

(Fisher, reagent grade) was dried over magnesium sulfate and distilled *in vacuo*; the fraction of bp 66–67° (1.0 mm) was retained. *N,N,N',N'*-Tetramethylazobisformamide (TMABFA) was prepared by lead tetracetate oxidation of the corresponding hydrazobisformamide suspended in methylene chloride maintained at 20 ± 2°. The crude TMABFA recrystallized from hexane–benzene (5:1, v/v) melted at 111–113° (lit.⁸ mp 112–113°).

Formamoylation of ABFA.—To a stirred slurry of ABFA (11.6 g, 100 mmol) in formamide (135 g, 3.0 mol) was added benzoyl peroxide (2.42 g, 10 mmol). The reaction mixture was then heated at 80 ± 2° under an oxygen-free nitrogen atmosphere for 4 hr. Additional peroxide (10 mmol) was then added and the reaction temperature was maintained for 24 hr.

Distillation of the clear, pale orange-amber reaction mixture *in vacuo* [pot temperature 85° (0.1 mm)] left a cream-colored solid residue. The residue was triturated consecutively with portions of alcohol and ether, leaving 13.9 g (81 mmol, 86.4%) of crude trisformamoylhydrazine (1), mp 214–222° dec. The crude cream-colored solid 1 was recrystallized twice from aqueous 75% alcohol and dried *in vacuo* (0.5 mm, 110°) to give an analytical sample melting at 220–225° dec.

Anal. Calcd for C₈H₇N₅O₃ (1): C, 22.36; H, 4.38; N, 43.47; mol wt, 161. Found: C, 22.21, 22.37; H, 4.39, 4.44; N, 43.56, 43.59; mol wt, 162 (determined cryoscopically in DMSO).

An ir spectrum (KBr) of 1 showed NH absorptions at 3475 (s), 3410 (shoulder, s), 3390 (s), 3350 (s), 3290 (s), and 3220 (m), a series of absorptions in the carbonyl region at 1695 (vs), 1660 (vs), 1630 (m), 1580 (m), and 1515 (m), and absorptions at 1360 (s), 1090 (w), 1063 (w), and 640 cm⁻¹ (m).

The uv spectrum (H₂O) of 1 exhibits no maxima above 200 nm (ϵ_{200} 7000 l. mol⁻¹).

The nmr spectrum (DMSO-*d*₆) of 1 showed absorptions at δ 6.11 (s, relatively sharp, 2 H), 6.97 (broad s, 2 H), 7.59 (broad s, 2 H), and 7.95 (s, 1 H). Addition of D₂O to the DMSO-*d*₆ solution of 1 caused greatest diminution in the absorption at δ 7.95.

The mass spectrum of 1 (20 eV, 170°) exhibits the following: *m/e* (rel intensity) 118 (95), 101 (100), 86 m (4), 75 (95), 45 (11), 44 (95), 31 (97), and 18 (32).⁹

Formamoylation of TMABFA.—A stirred solution of TMABFA (7.8 g, 45 mmol) in formamide (135 g, 3.0 mol) containing 2.42 g (10 mmol) of benzoyl peroxide was heated to 80 ± 2° under an oxygen-free nitrogen atmosphere for 4 hr. Additional peroxide (10 mmol) was added and heating was continued for 15 hr.

The clear, pale orange reaction mixture was distilled *in vacuo* (pot <80°, 0.15 mm) and left an orange-amber semisolid residue that was slurried with warm methylene chloride (80 ml) and filtered. The filter cake, crude 1-formamoyl-1,2-bis(*N,N*-dimethylcarbamoyl)hydrazine (2) (3.15 g, 32%), mp 180–185°, was recrystallized twice from absolute alcohol to afford analytically pure 2: mp 183–184.5°; ir (KBr) 3430 (s, NH), 3220 (m), 2930 (w), 1690 (s, shoulder, C=O), 1675 (vs, C=O), 1690 (s, shoulder, C=O), 1365 (m), and 1272 cm⁻¹ (w); uv (H₂O) exhibits no maxima above 200 nm (ϵ_{200} 14,600 l. mol⁻¹); nmr (DMSO *d*₆) δ 2.80 (s, 6 H, CH₃), 6.60 (s, 2 H), and 8.77 (s, 1 H). *Anal.* Calcd for C₇H₁₅N₅O₃ (2): C, 38.70; H, 6.96; N, 32.24; mol wt, 217. Found: C, 38.55; H, 7.01; N, 32.44; mol wt, 210 (determined in THF by vapor phase osmometry).

