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907. *Reactions of Vibrationally Excited Molecules. Part III.*[1] *The Photolysis of Cyclohexanespiro-3-diazirine.*

By H. M. Frey and I. D. R. Stevens.

The photolysis of cyclohexanespiro-3-diazirine has been investigated in the pressure range 0·1—10·0 mm. The major hydrocarbon reaction-products are cyclohexene, butadiene, ethylene, bicyclo[4,1,0]hexane, and methylenecyclopentane. The compositions of the reaction mixtures are explained in terms of a mechanism involving the production of "hot" molecules, formed by a carbene rearrangement, which either decompose unimolecularly or are deactivated by collision. The average lifetimes of these molecules suggest that they have very high energy.

As described [1] in Parts I and II, highly vibrationally excited molecules may be produced by methylene-addition to olefins. It was hoped that the study of the reactions of such molecules would be helpful in testing the validity of the various theories of unimolecular transformations. Unfortunately, there are serious disadvantages; some may be overcome by careful and precise experimental work, or will be minimised when the necessary thermodynamic data become available, but others are inherent in the systems. Since methylene attacks a wide range of organic compounds extremely indiscriminately, a large excess of the reactant olefin is necessary, and so the total mixture will contain only a relatively small percentage of the reaction products. The simultaneous addition of methylene to the olefinic double-bond and attack on other bonds in the molecule leads to obvious complications and may considerably reduce the precision of the results. Thus it is virtually impossible to study the efficiencies of various "inert" gases (and there are relatively few that do not react with methylene) in deactivating the "hot" molecules, since the concentration of the former must be much greater than that of the reactants, leading to a total reaction-product constituting perhaps less than 1% of the total mixture. There are other less serious analytical difficulties which limit the experimental accuracy.

As well as analytical problems, there are difficulties of a more fundamental nature. The initial step in the photolysis of keten and diazomethane is the absorption of a light quantum followed by dissociation into methylene plus carbon monoxide or nitrogen. However, the fraction of the surplus light energy carried by the methylene is unknown. There is considerable evidence to indicate that the methylene does possess excess of translational and vibrational energy when first formed. How much is lost before reaction, and how much retained and hence available for producing excitation in the reaction-product, is uncertain. This alone makes the interpretation of inert gas effects extremely difficult. There is even uncertainty about the value of ΔH_f for methylene, which is a triplet [2] in its electronic ground state, whereas in most of the systems studied it reacts in its (excited) singlet state.

Many of these difficulties may not occur or may be less acute with the diazirines,[3] yet such systems may well yield the same kind of information as the methylene reactions. The work described in this paper was initiated in an attempt to investigate the reactions of highly excited cyclohexene formed by the photolysis of cyclohexanespiro-3-diazirine.

Experimental

Cyclohexanespiro-3-diazirine.—Cyclohexanespiro-3-diaziridine, prepared as described by Schmitz and Ohme,[4] was oxidised to the diazirine as follows. The diaziridine (5·84 g.) in potassium hydroxide solution (170 ml. 20%) was added dropwise with stirring at 0° to a

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[1] Frey, *Proc. Roy. Soc.*, 1959, *A*, **250**, 409 (Pt. I); **251**, 575 (Pt. II).
[2] Herzberg, *Proc. Roy. Soc.*, 1961, *A*, **262**, 291.
[3] Frey and Stevens, *J. Amer. Chem. Soc.*, 1962, **84**, 2647.
[4] Schmitz and Ohme, *Ber.*, 1961, **94**, 2166.

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mixture of aqueous silver nitrate (40 g. in 180 ml.) and isopentane (200 ml.). The mixture was stirred for 30 min. and the pentane layer separated. The aqueous layer was extracted with isopentane (50 ml.) and the whole organic layer dried ($MgSO_4$) and concentrated at atmospheric pressure. The residue was distilled under vacuum to give pentamethylene diazirine (2·5 g.), b. p. 64°/100 mm.

The ultraviolet spectrum is similar to those of other diazirines.[5] Fig. 1 shows the long-wavelength band (10 cm. gas-cell, 12 mm. pressure).

