Ph	Cl	c-C_6H_{10}	3.02×10^{-4}	28.00	16
7	Ph	Bu^n	Me_2SO	6.60×10^{-5}	28.08	8
8	Ph	Me	Me_2SO	5.61×10^{-5}	28.50	8
9	Cl_3C	Cl	CCl_4	4.61×10^{-5}	29.20	14
10	c-C_7H_{13}	Cl	c-C_6H_{10}	2.82×10^{-5}	29.11	15
11	$PhCH_2$	Cl	CCl_4	2.73×10^{-5}	29.60	4
12	Et	Cl	Gas (80 mmHg)	1.20×10^{-5}	30.45	17
13	Bu^t	Cl	Gas (4 mmHg)	1.09×10^{-5}	29.50	17
14	Pr^i	Cl	Gas (30 mmHg)	1.03×10^{-5}	30.59	17
15	Me	Cl	Gas (350 mmHg)	6.96×10^{-6}	31.07	18
16	Pr^n	Cl	Gas (30 mmHg)	5.48×10^{-6}	30.98	17
17	Ph	CF_3	c-C_6H_{12}	4.74×10^{-6}	31.00	2
18	$-(CH_2)_4-$		Gas (7 mmHg)	2.86×10^{-6}	30.50	19
19	$-(CH_2)_5-$		Gas (5 mmHg)	1.47×10^{-6}	30.87	19
20	Me	$-(CH_2)_2CO_2H$	*p*-Xylene	1.62×10^{-6}	29.26	This work
21	Me	$-(CH_2)_3OH$	Iso-octane	1.26×10^{-6}	31.81	This work
22	Et	Et	Gas (10 mmHg)	8.38×10^{-7}	31.89	19
23	F	F	Gas (300 mmHg)	1.26×10^{-7}	32.20	20



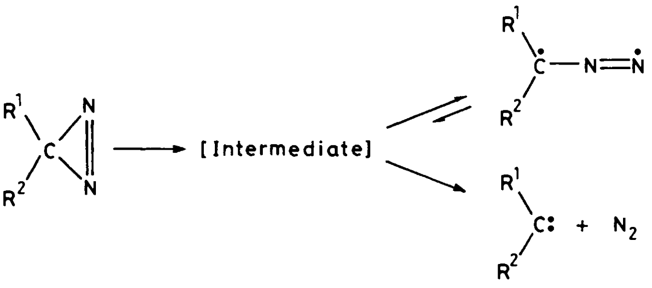
Scheme 2.

compound not being observable when its rate of breakdown is much greater than that of the diazirine—it is notable that diazo ketones are in general much more stable than α-ketodiazirines and yet, in the decomposition of the latter, the formation of diazo ketones is not observed; nor was diazo compound detectable in the thermolysis of 3-phenyl-3-trifluoromethyldiazirine, and of the compounds (**1**) and (**2**) reported here. These observations argue strongly against this isomerization being the single path involved.

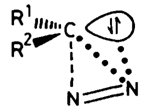
When addressing the second question, it should be recalled that Frey and Stevens[21] showed that in the gas-phase photolysis of alkyl diazirines two paths to product are essential in order to account for the energy distribution of the products. This conclusion has been confirmed by the more extensive analyses of Figuera[22] and also by the results of Frey and Penny[23] on 3-chloro-3-methyldiazirine. It is further noted that it is the change in the ratio of these two paths that gives rise to the change in product composition between photolysis and thermolysis. However, apart from the extra energy involved, the great similarity in overall results between photolysis and thermolysis strongly suggests that the intermediates involved are indeed the same. It is clear from the invariance of quantum yield with wavelength of irradiation that only a single electronic state is involved in photolysis, and that the change in product ratio is not a consequence of two different electronic states of the carbene[23,24] but must depend on other factors.

Both thermally and photochemically, diazirines are found to isomerize to diazo compounds, but this is by no means universal. For the single path of opening to the linear isomer followed by loss of N_2, photochemically one would anticipate the observable formation of diazo-compounds for all cases where these are less stable than the diazirines. However, particularly for halogenodiazirines, the formation of halogenodiazomethanes has only been detected under matrix conditions.