Hydrolysis of Trisformamoylhydrazine (1).—A clear solution of 1 (1.0 g, 6.2 mmol) in 75 mol of water was heated to reflux. After 4.5 hr, the reaction mixture contained some insolubles and ammonia was detected. The reaction mixture was refluxed for an additional 2 hr, cooled, and filtered. The dried filter cake (0.7 g) was identified as biurea (5.9 mmol) by melting point, mixture melting point, and ir. Evaporation of the weakly basic aqueous filtrate left a solid residue (undetermined amount) identified by ir as urea.

Basic Hydrolysis of Trisformamoylhydrazine (1).—To a slurry of 1 (1.0 g, 6.2 mmol) in 50 ml of water was added 5 ml of aqueous 40% sodium hydroxide, causing immediate solution of 1. After several minutes at room temperature, the reaction mixture became turbid and a finely divided solid precipitated. The filtered and dried solid (0.7 g) was identified as biurea (5.9

mmol). An acidulated aqueous solution of benzoyl hydrazide was added to the clear, pale yellow basic filtrate from the main reaction mixture. Upon cooling the mixture, 4-benzoylsemicarbazide precipitated; it was identified by melting point (222–225° dec), mixture melting point, and ir.

Aminolysis of Trisformamoylhydrazine (1).—To a suspension of 1 (1.0 g, 6.2 mol) in water (25 ml) at room temperature was added a solution of diethylamine (2.0 g, 41.0 mmol) in water (*ca.* 15–20 ml). After *ca.* 15 min, a solid precipitated from the turbid reaction mixture. After an additional 30 min at room temperature, the solid was filtered and the filter cake was washed consecutively with alcohol and ether. The dried filter cake (0.7 g) was identified as biurea (6.0 mmol) by melting point and ir.

The aqueous filtrate was evaporated to dryness, and the residual solid was extracted with ether. Concentration of the combined ether extracts gave diethylurea, mp 65–69°, identified by ir and nmr.

Thermolysis of Trisformamoylhydrazine (1).—A solution of 1 (6.5 mmol) in 25 ml of DMSO was heated at 115° for 21 hr. The solvent was removed by distillation *in vacuo* (pot temperature <80°, 0.1 mm). The solid residue was found to contain biurea (5.1 mmol) and cyanuric acid (2.1 mmol), as determined by nmr.

Registry No.—1, 39981-78-7; 2, 40081-62-7; ABFA, 123-77-3; formamide, 75-12-7; TMABFA, 10465-78-8; biurea, 110-21-4; benzoyl hydrazide, 613-94-5; 4-benzoylsemicarbazide, 39981-79-8; diethylamine, 109-89-7; diethylurea, 623-76-7; cyanuric acid, 108-80-5.

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The Electrocyclodimerization of *N*-Vinylcarbazole

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Passage of electric current through solutions of *N*-vinylcarbazole (VCZ), for example, with silver perchlorate in nitrobenzene¹ or with zinc bromide in acetone,² has been shown to result in polymerization. However, Breitenbach³ also reported that electroinitiation with Hg^{II} cyanide, in acetonitrile, gave a cyclic dimer. Similarly, photoirradiation in the presence of organic electron acceptors results in the production of polymer or cyclic dimer depending on the acceptor and the solvent. Tada, *et al.*,⁴ found that the basic character of the solvent was a critical factor in determining the production of cyclic dimer or polymer. In copolymerization studies with electron-accepting monomers,⁵ it was found that as the concentration of the electron-accepting monomer decreased the proportion of cyclodimer product increased. It was con-

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(2) D. C. Phillips, D. H. Davies, and J. D. B. Smith, *Macromolecules*, **5**, 674 (1972).

(3) J. W. Breitenbach, O. F. Olaj, and F. Wehrman, *Monatsh. Chem.*, **95**, 1007 (1964).

(4) K. Tada, Y. Shirota, S. Kusadazashi, and H. Mikawa, *Chem. Commun.*, 1169 (1971).

(5) K. Tada, Y. Shirota, and H. Mikawa, *J. Polym. Sci., Part B*, **10**, 691 (1972).

(8) R. J. Crawford and R. Raap, *J. Org. Chem.*, **28**, 2419 (1963).