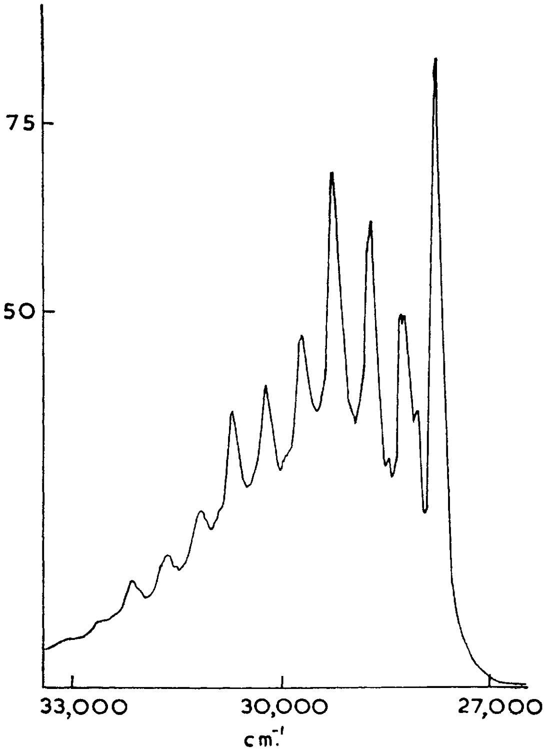

FIG. 1. The long-wavelength absorption band of cyclohexanespiro-3-diazirine.
[ord] Percentage absorption.
[abs] Wave numbers cm.$^{-1}$.

Apparatus.—A conventional high-vacuum apparatus was used for preparing all mixtures for photolysis and for the various gas-transfer operations. Greaseless stopcocks with Viton A diaphragms were used throughout to minimise absorption problems associated with the use of conventional greased stopcocks. Photolyses were carried out in cylindrical Pyrex reaction vessels of various sizes, using the unfiltered radiation of a medium-pressure mercury-arc (Hanovia UVS 500).

Analysis.—Gas chromatography was employed, the column being packed with 40/60 mesh Chromosorp P containing 20% w/w of di-2-cyanoethyl ether and operated at room temperature. Hydrogen was the flow gas and the detector was a Gow-Mac tungsten-filament katharometer in a conventional Wheatstone bridge network. Signals were fed *via* a variable attenuator to a 1 mv recorder, and were integrated electronically (Perkin-Elmer model 194). Stopcocks on the analytical apparatus were lubricated with a special fluorocarbon grease to reduce absorption errors. Products were identified in the first instance by comparison of their retention times with those of known compounds (either obtained commercially or synthesised during this work). Later, individual chromatographic peaks were trapped and analysed by mass-spectrometry (A.E.I.—M.S.3) and infrared spectroscopy (microgas-cell). Calibration factors were determined by preparing known mixtures of the appropriate compounds in a specially constructed apparatus, essentially a volume with thermostat and manometer, and a series of vessels for storage purposes. Greaseless stopcocks only were used. The mixtures were then analysed in the gas-chromatographic apparatus.

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[5] Frey and Stevens, *J.*, 1963, 3514.