It is here suggested that the mechanism shown in Scheme 3 reconciles all the available evidence in relation to the influence of substituents on the rate of decomposition, the effects of solvent, and the effect due to the stability of the diazo compound and the carbene formed. The intermediate shown may be described as an encounter complex and must be postulated to have a finite, though short, lifetime. Structurally it would resemble the intermediate involved in carbene addition to carbon–carbon bonds, with the plane of the σ-skeleton nearly parallel to the N–N axis, (**6**). It is then similar to the complex detected theoretically by Devaquet,[25] and also to the intermediate between cyclopropylcarbene and carbon monoxide proposed by Skell[26] to account for his results on the deoxygenation of cyclopropanecarboxaldehyde with atomic carbon.



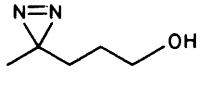
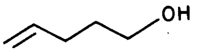
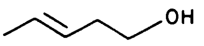
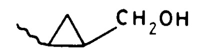
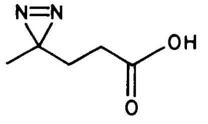
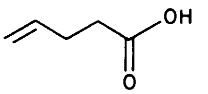
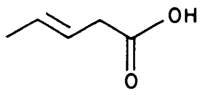
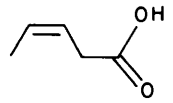
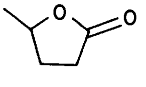
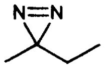
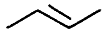
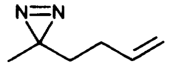
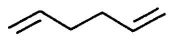
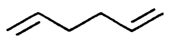
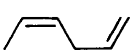
Scheme 3.



(**6**)

This encounter complex then allows a single rate-determining

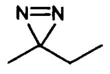
Table 3. Products from diazirine decompostion.

Diazirine	Conditions	Composition (%)			
 (1)	Δ[a] hν[b]	 2 15.0	 74 51.9	 24 23.4	 <0.5 4.7
 (2)	Δ hν	 18.7 25.4	 56 49.7	 20 17.5	 5.3 7.4
 (7)	Δ hν	 3.3 23.2	 66.6 38.0	 23.5 34.7	 0.5 3.7
 (8)	Δ hν	 5.0 22.8	 75.2 46.0	 18.2 27.2	 1.0 4.0

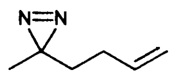
[a] Thermolysis at 100 °C. [b] Photolysis.

step with subsequent partitioning by two competitive product-forming processes. For differing substituents R^1 and R^2 on the diazirines, this mechanism then gives results which depend on the interplay of the rate coefficients and the compound stabilities. Photochemically, the rates and equilibria are affected by the light quanta and are not necessarily the same as for the thermal reactions.

Product Studies.—The products of thermolysis of (**1**) and (**2**) and of the photolysis of (**1**) were analysed by a combination of GC–MS and NMR methods together with a comparison with authentic materials. The results are reported in Table 3. For comparison purposes, data on the products from 3-ethyl-3-methyldiazirine (**7**)[27] and 3-(buten-3-yl)-3-methyldiazirine (**8**)[28] are also included.

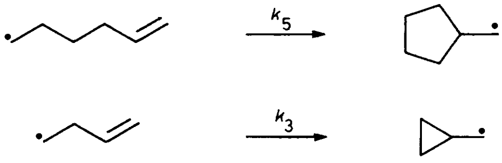


(**7**)



(**8**)

