Thermal Decomposition of the Diazirines. Part II.[1] 3,3-Tetramethylenediazirine, 3,3-Pentamethylenediazirine, and 3,3-Diethyldiazirine

By H. M. Frey and A. W. Scaplehorn

Thermal decomposition of 3,3-tetramethylenediazirine, investigated in the temperature range 100—139°, yields cyclopentene and nitrogen; of 3,3-pentamethylenediazirine (101—137°) gives cyclohexene and nitrogen; of 3,3-diethyldiazirine (118—149°) gives *cis*- and *trans*-pent-2-ene, ethylcyclopropane, and nitrogen. In all cases the reactions were homogeneous and of first order. The Arrhenius parameters for these decompositions, which are probably unimolecular, have been determined.

In Part I[1] the thermal decomposition of 3,3-dimethyldiazirine was reported. The results indicated that the decomposition was probably unimolecular and although it was not possible certainly to define the reaction path, a carbene was probably an intermediate. We now present work on three other diazirines, whose thermal and photochemical decomposition may enable the path to be defined more closely.

EXPERIMENTAL

Diazirines were obtained from the diaziridines, which were synthesised by essentially the method of Schmitz and Ohme;[2] hydroxylamine-*o*-sulphonic acid is added to a ketone and dry methanol in liquid ammonia. The purity of the hydroxylamine-*o*-sulphonic acid was important and unless traces of sulphuric acid were well washed out with ether poor yields were obtained. Other modifications which improved the yields were that the temperature was −70° rather than −40°, the ketone, liquid ammonia, and methanol were allowed to react for up to 1 hr. before addition of sulphonic acid, and that the sulphonic acid was added slowly, rather than in 10 min. After evaporation of the ammonia, the mixture was extracted with methylene chloride and crude diaziridine was obtained by evaporation of the methylene chloride and methanol in a vacuum. The crude diaziridines, recrystallised from light petroleum (b. p. 30—40°), were sublimed *in vacuo*, and if stored in dark bottles in absence of CO_2 were stable for several months. If sublimation was omitted the diaziridines partially decomposed on storage, and diazirines prepared from them then contained appreciable quantities of ketones.

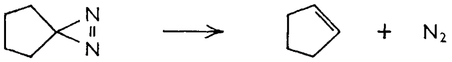
The diaziridines were treated with alkaline silver oxide and the diazirines swept out in nitrogen or extracted with ether. Ketones were removed with alkaline hydroxylamine solution. All diazirines were distilled under reduced pressure. This step gave good yields.

Apparatus and Procedure.—A conventional high-vacuum static system was used having greaseless stopcocks with Viton diaphragms. Pyrex reaction vessels were used, immersed in a high-temperature oil thermostat.* Analysis was by gas chromatography (Aerograph 600C, with a gas sampling valve and a flame ionisation detector). With tetra- and penta-methylenediazirines a 15 ft. column was used containing ββ'-oxydipropionitrile as the liquid phase at 35°. For 3,3-diethyldiazirine this column was extended by 6 ft. containing ethylene glycol saturated with silver nitrate as the liquid phase and the whole was at room temperature.

Products were removed from the reaction vessel by expansion into an evacuated gas pipette. Nitrogen was then added to the pipette to raise the total pressure to 150 mm. All analyses were performed in duplicate, and if an acceptable degree of reproducibility was not obtained between the two analyses the run was repeated. Between 7 and 16 runs were carried out at every temperature investigated.

RESULTS

Tetramethylenediazirine.—Cyclopentene and nitrogen were the only volatile pyrolysis products:



Plots of the logarithm of the undecomposed diazirine against time were linear even for decompositions taken to over 90%. Rate constants, determined from these plots by method of least squares, are in Table 1. These results were obtained with an initial reactant pressure of 7 mm., but experiments with various pressures from 1 to 10 mm., also with 150 mm. of added nitrogen, and runs in a packed and in the unpacked vessel gave the same rate constant. The decomposition is thus homogeneous and of first order. It is unlikely that any chain reaction is involved in the decomposition, especially since the cyclopentene formed is a good chain inhibitor. The transformation is probably unimolecular and at above 1 mm. is in its high-pressure region.