(9) The mass spectrum of authentic biurea (obtained from Aldrich Chemical Co., Inc.) exhibits the following fragmentation pattern (20 eV, 210°): *m/e* (rel intensity) 118 (2), 101 (89), 75 (100), 60 (21), 45 (85), 44 (90), 31 (90), 30 (54), 18 (82), and 17 (41).

cluded that cation solvation of a radical cation species was responsible for the cyclodimerization reaction. Ledwith, *et al.*⁶ reached similar conclusions when studying the metal salt catalyzed reactions of a number of aromatic enamines. It has been generally accepted that the cyclic dimer, in the *N*-vinylcarbazole system, is *trans*-1,2-dicarbazylcyclobutane (TCB).^{2,3}

In this note, we report that the electroinitiated reaction of VCZ, using zinc bromide as electrolyte in acetone solution, can result in either linear polymer or TCB in high yield. The product depends only upon the current density used in the electrolytic cell. The work reported here is largely confined to the current density regions where both products are obtained. The conventional polymerization process has been discussed previously.²

Experimental Section

The electrolytic experiments were conducted in a 50-ml darkened reaction flask to avoid the possible occurrence of any extraneous photochemical reactions. The vessel, which was maintained at 25° by means of a jacket through which water flowed, was equipped with stirrer and nitrogen inlet and outlet. The standard electrolytic cell contained two identical platinum foil electrodes (2.0 × 5.0 cm) separated by 4.0 cm. Similar cells modified with porous battery cup separation of anode and cathode compartments were also used. All reactions were performed under conditions of constant current using a dc power supply (Northeast Scientific Corp. Model RI233, 0–233 mA/0–360 V).

The purification of starting materials is reported elsewhere.^{2,7} The zinc bromide and *N*-vinylcarbazole monomer were separately dissolved in two equal volumes of acetone contained in darkened vessels. Equal quantities of each solution were mixed just prior to the application of current. After passage of electrolytic current, the products of the reaction were isolated by precipitation into a large excess of absolute methanol. This procedure served to separate the products from monomer, since the monomer is readily soluble in methanol. The crude product was further purified by reprecipitation from toluene solution into excess methanol followed by several methanol washes. Total yield was then determined gravimetrically.

The product was separated into polymer and dimer fractions using gel permeation chromatography, the product being dissolved in toluene and passed through a bank of four Styragel columns at 75° using a flow rate of 1 ml/min. Under these conditions the two peaks were well resolved and the percentage of each product was then determined through calibration of the chromatogram using a known mixture. Some product samples were separated by acetone extraction (the dimer being soluble in acetone) and analyzed gravimetrically. Both techniques gave good correlation.

The cyclic dimer was characterized using a number of techniques. Elemental analysis gave the following results: C, 87.1; H, 5.7; N, 6.9; calcd C, 87.3; H, 5.8; N, 6.8. Nmr analysis, in CDCl₃ on a Varian A-60 instrument, gave the results shown in Table I. These data are close to those reported by Ellinger⁸ for the dimer.

Mass spectral fragmentation (Perkin-Elmer Model 270) indicated a molecular weight of 386 and confirmed the adjacent position of the carbazole rings by the presence of significant levels of 1,2-dicarbazyl ethylene fragments. The crystalline solid dimer had a melting point of 191–192° (uncorrected) close to that reported by Breitenbach. The polymer was also studied and is discussed in more detail elsewhere.⁷ The polymer average molecular weight ranged between 3000 and 20,000 and was independent of the current strength and the zinc bromide concentration. Analysis of the major products for bromine or zinc

(6) F. A. Bell, R. A. Crellin, H. Fujii, and A. Ledwith, *Chem. Commun.*, 251 (1969).

(7) D. C. Phillips, J. D. B. Smith, and D. H. Davies, *Makromol. Chem.*, in press.

(8) L. P. Ellinger, J. Feeney, and A. Ledwith, *Monatsh. Chem.*, **96**, 131 (1965).

TABLE I

NMR ANALYSIS OF *trans*-1,2-DICARBAZYL CYCLOBUTANE^a

Protons	Nmr, τ	Rel intensities	
		Calcd	Found
Aromatic (1,8 positions)	1.98 (m)	2	1.8
Aromatic	2.69 (m)	6	5.9
CH cyclobutane ring	3.77 (m)	1	1.0
CH ₂ cyclobutane ring	7.25 (m)	2	1.7

^a TMS as internal reference.

proved negative. No significant amounts of other products were found.