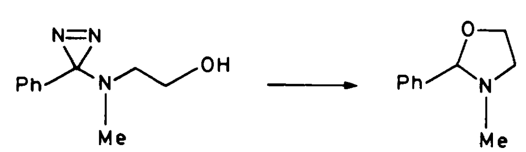
For the hydroxydiazirine (**1**), the product composition is very similar to that from the alkyl (**7**) and alkenyl (**8**) diazirines, both thermally and photochemically, not only in the nature but also in the proportions of the alkenes. The photolysis products exhibit the typical hot-radical effect previously observed for other photolytic decompositions of diazirines.[21,27] Very surprising is the lack of any product derived from interaction of the carbene centre in (**3**) with the OH group. 2-Methyltetrahydrofuran, the product of such a reaction, would have been detected at 0.5% in the products. The absence of such a product is surprising on two counts. Firstly, the bimolecular reactions of $Ph\ddot{C}Cl$ and $PhCH_2\ddot{C}Cl$ with methanol are known to be very fast,[3a,c] and for $PhCH_2\ddot{C}Cl$ to compete with 1,2 hydrogen transfer.[3b,c] Secondly, the OH insertion process would occur *via* a five-membered ring transition state, and these are known to be favoured over three-membered ring transition states as exemplified in radical ring closures (Scheme 4), when $k_5 = 10^5$ s^{-1} and $k_3 = 5 \times 10^3$ s^{-1}.[29,30] Yet diazirine (**1**) does form cyclopropanes (**11**) and does not give any tetrahydrofuran. That closure to a five-membered ring is in some way inhibited is improbable in view of the results of Moss[31] on diazirine (**9**), which gives the oxazolidine (**10**) in good yield.



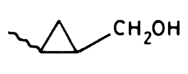
Scheme 4.

In accounting for these differences, it must be noted that the reaction of $Ph\ddot{C}Cl$ with methanol is known to occur about two orders of magnitude faster with the alcohol dimers than with the monomer[3a] and that the intramolecular reaction of carbene (**3**) with the OH group must occur with the monomeric form and also that the carbene formed from (**9**) cannot undergo a 1,2 hydrogen shift.

For the case of the acid diazirine (**2**), the product studies show that cyclic product [γ-valerolactone (**12**)] is formed to the extent of *ca.* 5% in the thermal decomposition. This is most readily accommodated as being due to intramolecular capture of the carbene (**4**) by the carboxylic acid group. However, close examination of the products reveals that about 10% of a dimeric product (**13**) is also formed. This is formally the result of capture of the carbene by the carboxy group of another molecule, either



(9) (10)



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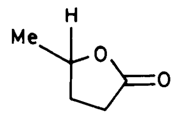
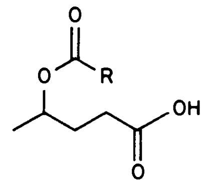


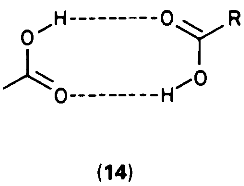
(12)



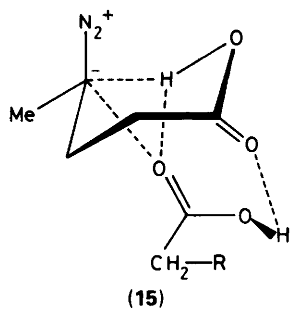
(13)

starting material (2) or product, but (13) could also be formed by the capture of an intermediate diazo compound (5; R^1 = Me, R^2 = $CH_2CH_2CO_2H$) by the carboxylic acids present.

Photolysis of (2) results in a change in the product composition and the differences between the thermal and the photochemical reactions would again appear to be characteristic of the hot-radical effect. As in thermolysis, dimeric product (13) is formed, this time to the extent of 24% of the total products. This increase is consistent with the photochemical transformation of the diazirine (2) into the diazo compound (5; R^1 = Me, R^2 = $CH_2CH_2CO_2H$), as observed for (1), and capture of (5) by acid. The diazo compound ought also to be captured intramolecularly to give the lactone, but the change in the amount of lactone formed on photolysis is much smaller than the change in the amount of dimer: the dimer to lactone ratio changes from 2 in thermolysis to 4 in photolysis. For either the carbene (4) or the diazo compound (5; R^1 = Me, R^2 = $CH_2CH_2CO_2H$), the rate of intramolecular capture would be expected to be much greater than that for intermolecular capture. We suggest that this apparent anomaly is caused by the extensive dimerization of carboxylic acids (14) in aprotic solvents. This would mean that intramolecular proton transfer from acid to diazo carbon would result in the second molecule of carboxylic acid being held in a position where it is ideally positioned to take part in a pseudo-intramolecular displacement of the diazonium ion generated by the proton transfer as shown in (15). In agreement with this hypothesis, the product ratios are invariant with dilution, but the ratio of lactone to dimeric product is markedly affected by solvent, changing from 1:4 in pentane to 1:1 in ether, although the total amount of (lactone + dimer) is not much altered (Table 4).