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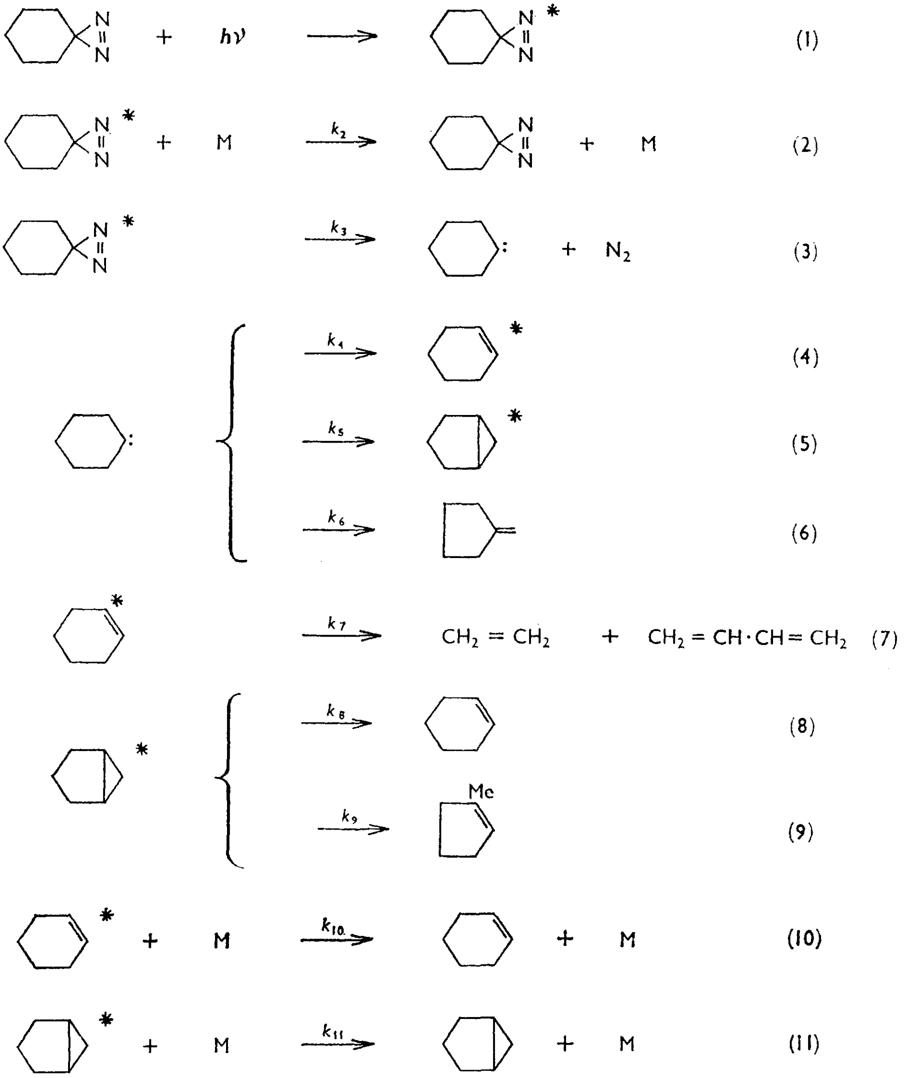
RESULTS AND DISCUSSION

Photolysis was carried out in cylindrical Pyrex reaction vessels whose volumes ranged from 25 to 500 ml. Results obtained at 0 and 65° were identical within experimental error. Accordingly, no attempt was made in the majority of runs to control the temperature, other than to ensure that it remained below 65°. In a series of runs with 5 mm. of the diazirine, the time of photolysis was varied so that the decomposition covered the range 10—90%. The relative ratios of products were found to be quite insensitive to the percentage decomposition in this range. In other runs photolysis was usually allowed to continue until at least 75% of the diazirine had reacted.



Runs were carried out with initial pressures of pentamethylenediazirine in the range 0·14—11·0 mm. After photolysis the entire reaction mixture was transferred by toepler pump to the analytical system. A fraction of this mixture (usually about one-third) was then analysed. Most reaction mixtures were analysed in duplicate. In a few runs varying

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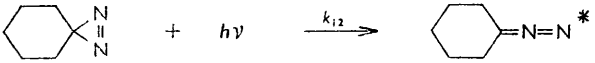
pressures of nitrogen were added to 10 mm. of the diazirine before photolysis. In these cases, after photolysis, the reaction vessel was cooled in liquid oxygen and the bulk of the nitrogen removed by pumping before the reaction mixture was transferred to the analytical system.

No attempt was made to filter the light from the mercury arc. With the medium-pressure mercury-arc and a Pyrex reaction vessel, the only " active " radiation is that at 3660, 3340, and 3130 Å. Similarly, in this initial study no attempt was made to determine quantum yields. However, by comparison of the time taken for decomposition of the cyclohexanespirodiazirine with that taken for the decomposition of diazomethane (in the presence of an excess of ethylene), allowance being made for the difference in extinction coefficients of these compounds, it appears that the quantum yield must be less than unity. Some semiquantitative evidence was also obtained that the quantum yield increased as the total pressure decreased.

On the basis of previous work with diazirines and studies of vibrationally excited molecules produced by methylene reactions,[1,3,6,7] together with the product analyses given here, the following mechanism is suggested for the reactions occurring when the cyclohexanespirodiazirine undergoes photolysis at pressures below 10 mm. In addition, recent experiments in this laboratory[8] have shown that in the liquid phase, photolysis of the diazirine leads to the transient formation of some diazocyclohexane. It is possible that this reaction also occurs in the gas phase.



