The Synthesis and Photoisomerization of Homo-1H-azepine Derivatives[1,2]

LEO A. PAQUETTE AND ROBERT J. HALUSKA[3]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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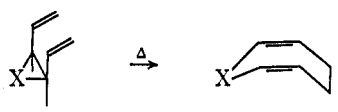
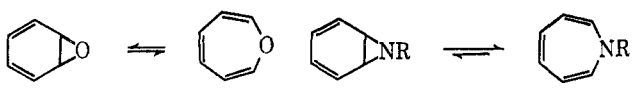
The reaction of cycloheptatriene with methoxycarbonylnitrene has been found to afford 2,3- and 4,5-homo-1H-azepines **4** and **5** in a combined yield of 35% and in a ratio of 2.2:1. The homo-1H-azepines most likely result from valence-bond rearrangement of initially formed methoxycarbonylaziridines. Irradiation of **4** with an unfiltered mercury arc has been found to give 5-carbomethoxy-5-aza-1α,2α,4α,6α-tricyclo[4.2.0.0^{2,4}]oct-7-ene and 2-carbomethoxy-2-azabicyclo[3.3.0]octa-3,6-diene. This photochemical reaction presumably occurs from the $\pi \rightarrow \pi^*$ singlet manifold of **4**. The relationship of the excited-state behavior of **4** to related structures is discussed.

The facility with which the thermal valence isomerization of *cis*-divinyl substituted three-membered rings occurs is now recognized to decrease in the order carbon

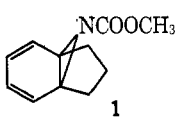


> nitrogen > oxygen > sulfur, with a sizable gap existing between carbon and nitrogen on the one hand, and oxygen and sulfur on the other. This widely differing thermal stability is revealed by the findings that *cis*-2,3-divinylcyclopropane[4,5] and aziridine[6] rearrange as rapidly as they are formed, even at low temperatures, whereas the oxygen[7] and sulfur[6] analogs rearrange at 60 and 100°, respectively.

Similar differences in valence tautomeric equilibria separate the 1H-azepine and oxepin groups.[8] Thus, while most oxepins exist in mobile equilibrium with their arene oxide forms,[9] the only authentic azanorcaradiene known at this time is **1**,[10] the 1H-azepine tautomers being greatly preferred in the absence of such a constraining annelation effect of the trimethylene bridge. As a result, oxepins react almost exclusively as



arene oxides,[11] while azepines undergo chemical transformations in the monocyclic triene form.[12]



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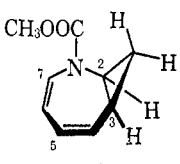
2 **3**

Other than **1**, the adduct (**2**) of ethoxycarbonylnitrene and cyclooctatetraene is the only other example of a *cis*-2,3-divinylaziridine which is stable at room temperature.[13] At 80°, **2** rearranges to **3**. The comparatively greater thermal stability of **2** may be steric in origin or may possibly be due to secondary orbital interactions (with the $\Delta^{4,5}$ bond) which would render the direct conversion of **2** into **3** a symmetry-disallowed process.[14]

The purpose of the present study was to examine the reaction of cycloheptatriene with methoxycarbonylnitrene for the twofold purpose of obtaining information on valence-bond rearrangements of the expected aziridines and making available homo-1H-azepines for further investigation.[15,16]

When a 7% solution of methyl azidoformate in cycloheptatriene was heated in a sealed tube at 127–128° for 4 hr, there was obtained, after recovery of the excess hydrocarbon, a mixture of nitrene insertion products. Careful distillation of this mixture afforded **4** and **5** in a combined yield of 35%. The ratio of **4** to **5**



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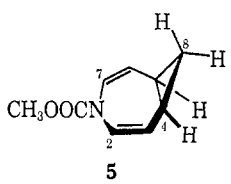

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was 2.2:1 (vpc analysis). Final separation was achieved by preparative-scale gas chromatography.