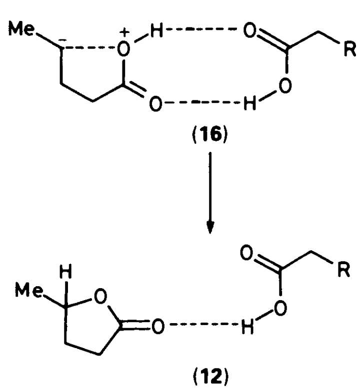


(14)



(15)

By contrast, the internal insertion of the carbene carbon into the O–H bond of the acid group would not be affected by the dimeric nature of the starting material (2), because either the transition state, or the intermediate formed, is an ylide (16) in which C-4 bears a negative charge and the other carboxylic acid is held out of the way. Proton transfer to complete the reaction from (16) would be expected to be rapid.



(12)

At this stage, we incline to the view that all of the dimeric product (13) is formed by reaction of diazo compound (5) and that most of the lactone (12) is formed by the internal insertion of the carbene carbon into the O–H bond of the acid group.

The photolysis of diazirines in acid solution has already been observed to give rise to unusual results,[1b] and it is clear that much further work will be needed to unravel the details of the path(s) followed.

Until the situation regarding the source of each product is clearer, any further conclusions would not be warranted.

Experimental

Syntheses.—3-(3-*Methyldiazirin-3-yl*)*propan*-1-*ol* (1). A solution of 5-hydroxypentan-2-one (13.26 g) in liquid ammonia (200 cm^3) was stirred for 5 h at reflux. After cooling of the mixture to −78 °C, a solution of hydroxylamine-*O*-sulphonic acid (16.0 g) in methanol (100 cm^3) was added in small portions. The reaction mixture was stirred for 1 h at reflux, then allowed to warm to room temperature overnight. The residue was washed with several small portions of methanol and the filtrate concentrated until NH_3 could not be detected. This yielded 3-(3- methyldiaziridin-3-yl)propan-1-ol (5.3 g). The crude diaziridine was dissolved in methanol (30 cm^3), triethylamine (6 cm^3) added and the solution cooled in ice with constant stirring. Solid iodine (6.8 g) was added in small portions and the mixture was then poured into brine (800 cm^3) and extracted with diethyl ether (4 × 50 cm^3). After removal of the solvent, the residue was distilled at reduced pressure to afford 3-(3-methyldiazirin-3-yl)propan-1-ol (1) (2.30 g; 15%) as a colourless liquid, b.p. 61 °C/0.03 mmHg; ν_{max} 1 582 cm^{-1}; λ_{max} 365 nm (ε = 52).

3-(3-*Methyldiazirin*-3-*yl*)*propanoic acid* (2). The hydroxy diazirine (1) (2.3 g) was added dropwise, with constant stirring, to a solution of chromic acid [from CrO_3 (5.2 g) and 5:1 v/v acetic acid–water (60 cm^3)] cooled in an ice-bath. This solution was stirred for 1 h at 0 °C and then at room temperature overnight. The mixture was diluted with brine (800 cm^3) and extracted with diethyl ether (4 × 50 cm^3). Removal of solvent left a yellow oil which was chromatographed on silica gel in hexane to give 3-(3-methyldiazirin-3-yl)propanoic acid (2) (0.67 g; 29%) as a pale yellow liquid, ν_{max} 1 700, 1 590 cm^{-1}; λ_{max} 363 nm (log ε = 1.73); δ_H(360 MHz) 2.24 (2 × H-2, t, J = 7.7 Hz), 1.72 (2 × H-3, t, J = 7.7 Hz), and 1.05 (3 H, s); δ_C(360 MHz) 178.6 (CO_2H), 29.47 (C-3), 28.63 (C-2), 25.14 (C-4), and 19.76 (methyl). Identical material could be prepared from laevulinic acid by using the method given for (1).