(12)

At high pressures, molecules formed by reactions (4) and (5) should all be stabilised by collision and hence cyclohexene, bicyclo[3,1,0]hexane, and methylene cyclopentane should be the only hydrocarbon products. In photolyses of the pure diazirine, the highest pressures used (*ca.* 11 mm.) were insufficient to completely suppress the formation of some butadiene and ethylene in reaction (7). However, in the presence of a large excess of added nitrogen (10 mm. of diazirine, 200 mm. nitrogen) no butadiene was formed. (The procedure employed with added nitrogen would in any case eliminate most of the ethylene.) The relative yields of cyclohexene, bicyclohexane, and methylenecyclopentane under these conditions were 97·0; 2·5; 0·4%. Hence, the predominant mode of decomposition of the carbene formed by reaction (3) is to yield cyclohexene. It follows that the reactions of the bicyclohexane are of minor importance. (Experiments on the thermal decomposition of the diazirine in the gas phase at 160° showed that cyclohexene was the *only* hydrocarbon product. This provides another example of the product-dependence from carbene rearrangements on the mode of formation of the carbene.) The analytical data for a representative selection of experiments are shown in the Table.

Percentage of hydrocarbon products at various initial pressures.

Initial pressure (mm.)	Cyclohexene	Butadiene	Bicyclo-hexane	1-Methyl-cyclopentene	Methylene-cyclopentane
10·2	88·2	8·3	2·5	0	0·4
8·1	87·6	9·4	2·5	0	0·4
5·9	86·4	10·8	2·3	0·1	0·4
3·0	80·2	17·1	2·1	0·2	0·5
1·1	71·2	26·4	1·8	0·3	0·3
0·34	61·6	36·3	1·4	0·3	0·4
0·17	57·2	41·1	0·9	0·4	0·4

Note: Since one molecule of cyclohexene yields a molecule of ethylene in addition to a molecule of butadiene, the yield of the former has been neglected in the Table. At pressures below 1 mm., cyclohexadiene was detected but could not be determined quantitatively and has not been recorded in the Table.

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[6] Knox, Trotman-Dickenson, and Wells, *J.*, 1958, 2897.
[7] Frey, *Trans. Faraday Soc.*, 1962, **58**, 516; 1961, **57**, 951.
[8] Evans and Stevens, to be published.

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Neglecting the reactions of the bicyclohexane, the suggested mechanism yields the equation

$$[\text{cyclohexene}]/[\text{butadiene}] = k_{10}M/k_7 \tag{13}$$

We may take M to be directly proportional to the initial pressure of the system. Since at 5 mm. the relative yields of products was essentially independent of the extent of decomposition, we have direct experimental evidence of the validity of this approximation. Hence, a plot of the ratio of cyclohexene to butadiene against pressure should give a straight line which passes through the origin. The experimental results are shown in Fig. 2.

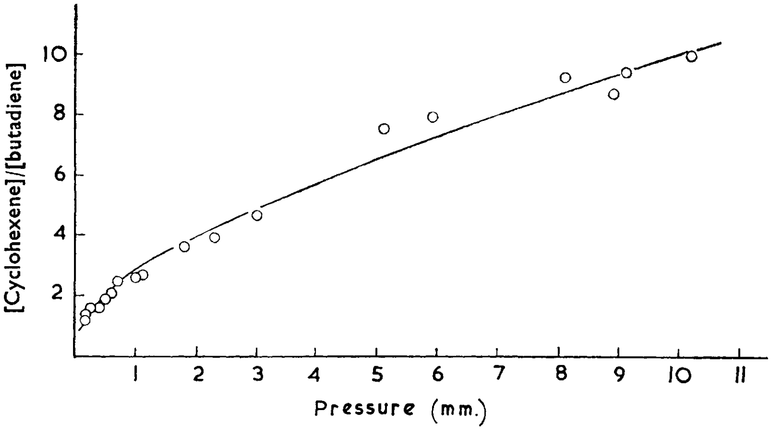

FIG. 2. Ratio of cyclohexene to butadiene as a function of the pressure. [ord] Cyclohexene : butadiene. [abs] Pressure in mm.

It will be seen that the experimental results do not yield this linear relationship. Indeed the plot at low pressures shows such considerable curvature that an extrapolation to zero pressure cannot be made. Curvature of this type has been noted previously in studies of the decomposition of vibrationally excited molecules produced by methylene reactions and also in studies of the photochemical decomposition[9] of 2,3-diazabicyclo-[2,2,1]hept-2-ene. It has been ascribed to the production of excited molecules with a range of energy contents and hence a range of lifetimes. In the present work this would correspond to a range of values of k_7. What is surprising is the extent of the effect, which is considerably greater than in previously reported work. Before we consider the major causes of energy spread it will be convenient to discuss some minor contributory effects.