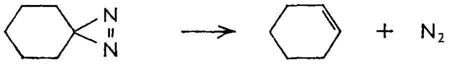
Table 1

Rate constants for the decomposition of tetramethylenediazirine

Temp.	100·5°	109·55°	114·6°	118·7°
10^4k (sec.$^{-1}$)	0·337	0·917	1·635	2·47
Temp.	124·45°	129·6°	134·2°	139·15°
10^4k (sec.$^{-1}$)	3·99	6·485	10·56	16·55

From the results in Table 1 the Arrhenius parameters were calculated by the method of least squares, whence $k = 10^{13\cdot 40}\exp(-30{,}500/\boldsymbol{R}T)$sec.$^{-1}$. Probable errors in the Arrhenius parameters are not quoted for reasons given in ref. 1.

Pentamethylenediazirine.—The decomposition, studied at nine temperatures in the range 101—137°, showed first-order kinetics and the only volatile products were cyclohexene and nitrogen.



The results shown in Table 2 refer to runs with an initial reactant pressure of 5 mm. but the rate constant was independent of pressure down to 1 mm. and independent of

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* Temperatures were measured using mercury-in-glass thermometers calibrated against N.P.L. standardised thermometers.

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

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

added nitrogen (150 mm.). Arrhenius parameters, determined by the method of least squares, gave $k = 10^{13\cdot34}$ exp$(-30{,}870/\boldsymbol{R}T)$sec.$^{-1}$.

TABLE 2

Rate constants for the decomposition of pentamethylenediazirine

Temp.	101·4°	104·6°	110·0°	114·8°	119·0°
10^4k (sec.$^{-1}$)	0·216	0·312	0·536	0·902	1·35
Temp.	124·85°	127·9°	132·4°	137·2°	
10^4k (sec.$^{-1}$)	2·48	3·48	5·14	8·05	

Diethyldiazirine.—The decomposition, studied at five temperatures in the range 118—149°, gave good straight lines in plots of the logarithm of undecomposed diazirine against time. The volatile products were *cis*- and *trans*-pent-2-ene, ethylcyclopropane, and nitrogen; the relative yields of hydrocarbon products were 30·6, 67·5, and 1·6, respectively, and these relative yields did not vary with percentage decomposition or with temperature in the range studied. The rate constant was independent of pressure from 1 to 20 mm. and was unaffected by the addition of nitrogen. The rate constants for various temperatures (initial reactant pressure 10 mm.) are in Table 3. A least-squares analysis yielded the following Arrhenius equation $k = 10^{13\cdot73}$exp $(-31{,}890/\boldsymbol{R}T)$sec.$^{-1}$.

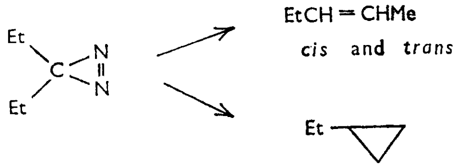

TABLE 3

Rate constants for the decomposition of diethyldiazirine

Temp.	118·65°	129·45°	136·9°	143·4°	149·0°
10^4k (sec.$^{-1}$)	0·860	2·61	5·34	9·96	16·5

DISCUSSION

The results are consistent with the decompositions' being truly unimolecular. The lower energies of activation for the tetra- and penta-methylenediazirine than the diethyl (and dimethyl) compound may be due to the ring strain in these cyclic diazirines. Thus in diazirine itself[3] the ∠HCH is 117°, so there will be appreciable ring strain in the five- and six-membered rings in the tetra- and penta-methylene derivatives (with slightly more in the five- than the six-membered ring).

The formation of some ethylcyclopropane in the pyrolysis of the diethyldiazirine is good evidence for the intermediacy of a carbene, and all the decompositions can be rationalised by assuming such an intermediate. The hydrocarbon products then result from the well known intramolecular rearrangements of the carbenes.

