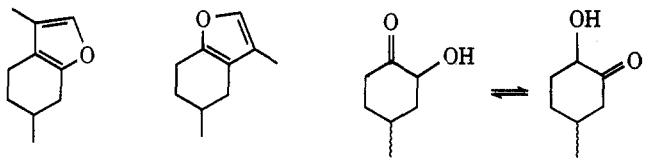
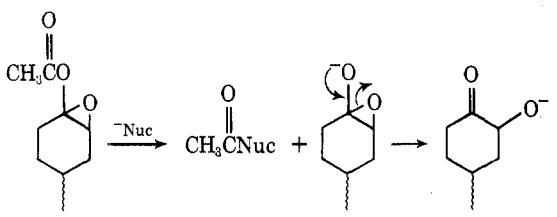


10 11 12 13

To circumvent this isomerization problem, we attempted to generate and trap the specific acyloin anion putatively generated by reaction of epoxyacetate **14**[20] with nucleophilic reagents, as shown in Scheme III. Treatment of **14** with various amounts of butyllithium followed by 3 afforded no furan, although the formation of 56% 5-methylnonan-5-ol plus 15% hexan-2-one in one reaction suggested that at least the initial stages of the desired reaction sequence were occurring. Treatment of **14** with sodium ethoxide in an aprotic medium afforded 30% of the familiar mixture of **10** and **11**. Efforts to overcome this acyloin isomerization limitation to the furan synthesis are in progress, as are studies of the use of β-alkoxyvinylphosphonium salts in the synthesis of other heterocycles.

Scheme III



14

Typical Procedure for Furan Synthesis. The following procedure is suitable for any of the three phosphonium salt reagents. A mixture of 0.300 g (6.5×10^{-4} mol) of **2**, 0.025 g (5.5×10^{-4} mol) of a 50% mineral oil dispersion of sodium hydride, and 0.165 g (5×10^{-4} mol) of **6** in 25 ml of anhydrous dimethoxyethane was stirred for 72 hr at room temperature under nitrogen until tlc no longer showed **6**. The mixture was filtered and evaporated, and the residue was dissolved in 50 ml of benzene to which was then added a pinch of *p*-toluenesulfonic acid and 4 g of Linde 4A Molecular Sieves. This mixture was heated at reflux for 2 hr and filtered rapidly through 20 g of Florisil, which was then washed with five 30-ml portions of ether. The filtrates were evaporated and the residue was purified by preparative layer chromatography on silica gel which had been treated with potassium hydroxide[21] to afford 0.113 g (70%) of **5**: mp 117–119°; ir (KBr) 6.0, 6.2, 11.5, and 11.55 μ; nmr ($CDCl_3$) 0.55 (s), 0.7–2.8 (m), 1.2 (s), 5.8 (s, 1), 6.25 (s, 1), and 7.1–7.4 ppm (m, 2).

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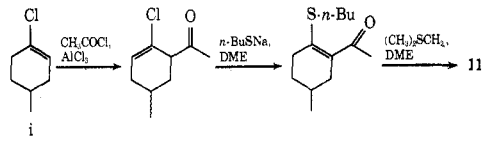

i

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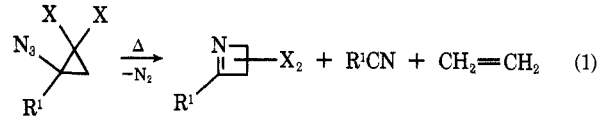
Stereochemical Aspects of the Photochemical and Thermal Fragmentation of Cyclopropyl Azides[1]

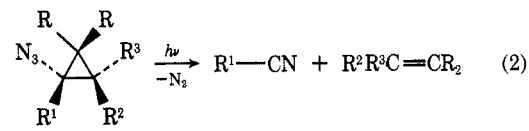
Summary: Photolysis of cyclopropyl azides results in high yields of nitrile and olefin derived from fragmentation of the cyclopropane ring in contrast to their thermal decomposition which leads to 1-azetine and/or fragmentation; both the photochemical and the thermal fragmentation are stereospecific.

Sir: Several examples[2-4] of the thermal decomposition of cyclopropyl azides **1** have recently been reported. In most of these cases formation of the ring-expanded 1-azetine predominates with minor amounts of nitrile and olefin present (eq 1). The availability of stereochemically pure



(1)

1



(2)

1a, R^1 = Ph; R^2 = R^3 = H; R = Cl
b, R^1 = Me; R^2 = Me; R^3 = H; R = Cl
c, R^1 = Me; R^2 = H; R^3 = Me; R = Cl
d, R^1 = R^2 = R^3 = Me; R = H
e, R^1 = Ph; R^2 = R^3 = Me; R = H

cyclopropyl azides[5] led us to investigate their photochemical and thermal fragmentation. The effect of ring substituents and determination of the stereochemistry of the resultant olefins provide an insight into the scope and mechanism of these reactions.