Homoazepine **4** was obtained as a pale yellow liquid exhibiting infrared bands (film) at 1730, 1655, and 1635 cm^{-1} and ultraviolet absorption (ethanol) at 262 nm (ϵ 8430). The nmr spectrum of this substance ($CDCl_3$) shows a doublet (J = 9.5 Hz) at δ 6.65 attributable to H-7 and three doublets of doublets centered at δ 6.12 (H-4, J = 11.1 and 3.1 Hz), 5.66 (H-5, J = 11.1 and

(1) Unsaturated Heterocyclic Systems. LXIV. For the previous paper in this series, see L. A. Paquette and G. R. Krow, *J. Amer. Chem. Soc.*, **91**, 6107 (1969).

(2) This work was supported in part by the National Institutes of Health, Grant GM 14853.

(3) National Institutes of Health Predoctoral Fellow, 1966–1969.

(4) E. Vogel, K. H. Oh, and K. Gajek, *Ann.*, **644**, 172 (1961).

(5) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(6) E. L. Stogryn and S. J. Brois, *J. Org. Chem.*, **30**, 88 (1965).

(7) E. L. Stogryn, M. H. Gianni, and A. J. Passanate, *ibid.*, **29**, 1275 (1964).

(8) For a recent comprehensive review of the 8-π-electron heterocycles, see L. A. Paquette in "Non-Benzenoid Aromatics," J. P. Snyder, Ed., Academic Press, New York, N. Y., in press.

(9) E. Vogel and H. Günther, *Angew. Chem.*, **79**, 429 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 385 (1967).

(10) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and R. J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969).

(11) The sole *chemical* indication of the existence of oxepins is the formation of 2-oxabicyclo[3.2.0]hepta-3,6-dienes on photolysis: (a) L. A. Paquette and J. H. Barrett, *J. Amer. Chem. Soc.*, **88**, 1718 (1966); (b) J. M. Holovka and P. D. Gardner, *ibid.*, **89**, 6390 (1967); (c) ref 9.

(12) (a) L. A. Paquette, J. H. Barrett, and D. E. Kuhla, *J. Amer. Chem. Soc.*, **91**, 3616 (1969); (b) L. A. Paquette and D. E. Kuhla, *J. Org. Chem.*, **34**, 2885 (1969); (c) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and L. M. Leichter, *ibid.*, **34**, 2888 (1969).

(13) S. Masamune and N. T. Castellucci, *Angew. Chem.*, **76**, 569 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 582 (1964).

(14) For a discussion of this point, see A. G. Anastassiou, *J. Amer. Chem. Soc.*, **90**, 1527 (1968).

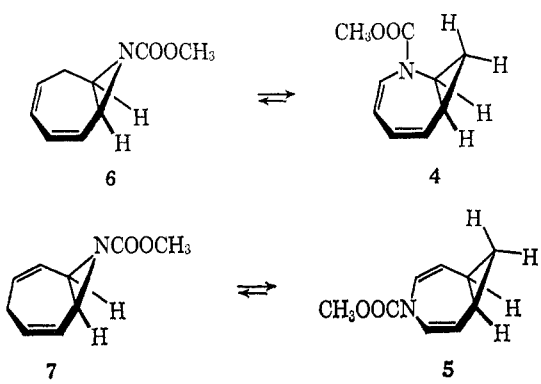
(15) A preliminary account of a portion of this work has appeared: L. A. Paquette and R. J. Haluska, *Chem. Commun.*, 1370 (1968).

(16) A recent report of an analogous nitrene reaction has also appeared: W. H. Okamura, W. H. Snider, and T. J. Katz, *Tetrahedron Lett.*, 3367 (1968).