The ratio of hydrocarbon products produced by the thermal and photochemical decompositions of some diazirines differ.[4,5] With methylethyldiazirine the differences are quite marked and have been ascribed to the production of a vibrationally excited carbene in the photochemical decomposition.[4] Similar differences occur with diethyldiazirine; thus the photochemical decomposition yields[5] *trans*- and *cis*-pent-2-ene and ethylcyclopropane in the relative yields of 57·0, 38·4, and 4·0% (together with traces of 2-methyl-but-2-ene and -but-1-ene). Similarly the photochemical decomposition of pentamethylenediazirine yields some bicyclo[3,1,0]-hexane and methylenecyclopentane, neither being formed in thermal decomposition.[6]

Our results for diethyldiazirine show that, within experimental error, the energy of activation for the formation of the three hydrocarbon products is the same. We now consider if this finding can be reconciled with the suggested "hot" carbene hypothesis. There are two distinct possibilities with respect to the carbenes formed thermally. They may rearrange so rapidly that their energy content is entirely determined by the energetics of the primary (decomposition) step, or they may be in temperature equilibrium with their surroundings. The absence of any addition of the carbenes to olefins suggests that the rearrangements are fast, since the addition reactions are expected to have low energies of activation.

If the carbene is in temperature equilibrium with its surroundings in the pyrolyses, we may proceed as follows; first we assume that the photochemically produced carbenes have such a high energy content that the relative rates of isomerisations to the various hydrocarbons is determined solely by the *A* factors of the reactions. For diethyldiazirine this gives the relative *A* factors for the isomerisations to *trans*- and *cis*-pent-2-ene and ethylcyclopropane as 57·0 : 38·4 : 4·0. Using these ratios and the product yields obtained in the pyrolysis of diethyldiazirine at 119° we can calculate a difference in energy of activation for the reactions leading to the *cis*- and *trans*-pent-2-enes of 300 cal./mole and between the *cis*-olefin and the ethylcyclopropane of about 500 cal./mole. Over the temperature range studied these small differences would only produce a minor change in the isomer ratios which would be masked by experimental errors. (We have chosen the most favourable situation; if the photochemically produced carbene is not assumed to be so energetic that small differences of energy of activation are unimportant then larger values will be obtained.) Thus we see that the thermal results are not inconsistent with the hot-radical hypothesis, if the thermally produced carbene is in temperature equilibrium with its surroundings.

If the pyrolytically produced carbene is not in temperature equilibrium with its surroundings then one extreme case can be considered; that in which its rate of reaction is entirely determined by its energy content resulting from its genesis. The reaction paths are envisaged as shown in the Figure. According to Kassel's

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[3] L. Pierce and Sr. V. Dobyns, *J. Amer. Chem. Soc.*, 1962, **84**, 2651.

[4] H. M. Frey and I. D. R. Stevens, *J. Amer. Chem. Soc.*, 1962, **84**, 2647.

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

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

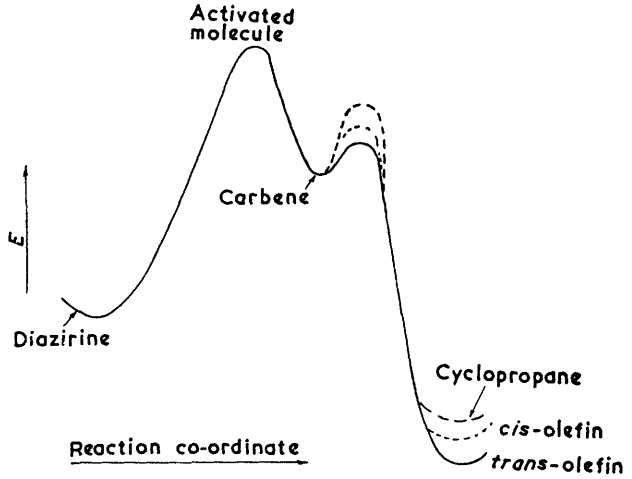
classical theory of unimolecular reactions, the most probable energy of an activated molecule undergoing a unimolecular reaction is given by

$$E = E_0 + (S - 1)\boldsymbol{R}T \qquad (1)$$

where E_0 is the minimum energy required for reaction (the energy of activation) and S is the number of effective oscillators in the molecule. Thus the difference in the most probable energy contained in an activated molecule at two different temperatures is given by

$$E_1 - E_2 = (S - 1)\boldsymbol{R}(T_1 - T_2) \qquad (2)$$

For nearly all unimolecular reactions so far investigated in the " fall off " region S is between one half and two thirds of the total number of oscillators in the reactant. For diethyldiazirine we may take $S \approx 25$. Thus in our temperature range the most probable energy of the activated molecules increased by approximately 1500 cal./mole.



