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.

[15] M. Albeck, M. Konigsbuch, and J. Relis, *J. Polym. Sci., Part A-1*, **9**, 1375 (1971).

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

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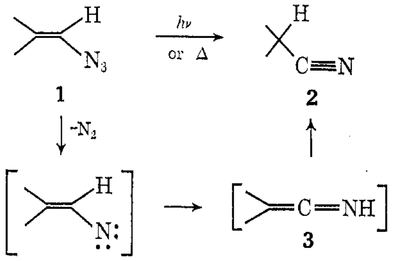
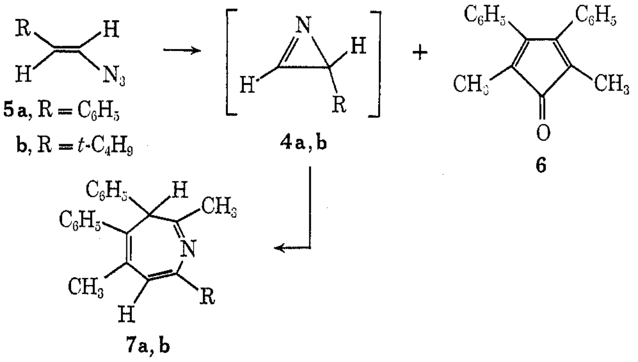
We have recently described the formation[2] of azepines from 1-azirines and cyclopentadienones, and discussed the mechanistic implications.[3] We now demonstrate the effectiveness of cyclopentadienones as a general reaction, to intercept (in a Diels–Alder fashion) 1-azirines possessing only a fleeting existence, formed during the thermolysis of particular vinyl azides.

When terminal vinyl azides **1** are decomposed, frequently the major product is the nitrile **2** believed[4] to be formed *via* the vinyl nitrene and ketenimine **3**.

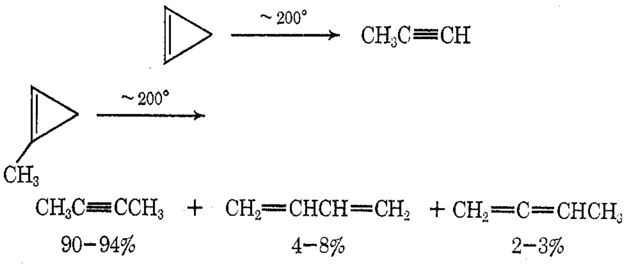


However, spectroscopic and chemical evidence[5] have indicated the presence of 1-azirines **4** in these reactions. Indeed, one such azirine, unsubstituted on carbon 2, has been isolated[6] and found to rearrange to both nitrile and isonitrile.

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**

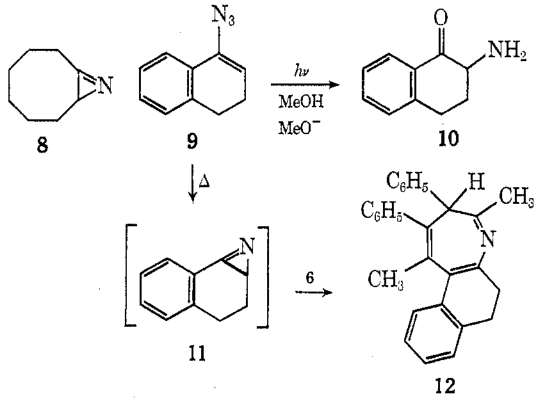


and hence are intermediates in the formation of nitriles and ketenimines. By analogy, cyclopropene rearranges thermally[7] to 1-propyne, and 1-methylcyclopropene affords 2-butyne, butadiene, and methyl allene.



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 prepared[8] 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 led[9] to the formation of the isoxazole **14** and benzoylacetonitrile (**15**). We were unable to trap the possible

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

[2] D. J. Anderson and A. Hassner, *J. Amer. Chem. Soc.*, **93**, 4339 (1971).

[3] A. Hassner and D. J. Anderson, *ibid.*, **94**, 8255 (1972).

[4] J. H. Boyer, W. E. Krueger, and G. J. Mikol, *ibid.*, **89**, 5504 (1967).