Concurrently with the thermolysis of **1**,[2] we investigated the photolysis of azides **1a–e** (sealed tube) at 3500 Å. Only the corresponding nitriles and olefins in yields of ~90% were obtained. No 1-azetines could be observed in the pmr spectra of the products.[6] This is in sharp contrast to

Table I
Pyrolysis of Cyclopropyl Azides. Fragmentation vs. Ring Expansion as a Function of Substituents

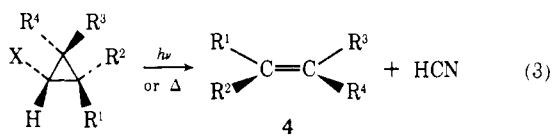
Azide	Pyrolysis temp, °C	Yield[a] of 1-azetine, %	Yield[a] of olefin and nitrile, %
1a	120	55	
1b	120	74	5
1c	120	79	8
1d	97		28[b]
1e	90	51	45
2a	120		85
2b	120		100
2c	120		72
2d	120		87

[a] Absolute yields, by nmr integration of distilled product or isolation of the azetine. [b] The remainder was unreacted azide (after 6 hr).

Table II
Rate of Disappearance of Cyclopropyl Azides at 95°

Compd	Relative rate
2b (trans)	8.3
2d (cis)	1.5
2a (trans)	2.3
2c (cis)	1.0

the thermal decomposition of these azides which leads predominantly to 1-azetines.[2] In one reported example of photolysis of a cyclopropyl azide only fragmentation to olefin and nitrile was observed.[4] Photolysis of the stereoisomerically pure azides **2a-d** gave the phenylpropenes **4a-d** of retained configuration in high yield (eq 3).



(3)

4

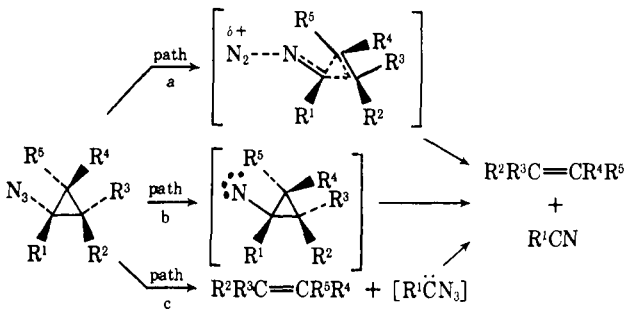
2, X = N_3
3, X = C = O

a, R^1 = Ph; R^2 = R^3 = H; R^4 = Me (trans)
b, R^1 = Me; R^2 = R^3 = H; R^4 = Ph (trans)
c, R^1 = Ph; R^2 = R^4 = H; R^3 = Me (cis)
d, R^2 = Me; R^1 = R^3 = H; R^4 = Ph (cis)

In contrast to the photochemical reaction, we found that ring substituents have a pronounced effect on the path of the thermal reaction.[7] In general, halogen substituents (R = Cl or Br) guide the pyrolysis of 1 almost totally toward 1-azetine formation when R^1 is phenyl or methyl. Without halogen the yields of nitrile and olefin increase and, when R^1 is hydrogen, no 1-azetine is observed. These results are summarized in Table I. The resultant 1-azetines were found to be stable to the reaction conditions indicating they are not precursors in the fragmentation process.[8] In an investigation of the pyrolysis of **2a-d** as a function of temperature higher yields of olefin were obtained as the temperature was raised. The pyrolysis of **2a-d** afforded olefins **4a-d** with complete retention of stereochemistry.[9]

These and previously published results do not definitively prove a mechanism for the thermal fragmentation[10] but they permit us to exclude certain pathways.[11] Three plausible mechanisms are outlined in Scheme I. A nitrene intermediate, as indicated in path b, seems unlikely since the absolute rate of decomposition of cyclopropyl azides is much greater than that of simple alkyl azides.[12] Furthermore the rate of decomposition of azides **2a-d** depends on the substituents and their stereochemistry (Table II). If the rate-determining step is formation of the nitrene, the rate should not be affected by ring substituents. In general trans 2,3-disubstituted isomers pyrolyzed somewhat

Scheme I



faster than their cis isomers, suggesting a partial rupture of the cyclopropane ring in the transition state leading to olefin.

While we favor path a because of the presumably higher energy of a carbene intermediate in pathway c, we cannot eliminate the latter at the present time.

On the other hand the photolysis of these azides more likely involves a nitrene intermediate (path b). Lending credence to this idea is the photolysis of cyclopropyl isocyanate **3a** at 2554 Å which, like **2a**, produced phenylpropene and hydrogen cyanide. Since such reactions presumably proceed *via* a nitrene,[13] a common intermediate in the photolysis of **2a** and **3a** is suggested.

Further work is in progress to elucidate the detailed mechanism of decomposition of cyclopropyl azides.

Acknowledgment. Support of this research by a grant from the National Science Foundation is gratefully acknowledged.

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(8) The failure of azetines to fragment in a retro [2 + 2] process does not rule out an azetine intermediate possessing residual excess energy from the prior loss of N_2.
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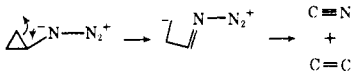

(12) For instance the rate constant for decomposition of *n*-propyl azide at 200° is 9.58 × 10^{-5} sec^{-1}, E_{act} = 39.4 kcal/mol [G. Geiseller and W. Koenig, *Z. Phys. Chem.*, **227**, 81 (1964)], while for cyclopropyl azide **1b** at 121° it is 8.2 × 10^{-4} sec^{-1}, E_{act} = 22 kcal/mol.[2]
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