The excess of energy present in the carbene will depend on the difference between the heat of formation of the diazirine plus the energy of activation less any energy carried away by the nitrogen. While the nitrogen may carry a different fraction of the total energy depending on the exact energy of the activated molecule, this effect is likely to be small. We can therefore set an upper limit on the difference between the excess of energy carried by the carbene at the lowest and highest temperature used of 1500 cal./mole.

The rate of isomerisation of the carbene can be approximated by

$$k = A\left(\frac{E - E_0}{E}\right)^{S-1} \qquad (3)$$

The use of equation (3) can lead to quite considerable errors [7,8] but it is sufficiently precise for our rather crude calculations. Thus the relative rates of isomerisation to *cis*- and *trans*-pent-2-ene will be given by

$$\frac{k_{cis}}{k_{trans}} = \frac{A_{cis}}{A_{trans}}\left(\frac{E - E_0^{cis}}{E - E_0^{trans}}\right)^{S-1} \qquad (4)$$

If we proceed as before and assume that the photochemical yields of *cis*- and *trans*-pent-2-ene reflect the A factors of the reaction, and we take $E_0^{cis} - E_0^{trans} = 300$ cal./mole, then equation (4) yields the result $E - E_0^{trans} \approx 18$ kcal./mole. A consideration of the probable difference between the heat of formation of the diazirine and the carbene suggests that this is by no means an unreasonable value. If equation (4) represents the isomerisation of the carbene at the lowest temperature investigated in the pyrolysis of diethyldiazirine then the corresponding ratio of *cis*- to *trans*-pent-2-ene at the highest temperature will be given by

$$\frac{k_{cis}}{k_{trans}} = \frac{A_{cis}}{A_{trans}}\left(\frac{E + 1500 - E_0^{cis}}{E + 1500 - E_0^{trans}}\right)^{S-1} \qquad (5)$$

Combining equations (4) and (5) we obtain for the change in ratio of the pent-2-enes from the lowest to the highest temperature

$$\frac{R_1}{R_2} = \left(\frac{E - E_0^{cis}}{E - E_0^{trans}} \times \frac{E + 1500 - E_0^{trans}}{E + 1500 - E_0^{cis}}\right)^{S-1} \qquad (6)$$

Using the previously calculated values for $E - E_0^{trans}$ and $E_0^{cis} - E_0^{trans}$ we find $R_1/R_2 = 1{\cdot}04$. Thus a change in the ratio of the two pentenes of only 4% is predicted in the temperature range studied, and again this would probably have escaped detection.

It should be noted that the chosen value of $E_0^{cis} - E_0^{trans} = 300$ cal./mole is arbitrary in the case just considered. It was chosen as the smallest probable value for this difference. If a value of between 400 and 600 cal./mole is used (as such a value would be closer to that expected from considerations of the enthalpy differences between *cis*- and *trans*-pent-2-ene) then the predicted ratio R_1/R_2 is even closer to unity.

A somewhat larger effect for the relative yields of ethylcyclopropane is predicted. But again, owing to the very small yields of the compound that were observed experimentally, the effect would again be too small to be definitely observable.

As a result of these crude calculations, it can be seen that the absence of an appreciable temperature-dependence of the ratios of the hydrocarbon products observed in the pyrolysis of diethyldiazirine does not rule out the hot-radical hypothesis in the photochemical system, though the thermal experiments cannot be considered to support this hypothesis. Alternative explanations to account for the differences observed between the photochemical and thermal systems, such as the occurrence of some triplet-state carbenes,[9] can neither be substantiated or disproved by thermal studies.

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[7] H. M. Frey, *Trans. Faraday Soc.*, 1960, **56**, 1201.

[8] B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, 1959, **60**, 735; R. E. Harrington, B. S. Rabinovitch, and R. W. Diesen, *ibid.*, 1960, **32**, 1245.

[9] H. M. Frey, " Advances in Photochemistry," vol. 4, ed. Noyes, Hammond, and Pitts, Interscience, New York, 1966.