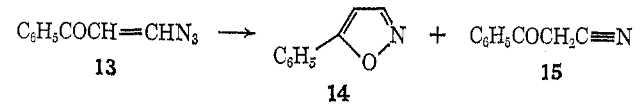
[5] K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Lett.*, 3499 (1968); A. Hassner and A. B. Levy, *J. Amer. Chem. Soc.*, **93**, 5469 (1971).

[6] W. Bauer and K. Hafner, *Angew. Chem., Int. Ed. Engl.*, **8**, 772 (1969).

[7] R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 6250 (1969).

[8] A. Hassner and F. W. Fowler, *ibid.*, **90**, 2869 (1968).

[9] S. Sato, *Bull. Chem. Soc. Jap.*, **41**, 2524 (1968).



1-azirine intermediate in this reaction, using the cyclone **6** in refluxing chloroform or benzene. In fact the reaction path of **13** → **14** + **15** was completely unaltered by addition of **6**.

It is noteworthy that the *in situ* generation of the azirines lacking a 2 substituent, from the terminal vinyl azides **5a** and **5b**, produces species with greatly enhanced dienophilic properties when compared to those possessing a 2 substituent.[2,3] Details of this enhanced property will shortly be revealed.

Experimental Section[10]

Reaction of Cyclone 6 and 1-Azido-2-phenylethylene (5a).—The vinyl azide (0.8 g, 5.5 mmol) and the dienone (1.4 g, 5.5 mmol) were heated under reflux in toluene (25 ml) for 2 hr. Removal of the solvent yielded an orange oil, which rapidly solidified (1.30 g, 69%). Recrystallization from ethanol gave colorless needles of **2,5-dimethyl-3,4,7-triphenyl-3*H*-azepine (7a)**: mp 108°; τ ($CDCl_3$) 7.91 (s, 3 H), 7.72 (s, 3 H), 4.59 (s, 1 H), 3.87 (s, 1 H), 2.94–2.45 (m, 15 H); mass spectrum *m/e* (rel intensity) 350 (25), 349 (100), 348 (52), 334 (10), 308 (20), 293 (12), 272 (11), 246 (8), 231 (8), 229 (9), 215 (34), 115 (7) 91 (13).

Anal. Calcd for $C_{28}H_{23}N$: C, 89.4; H, 6.6. Found: C, 89.1; H, 6.8.

Reaction of Cyclone 6 and 1-Azido-2-*tert*-butylethylene (5b).—The vinyl azide (1.25 g, 10 mmol) and the dienone (2.60 g, 10 mmol) were heated under reflux in toluene (25 ml) for 5 hr. Removal of the solvent afforded an orange oil. Chromatography using dichloromethane–pentane (1:4) eluent afforded a pale yellow oil which solidified (2.35 g, 71%) on trituration. Recrystallization from ethanol afforded large, pale yellow crystals of **7-*tert*-butyl-2,5-dimethyl-3,4-diphenyl-3H-azepine (7b)**: mp 97°; nmr ($CDCl_3$) τ 9.14 (s, 9 H), 7.97 (s, 3 H), 7.72 (s, 3 H), 4.74 (s, 1 H), 4.20 (s, 1 H), 2.89 (s, 5 H), 2.65 (s, 5 H); mass spectrum *m/e* (rel intensity) 330 (25), 329 (100), 328 (25), 314 (55), 287 (27), 273 (50), 258 (77), 257 (58), 246 (30), 231 (25), 215 (20), 91 (17).

Anal. Calcd for $C_{24}H_{27}N$: C, 87.5; H, 8.3. Found: C, 87.8; H, 8.2.

Reaction of Cyclone 6 and 4-Azido-1,2-dihydronaphthalene (9).—The vinyl azide (1.71 g, 10 mmol) and the dienone (2.60 g, 10 mmol) were heated under reflux in toluene (25 ml) for 8 hr. Removal of the solvent and chromatography of the residue (dichloromethane) afforded **2,5-dimethyl-3,4-diphenyl-1,2-dihydronaphtho[3,4-*f*]-3*H*-azepine (12)**[11] (1.2 g, 32%) as golden plates from ethanol: mp 163°; nmr ($CDCl_3$) τ 8.04 (s, 3 H), 7.68 (s, 3 H), 8.35–6.55 (m, 4 H), 4.92 (s, 1 H), 3.15–2.56 (m, 14 H); mass spectrum *m/e* (rel intensity) 376 (32), 375 (100), 374 (44), 360 (12), 284 (60), 178 (10), 115 (7), 91 (17).