Results and Discussion

The current density was varied while maintaining other variables constant and holding a 5:1 VCZ:ZnBr₂ constant mole ratio. The results, presented in Table II, show that as the current density is decreased the cor-

TABLE II

ELECTROINITIATION OF VCZ-ZnBr₂-ACETONE SOLUTIONS^a

Current density, mA cm ⁻²	Time, hr	Product formation as percentage of initial monomer	
		TCB	Poly VCZ
4.0	2	0.2	83.5
1.0	2	0.8	66.6
0.20	2	13.0	46.2
0.05	2	13.8	0.1
0.05	8	34.0	0.1
0.05	18	61.3	0.2

^a VCZ:ZnBr₂ = 5:1, VCZ:acetone = 1:40.

responding proportion of the dimer is increased. Above 1.0 mA cm⁻² the reaction produces almost exclusively polymer. Below 0.05 mA cm⁻² the cyclic dimer, TCB, was produced in high yield.

Also shown in Table II is the effect of increased time at the lowest current density. Even at extremely long reaction times no significant levels of polymer could be found. Increasing the VCZ monomer concentration, while maintaining the current density, reaction time, and zinc bromide concentration constant, decreased the polymerization rate while increasing the rate of cyclodimerization. For example, using a 10:1 VCZ:ZnBr₂ mole ratio and 2 hr of 4.0 mA cm⁻² current passage gave 24% polymer product and 0.5% dimer. At a current density of 0.05 mA cm⁻² a similar decrease in polymer yield, accompanied by an increase in TCB formation, was observed. The exponent (α) and the constant (k) in the rate equation $R_n = kI^\alpha + c$ were determined. (c and k are constants and I the electrolytic current density.) R_n is the rate of cyclodimerization (R_c) or the rate of polymerization (R_p). Also determined was the equivalent function for photoirradiation of the same system with 254-nm uv, I being the uv intensity in this case. The experimental conditions for irradiation are similar to those reported elsewhere.⁹ The result of irradiation as was expected from the results of Tada, *et al.*⁴ The TCB was always the major product and only small amounts of polymer were found. Table III shows the results of irradiation, and Table IV the rate equation determination data.

(9) D. H. Davies, D. C. Phillips, and J. D. B. Smith, *J. Polym. Sci., Part A-1*, **10**, 3253 (1972).

TABLE III
UV IRRADIATION OF VCZ-ZnBr₂-ACETONE SOLUTIONS^a

Intensity of 254-nm uv, $\mu\text{A cm}^{-2}$	Time, hr	Product formation as percentage —of initial monomer—	
		TCB	Poly VCZ
30×10^3	1	8.6	2.4
30×10^3	2	61.5	1.8
30×10^3	5	99.5	0.2
16×10^3	5	73.0	<0.1
10×10^3	5	55.0	<0.1

^a VCZ:ZnBr₂ = 5:1, VCZ:acetone = 40:1, under N₂.

TABLE IV
INTENSITY EXPONENT DATA FOR PHOTO- AND ELECTROINITIATED
REACTIONS OF VCZ IN ZnBr₂-ACETONE SOLUTIONS^a

System	β	α
Photodimerization	+0.52	+0.53
Electrodimerization	+1.56	-0.98
Electropolymerization	+1.92	+0.30

^a VCZ:ZnBr₂ = 5:1, VCZ:acetone = 40:1; photoirradiation 254 nm, 5 hr under N₂; electroinitiation, 2 hr, 0.05–4.0 mA cm⁻²

The intensity exponent for the photodimerization is very close to that obtained by Tazuke¹⁰ ($\alpha = 0.56$ – 0.45) in his analysis of a variety of photoinitiated VCZ polymerizations. This confirms the proposal that, in the absence of significant competing reactions, the initiation step for both photodimerization and photopolymerization is the same.

The very different data for the electroinitiated reactions must reflect the competitive processes of polymerization and cyclodimerization. The possibility of other initiation routes, however, cannot be ruled out and this will be discussed in more detail below. It should be noted that the data on the electroinitiated reaction refer only to the low current densities detailed above, *i.e.*, under conditions where both products are obtained. This analysis allows us to conclude tentatively that (a) the chemistry of the ZnBr₂-acetone-VCZ system will be similar to that of other VCZ systems since the photoinitiation results are clearly similar to those obtained by other workers on various photo VCZ systems,^{4,10} and (b) competition is occurring between the two product routes in low current density electroinitiation, *i.e.*, both products are not formed independently but arise from a common initiation process.