The thermal isomerisation[10] of bicyclo[3,1,0]hexane gives rise to cyclohexene and 1-methylcyclopentene in the ratio of 3 : 1. For this reason reactions (8), (9), and (11) have been included in the mechanism. We found that at pressures below 3 mm. the yield of bicyclohexane began to decrease and at the same time a very small peak with the same retention time as 1-methylcyclopentene was noted (the quantity was too small to allow trapping and secondary identification). We therefore suspected that some of the initially-formed bicyclohexane gave rise to cyclohexene. This would cause curvature in the plot shown in Fig. 2. However, since the total high-pressure yield of the bicyclohexane is only 2·5%, the effect will produce only a small deviation from linearity.

The thermal decomposition of cyclohexene has been studied in the gas phase between 425 and 535°. In this temperature range the initial decomposition proceeds by two paths, one leading to butadiene and ethylene and the other to cyclohexadiene and hydrogen. The rate constants for these two reactions are $1{\cdot}4 \times 10^{17} \exp(-72{,}700/\boldsymbol{R}T)$

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[9] Steel, *J. Phys. Chem.*, 1963, **67**, 1779.

[10] Frey and Smith, *Trans. Faraday Soc.*, 1962, **58**, 697.

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and $1{\cdot}9 \times 10^{16} \exp(-71{,}200/\mathbf{R}T)$ sec.$^{-1}$, respectively. In the temperature range investigated this leads to a butadiene : cyclohexadiene ratio of about 3 : 1.

In the present work at pressures below 1 mm. very small quantities of a compound with the same retention time as cyclohexadiene were detected. With the analytical column used, the retention time of this compound was so long (resulting in a very broad peak) that no accurate quantitative estimate of it could be made. However, it certainly could not be equivalent to more than 10% of the butadiene formed. The reason for the difference in the relative yields of butadiene and cyclohexadiene obtained in this work compared with the pyrolysis results will be discussed later. The formation of any cyclohexadiene (which was not allowed for in the calculated ratio of cyclohexene to butadiene in Fig. 2) will again produce curvature in the figure.

We now consider what factors will produce in the cyclohexene molecules a range of energy contents, and hence a range of values of k_7. With a Pyrex reaction vessel and the medium-pressure mercury-arc, the only radiation absorbed by the pentamethylene diazirine will be from the lines at 3130, 3340, and 3660 Å (relative intensities 7 : 1 : 12). Since Pyrex has an appreciable absorption at 3130 Å the actual relative intensities of the light entering the reaction vessels were more nearly in the ratio 3 : 1 : 12. At all pressures of the diazirine used experimentally only a fraction of the incident radiation was absorbed. The fraction of each wavelength of incident radiation that was absorbed cannot be estimated accurately since it is highly dependent on the extent of pressure-broadening of the mercury lines. [Thus the absorption of the diazirine (12 mm. pressure in a 10-cm. cell) is approximately 4% at 3660 Å but at 3600 Å has risen to 83%.] Nevertheless there is no doubt that each line does contribute to the photolysis. The difference in energy between radiation at 3130 and 3660 Å is equivalent to 13 kcal./mole. Thus the excited cyclohexanespirodiazirine molecules formed according to reaction (1) can have an energy spread of this magnitude. This in turn will lead to the production of the carbene with a spread of energy values. (It is indeed possible that the resulting carbenes have an even greater energy spread than the excited diazirine molecules from which they are formed. This is not, however, likely owing to the relatively long lifetime of the excited molecule, as evidenced by the pressure-dependent quantum yield.) Thus, while there is uncertainty about the actual magnitude of the energy spread, there is no doubt that such a range of values occurs. All recent theories of unimolecular decompositions predict that the lifetime of excited molecules will be strongly energy-dependent, and this prediction has been amply proved experimentally.[11-13] Thus the existence of an energy spread in the molecules of cyclohexene will lead to curvature in Fig. 2. As has already been remarked, this curvature is more marked than in previous work. We believe this arises from two causes. Firstly, a given energy spread gives a larger range of lifetimes with a complex than a simple molecule. Cyclohexene is more complex (in terms of the total number of normal modes of vibration) than the other molecules so far investigated. Secondly, the relative contribution of the various wavelengths of light causing photolysis is probably pressure-dependent. Since the quantum yield is less than unity and is pressure-dependent, steps (2) and (3) were included in the reaction mechanism; in such cases the quantum yield usually has a pressure-dependence which is also wavelength-dependent,[14] since k_3 depends on the wavelength of the light absorbed. Thus we expect the relative contribution of the long-wavelength radiation to the formation of the cyclohexyl carbene to increase with decreasing pressure; this will enhance the effects already discussed and lead to even more marked curvature.