Anal. Calcd for $C_{28}H_{25}N$: C, 89.6; H, 6.7. Found: C, 89.8; H, 6.8.

Ethyl acetate–dichloromethane (1:19) eluted unreacted dienone (1.5 g, 58%). Use of a threefold excess of the vinyl azide gave **12** in 45% yield.

Registry No.—**5a,** 16722-99-9; **5b,** 40168-86-3; **6,** 26307-17-5; **7a,** 40168-88-5; **7b,** 40168-89-6; **9,** 16719-58-7; **12,** 40168-91-0.

Acknowledgment.—Support of this work by a grant from NSF is gratefully acknowledged.

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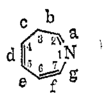
[10] All melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 457 spectrophotometer as KBr pellets. Nmr spectra were recorded with a Varian A-60A spectrometer using tetramethylsilane as an internal standard. The elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

[11] Since the numbering of the azepine system is not completely systematic,[12] the lettering system adopted in this paper follows the numbers shown.



3 H

[12] L. A. Paquette in "Nonbenzenoid Aromatics," Vol. 1, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, p 249.

Nitrogen Photochemistry. XIII. The Deoxygenation of Aniline and Naphthylamine *N*-Oxides

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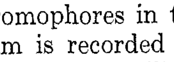
Received September 11, 1972

We are studying various aniline and naphthylamine *N*-oxide derivatives as potential sources of atomic oxygen in the liquid phase since these *N*-oxides are expected not to rearrange in contrast to the well-studied *N*-oxides where the nitrogen is part of the aromatic ring. It is important that a distinction be made between the amine oxide photochemistry described in this article, *e.g.*, of **1**, and that of the aromatic *N*-oxides such as **2**. Only the latter has been extensively studied. The former has a benzene chromophore and the latter a pyridine chromophore. *N*-Oxides such as **2** rearrange and undergo α cleavages on irradiation,[1–5] whereas we now wish to demonstrate that the excited state of **1** leads almost exclusively to β cleavages and, importantly, with little rearrangement. The nomenclature is that defined on structure **3**.[6] This article contains the descriptive work on aniline and naphthylamine *N*-oxide photochemistry.



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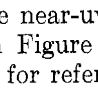

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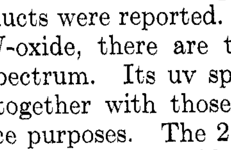

3

Previously Jerina, Boyd, and Daly[7] irradiated *N*,*N*-dimethylaniline *N*-oxide to gain deuterium retention data during the photochemical hydroxylation of 4-deuterioanisole and demonstrated that an undefined oxygen species was transferred to anisole forming *p*-hydroxyanisole. No other products were reported.

With *N*,*N*-dimethylaniline *N*-oxide, there are two chromophores in the near-uv spectrum. Its uv spectrum is recorded in Figure 1 together with those of benzene and aniline for reference purposes. The 260-nm chromophore of *N*,*N*-dimethylaniline *N*-oxide is essentially the π,π^* transition of benzene with slight modification for the functional group. This is expected because the parent amine *N*-oxide chromophore,

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[1] J. Streith, B. Danner, and C. Sigwalt, *Chem. Commun.*, 979 (1967).

[2] T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Lett.*, 2213 (1970).

[3] H. Igeta, T. Tsuchiya, M. Yamada, and H. Arai, *Chem. Pharm. Bull.*, **16**, 767 (1968).

[4] T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Lett.*, 2747 (1969).

[5] M. Ogata and K. Kano, *Chem. Commun.*, 1176 (1967).

[6] V. I. Stenberg and D. R. Dutton, *Tetrahedron*, **28**, 4635 (1972). This article is regarded as part XII of this series.

[7] D. M. Jerina, D. R. Boyd, and J. W. Daly, *Tetrahedron Lett.*, 457 (1970).