There are four mechanistic possibilities in the electroreaction that could explain the formation of the TCB. These follow. (1) Extraneous photochemical reaction could occur. This is a possibility considering the solvent system and the results of Tada.⁴ This likelihood was eliminated by careful exclusion of light in all stages of sample preparation and reaction. Also, the rate dependence on current density, as indicated in Table II, makes this unlikely. (2) Direct chemical catalysis could occur. This is similar to the results of Ledwith⁶ using Fe³⁺ and Cd⁴⁺. There was no significant reaction in blank solutions of the above compositions which were shielded from the light but through which no current was passed. (3) Cathodic electrolytic reaction could occur. Using the porous battery cup technique the locus of reaction was determined to be the anode. No product, TCB

or polymer, could be found at the cathode. (4) Anodic electrolytic reaction could occur. Both products were formed exclusively in the anode region. Some small filaments of product were found at the electrode with the higher current densities. Principally, however, the reaction occurred in the bulk and the product was only isolated upon extraction. Analysis of the reaction product from the anode cup indicated that a similar polymer:TCB product ratio was obtained for comparable single-cell data. The overall reaction rate was somewhat different, presumably because of diffusion rate limitations.

The role of radical cation species as the initiating activity in both VCZ polymerization and cyclodimerization has been proposed.^{2,6,10,11} Both photochemical and metal-catalyzed systems involve these intermediates. Complex formation (VCZ^{•+}+Fe^{II}X₃⁻) was proposed by Ledwith⁶ as the initial stage in the latter reaction. As we have proposed previously, for the ZnBr₂-catalyzed polymerization of VCZ at high current densities,² it is likely that donation from the basic carbazole nitrogen to the zinc salt (Lewis acid) occurs to give a complex. Similar complexes have been isolated for the analogous ZnBr₂-vinylimidazole system.¹² It was shown that conjugation of the vinyl unsaturation with the heteroaromatic ring occurs. The evidence for the existence of these complexes is discussed in more detail elsewhere.⁷

The formation of these charge-transfer donor-acceptor (D-A) complexes has been shown by Gaylord¹³ to be a very useful method for inducing reaction. Funt¹⁴ has further shown that such D-A complexes are readily susceptible to electrolytic reaction, although the exact nature of the electrode process is not known. The result of this process when applied to our system is the formation of a VCZ radical cation stabilized by a VCZ-metal salt radical anion system. The radical cation (VCZ^{•+}) results in either polymerization or cyclic dimerization. It is well established that the polymerization is a consequence of the cation function of this species.^{2,7} However, if the concentration of neutral VCZ molecules is high enough it is possible that they interact with VCZ^{•+} in the fashion proposed by Ledwith for chemical catalysis.⁶ The result is radical cyclic dimerization to give TCB, as was found in the chemical catalytic system. This mechanistic path can explain the unusual features of the results detailed above. At low current densities, the concentration of neutral VCZ molecules is high. The reaction path leading to TCB is therefore likely. However, at the higher current densities the concentration of available neutral VCZ molecules is significantly depleted relative to the electrode-produced radical cation. Therefore, the alternative, competitive, cationic polymerization is more likely. Similarly, the higher the VCZ monomer concentration, relative to ZnBr₂, the more likely is the process leading to cyclic dimerization, as was found. This mechanism, however, assumes that similar initiating species are produced at the electrode at both extremes of the range

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(12) S. Tazuke and S. Okamura, *J. Polym. Sci., Part A-1*, 7, 851 (1969).

(13) N. G. Gaylord and A. Takahashi, *Advan. Chem. Ser.*, 91, 94 (1969).

(14) B. L. Funt, I. McGregor, and J. Tanner, *J. Polym. Sci., Part B*, 8, 699 (1970).

(10) M. Asai, K. Kameoka, Y. Takeda, and S. Tazuke, *J. Polym. Sci., Part B*, 9, 247 (1971).

of current densities. Albeck, *et al.*,¹⁵ examined the electrode reaction potential, as a function of current density, for lithium acetate-methanol-acrylate systems. They found that changes in current density (0.2–1.6 mA cm⁻²) could more than double the electrode reaction potential. It is therefore feasible that alternative initiating species (possibly dications) are produced at the different current densities and that product formation is a function of this phenomenon rather than of monomer depletion.

Registry No.—VCZ, 1484-13-5; TCB, 1484-96-4.