If reaction (12) makes an appreciable contribution at low pressures, then the photolysis

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[11] Frey, *Trans. Faraday Soc.*, 1960, **56**, 1201.
[12] Butler and Kistiakowsky, *J. Amer. Chem. Soc.*, 1960, **82**, 759; 1961, **83**, 1324.
[13] Simons, Setser, and Rabinovitch, *J. Amer. Chem. Soc.*, 1962, **84**, 1758; Rabinovitch, Bubin, and Harrington, *J. Chem. Phys.*, 1963, **38**, 405.
[14] Smith and Gordon, *J. Phys. Chem.*, 1961, **65**, 1124.

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of the resulting diazocyclohexane will lead to cyclohexene by yet another path, but there is no reason to suppose that the latter will have the same energy content as that formed more directly from the diazirine. We do not, however, believe that this is a major factor here. Finally it must be realised that, to all other effects producing a spectrum of energy values in the cyclohexene, will be added that due to the normal spread of thermal energy originally present in the pentamethylene diazirine molecules.

A molecule of the complexity of cyclohexene undergoing a thermal unimolecular decomposition would not be expected to show a decrease in the high-pressure rate-constant until pressures well below 0·1 mm. had been reached. In the present work the initially-formed cyclohexene shows some decomposition even at 10 mm. This implies that the molecule initially possesses energy well in excess of the energy of activation for its decomposition. It is possible to make a rough estimate of the energy content of these cyclohexene molecules (say the most energetic ones in the present work) from the Kassel formulation as applied to monoenergetic species.[11] Assuming that cyclohexene has 28 effective oscillators, and adopting the Arrhenius parameters determined by Smith and Gordon [15] for the thermal decomposition of this compound, we compute the energy content of the cyclohexene to be 120 kcal. mole^{-1}. No great accuracy is possible in these calculations, and this value may easily be in error by ±10 kcal. mole^{-1}. However this energy content is certainly enormously in excess of the average energy of reacting cyclohexene molecules in the normal thermal experiments.

The energy corresponding to the shortest wavelength of the light absorbed by the pentamethyl diazirine (3130 Å) is 90 kcal. mole^{-1}. Even if all this energy found its way into the cyclohexene molecule (and this is improbable since some is almost certainly converted into vibrational and translational energy associated with the nitrogen molecule) there is still a discrepancy of 30 kcal. mole^{-1}. This would have to be less than or equal to the difference in heats of formation of pentamethylene diazirine and cyclohexene. While this difference is not known, it is easy to show that the inequality almost certainly holds. It has recently been shown [16] that diazirine is even more endothermic than diazomethane, with heats of formation of 79 and 49 kcal. mole^{-1}, respectively. It is probable that the difference between the heats of formation of diazirine and methane will be approximately the same as that for the cyclohexanespirodiazirine and cyclohexane. This yields a value for the further energy available to the cyclohexene molecule of 68 kcal. mole^{-1}. Thus we see that there is no difficulty in producing molecules with 120 kcal. mole^{-1} excess of energy.

In the thermal experiments the decomposition of cyclohexene gave butadiene and cyclohexadiene in the ratio of about 3 : 1. The considerably higher "*A*" factor for the formation of butadiene is partially compensated by a slightly greater energy of activation when compared with the reaction leading to cyclohexadiene. With the highly excited molecules produced in the present work, this small difference in energies of activation is of little consequence, and the ratio of the products will be determined only by the relative magnitudes of the "*A*" factors, *i.e.*, about 8 : 1. The experimental ratio was even smaller than this, which may be due partly to further reactions of the cyclohexadiene.

The studies here reported have not fulfilled the expectation that this system might furnish excited molecules with fewer theoretical and experimental difficulties than in the corresponding work with methylene and ethylidene. It is possible that studies with monochromatic radiation and with other diazirines may yet prove to have the predicted advantages.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY, SOUTHAMPTON. [*Received, December* 28*th*, 1963.]

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[15] Porter, *J. Amer. Chem. Soc.*, 1957, **79**, 827.

[16] Paulett and Ettinger, *J. Chem. Phys.*, 1963, **39**, 825.