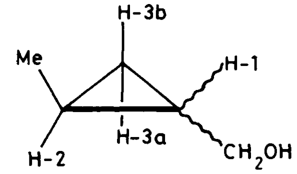
(*Z*)-*Pent*-3-*en*-1-*ol*. But-3-yn-1-ol (14.0 g) was added to a solution of dihydropyran (17.2 g) in diethyl ether (200 cm^3) containing toluene-*p*-sulphonic acid (0.2 g) and the mixture stirred overnight. The solution was washed with 5% potassium carbonate, dried, and distilled to give but-3-yn-1-ol tetrahydropyranyl ether (29.6 g), b.p. 88–89 °C/14 mmHg. This THP ether (10 g) in THF (10 cm^3) was added dropwise to sodamide

Table 4. Products of Photolysis of (**2**).

Solvent (concentration)	Pent-4-enoic acid	(*Z*)-Pent-3-enoic acid	(*E*)-Pent-3-enoic acid	5-Methyltetra-hydrofuran-2-one	$HO_2C(CH_2)_2CH(Me)OCOR$
Pentane (1 mg cm^{-3})	19.4	13.3	38.0	5.6	23.8
Pentane (0.1 mg cm^{-3})	17	13.5	38.5	6	25
Diethyl ether (0.4 mg cm^{-3})	15.4	15.4	30.8	18.8	19.7

[prepared from sodium (2.5 g) in liquid ammonia (200 cm^3)]. After the mixture had been stirred for 1 h, iodomethane (14 g) in THF (15 cm^3) was added over 15 min. After 3 h, diethyl ether (80 cm^3) was added and the mixture allowed to warm to room temperature overnight. Water (100 cm^3) was added, the ether layer separated, and the aqueous layer extracted with ether. The combined organic layers were washed and dried ($MgSO_4$). Removal of solvent and distillation gave pent-3-yn-1-ol THP ether (9.1 g; 87%), b.p. 95–98 °C/13 mmHg; δ_H(60 MHz) 4.6 (1 H), 4.1–3.2 (m, 4 H), 2.6–2.2 (m, 2 H), and 1.9–1.3 (m, 9 H). This THP ether (4.5 g) was dissolved in pentane (40 cm^3) and quinoline (0.25 g) and Lindlar catalyst (0.25 g) were added. Hydrogenation at 0 °C was continued until 1 equiv. of hydrogen (660 cm^3) had been taken up. After filtration, the solvent was removed at reduced pressure, methanol (35 cm^3) and toluene-*p*-sulphonic acid (0.5 g) were added, and the solution stirred overnight. Neutralization with KOH (0.18 g) followed by flash distillation at reduced pressure removed most of the methanol. The semisolid residue was extracted with diethyl ether and distilled. Careful fractionation afforded (*Z*)-pent-3-en-1-ol (1.0 g; 85%), b.p. 137–139 °C; δ_H(270 MHz) 5.60 (H-4, d of qt, *J* 10.87, 6.76, and 1.54 Hz), 5.40 (H-3, d of tq, *J* 10.87, 7.34, and 1.74 Hz), 3.63 (2 × H-1, t, *J* 6.8 Hz), 2.41 (OH, s), 2.35 (2 × H-2, q, *J* 7 Hz), and 1.65 (Me, dd, *J* 6.76 and 1.74 Hz).