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The Interception of Transitory 1-Azirines with Cyclopentadienones during the Thermal Decomposition of Certain Vinyl Azides. Formation of 3*H*-Azepines¹

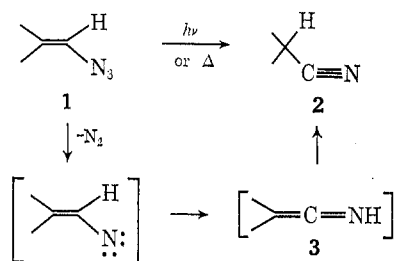
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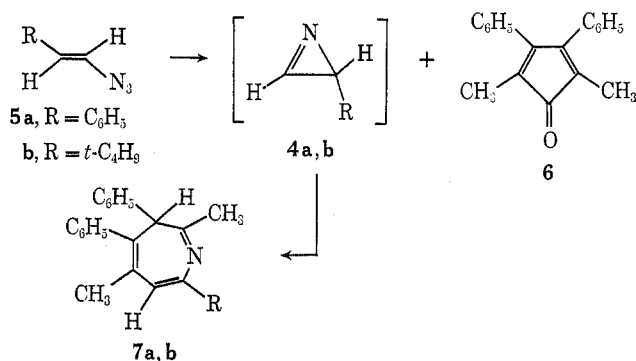
We have recently described the formation² of azepines from 1-azirines and cyclopentadienones, and discussed the mechanistic implications.³ We now demonstrate the effectiveness of cyclopentadienones as a general reaction, to intercept (in a Diels-Alder fashion) 1-azirines possessing only a fleeting existence, formed during the thermolysis of particular vinyl azides.

When terminal vinyl azides **1** are decomposed, frequently the major product is the nitrile **2** believed⁴ to be formed *via* the vinyl nitrene and ketenimine **3**.

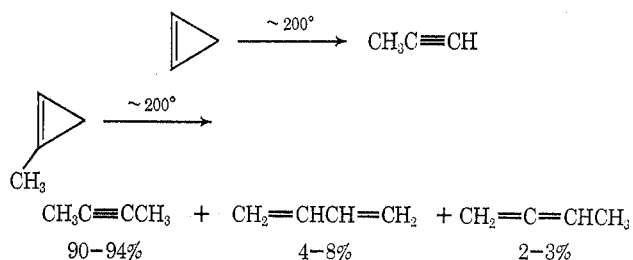


However, spectroscopic and chemical evidence⁵ have indicated the presence of 1-azirines **4** in these reactions. Indeed, one such azirine, unsubstituted on carbon 2, has been isolated⁶ and found to rearrange to both nitrile and isonitrile.

When the terminal vinyl azides **5a** and **5b** were decomposed in refluxing toluene in the presence of the cyclone **6**, the appropriate 3*H*-azepines **7a** and **7b** were isolated in high yield. It is apparent, therefore, that azirines **4** are formed in the thermal decomposition of **5**

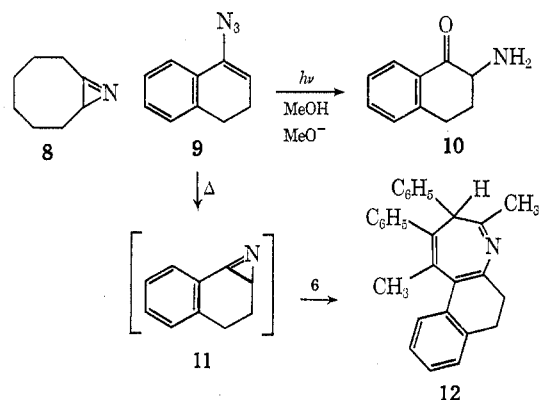


and hence are intermediates in the formation of nitriles and ketenimines. By analogy, cyclopropene rearranges thermally⁷ to 1-propyne, and 1-methylcyclopropene affords 2-butyne, butadiene, and methyl allene.



The structures of azepines **7** were inferred from their nmr and mass spectra in analogy to previous cases.^{2,3}

1-Azirines fused to eight-membered rings, for example **8**, have been prepared⁸ from the appropriate vinyl azides. However, decomposition of the six-membered ring vinyl azide **9** alone produced polymeric material. Photochemical decomposition of **9** in methanol, in the presence of methoxide, did produce the amino ketone **10**, suggesting the intermediacy of the fused azirine **11**. When **9** was allowed to decompose in refluxing toluene in the presence of the cyclone **6**, the 3*H*-azepine **12** was



formed together with much polymeric material, thus inferring the fused azirine **11** as an intermediate.

The decomposition of β -azidoacrylophenone (**13**) has led⁹ to the formation of the isoxazole **14** and benzoyl-acetonitrile (**15**). We were unable to trap the possible

(1) Cycloadditions. XIII. For previous paper in the series see J. Rasmussen and A. Hassner, *J. Org. Chem.*, **38**, 2114 (1973).

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