2-*Methylcyclopropylmethanol* (**11**). 2-Methylcyclopropanecarbonitrile (2 g; mixture of *E* and *Z*) was heated overnight at 100 °C with methanol (20 cm^3) and concentrated sulphuric acid (4 cm^3). The solution was slowly poured into aqueous K_2CO_3 and then extracted with dichloromethane (4 × 10 cm^3). After drying, distillation gave methyl 2-methylcyclopropanecarboxylate (1.2 g), b.p. 132 °C; δ_H(60 MHz) 3.66 (OMe), 1.4 (H-2), 1.33 (H-1), 1.16 (H-3a), 1.11 (Me, d, *J* = 5.8 Hz), and 0.67 (H-3b). This ester (1.2 g) in diethyl ether (2 cm^3) was added to a stirred suspension of $LiAlH_4$ (0.47 g) in ether (10 cm^3) at room temperature and then refluxed for 30 min. Careful addition of 10% NaOH (0.5 cm^3) and water (0.75 cm^3) followed by filtration gave a solution which was dried and distilled to give 2-methylcyclopropylmethanol (0.72 g), b.p. 134–135 °C. NMR analysis showed this to be a mixture of the *E*- and *Z*-isomers (87:13, *E*:*Z*). The *E*-isomer showed δ_H(360 MHz) 3.43 and 3.40 [C*H*$_2$OH, *J* = 11.2 (*gem*) and 7.0 Hz], 1.05 (Me, d, *J* 6.0 Hz), 0.79 (H-1, *J* 8.1, 4.3, 4.6, and 7.0 Hz), 0.62 (H-2, *J* 8.3, 6.0, and 4.6 Hz), 0.36 [H-3a, *J* 4.8 (*gem*), 8.3, and 4.5 Hz], and 0.25 (H-3b), *J* 4.8, 8.1, and 4.3 Hz). The *Z*-isomer showed δ_H 3.69 and 3.51 [C*H*$_2$OH, *J* 11.25 (*gem*), 8.4, and 6.7 Hz—these two protons show different couplings to the H-1 proton], 1.22 (H-1), 1.10 (Me, d, *J* = 6.2 Hz), 0.91 (H-2), 0.69 (H-3a), and −0.07 (H-3b). The mass spectrum of the mixture showed *m*/*z* (% base): 85 (0.6), 68 (15), 67 (15), 57 (63), 55 (41), 45 (base), 44 (96), and 41 (66).



(**11**)

Product Analyses.—Diazirine (**1**) (300 mg) in iso-octane solution was heated at 100 °C until all the diazirine was destroyed. The solvent was removed at reduced pressure and the residue was chromatographed on silica gel in hexane. The products were analysed using GC–MS and/or ^{1}H NMR (250 MHz) spectroscopy. The NMR spectra of both crude and chromatographed samples were comparable and similar to those of authentic materials. Quantification gave the results reported in Table 3. 2-Methyltetrahydrofuran was not detected in the product mixture but could be detected when 0.5% was added.

The products of photolysis of (**1**) were obtained in a similar way after irradiation of the solution of (**1**) with a medium-pressure mercury arc at 0 °C. The products were stable to the photolytic conditions.

Diazirine (**2**) (45 mg) in pentane (4 cm^3) was heated in a sealed tube at 125 °C fo 8 h (10 × $t_{\frac{1}{2}}$). The pentane was removed at reduced pressure and the residue analysed by ^{1}H NMR spectroscopy.

Photolysis of (**2**) was carried out at two concentrations—30 mg in 30 cm^3 and 8.6 mg in 90 cm^3—using a medium-pressure mercury arc at 0 °C.

Kinetics.—*By UV spectroscopy.* Solutions of diazirine (1.3 × 10^{-2} mol dm^{-3}) in iso-octane for (**1**) and in *p*-xylene for (**2**) were used for the kinetic measurements. The decomposition rates were obtained by following the disappearance of the UV absorption at 365 nm for (**1**) and at 363 nm for (**2**). The first-order rate coefficients were determined from least-squares analysis of plots of $\log(A_t - A_\infty)$ *v.* time (where A_t = absorbance at time *t* and A_∞ = absorbance at infinite time).

By nitrogen evolution. A known amount of diazirine was dissolved in *p*-xylene and the solution was connected to a gas burette and immersed in an oil bath. The volumes of nitrogen were measured at suitable time intervals, V_t, and at atmospheric pressure. The volume at infinite time, V_∞, was measured after 10 half-lives of the reaction. The first-order rate coefficients were determined by least-squares analysis of the plots of $\log(V_t - V_\infty)$ *vs.* time.

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