6.6 Hz), and 5.10 (H-6, J = 9.5 and 6.6 Hz). In addition, a methoxyl singlet is displayed at δ 3.80 and three multiplets assignable to H-2 (δ 3.15), H-3 and the *anti* C-8 proton (δ 1.1–1.6), and the *syn* proton at C-8 (δ 0.1–0.4) are also seen.[17]

Homoazepine **5** was isolated as a colorless oil, with infrared bands at 1725 and 1670 cm^{-1} and ultraviolet absorption (ethanol) at 231 nm (ϵ 11,430). The nmr spectrum of **5** reveals the symmetrical nature of the structure; thus, H-2 and H-7 appear together as a doublet (J = 9.8 Hz) at δ 6.65 and H-3 and H-6 are seen as a broad doublet (J = 9.8 Hz) at δ 5.15. The remainder of the spectrum consists of a singlet at δ 3.86 due to the methoxyl group, and multiplets centered at δ 1.0–1.6 (3 H) and 0–0.3 (1 H) attributable to H-4, H-5, and the *anti* proton at C-8 on the one hand, and the *syn* proton at C-8, respectively.

The temperature-invariant nmr spectra of **4** and **5** (40–170°) attest to the fact that the internal cyclopropyl bond in these structures is not prone to delocalization or to valence-bond isomerization. If equilibria of type **6** ⇄ **4** and **7** ⇄ **5** are operative, the concentrations of **6** and **7** do not rise above the detection

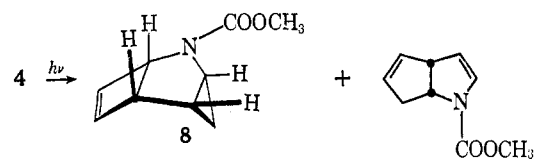


limits of the spectrometer, estimated in this instance to be *ca.* 3%. In view of the logical mechanistic conclusion that **4** and **5** result from valence-bond rearrangement of initially formed methoxycarbonylaziridine **6** and **7**, respectively,[18] it is clear that **6** and **7** exhibit a marked tendency for symmetry-allowed [1,5] sigmatropic and Cope rearrangements, respectively. The apparent irreversibility of the **7** → **5** rearrangement is in marked contrast to the ease with which bicyclo[5.1.0]-octa-2,5-diene undergoes rapidly reversible degenerate [3,3] sigmatropic change.[19] This observation clearly reveals the pronounced influence of the nitrogen substituent even when the molecules are so constructed that strain factors are closely balanced, as in **5** and **7**. The strong bias toward structures **4** and **5** may be the result of delocalization of the nitrogen electron pair which can only be made manifest in the homo azepines.

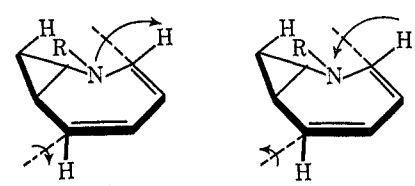
The minor products from the nitrene-insertion reaction appear to be a mixture of air-sensitive cycloheptatrienylurethans on the basis of infrared and nmr spectra. These substances have not been investigated further.

We have found homoazepines **4** and **5** to be singularly unreactive in cycloaddition reactions. For example, no cycloadducts were obtained when benzyne was generated in the presence of either homoazepine, nor when solutions of **4** containing diphenylisobenzofuran or N-phenylmaleimide were refluxed for varying periods of time.[20]

Irradiation of an ether solution containing a mixture of **4** and **5** with unfiltered light from a 200-W Hanovia mercury arc for 2.5 hr resulted in the complete disappearance of **4** and the simultaneous formation of two new products in the approximate ratio of 3:2. The 4,5 isomer (**5**) was virtually unaffected under these conditions. Separation of the various components of the photolysate was achieved by means of preparative thick layer chromatography on alumina.



The major component is an isomeric, colorless liquid displaying a strong infrared band (film) at 1710 cm^{-1} and end absorption in the ultraviolet region. In the nmr ($CDCl_3$, 100 MHz), this substance exhibits a narrow multiplet centered at δ 6.23 (2 H), a broadened doublet centered at δ 4.47 (1 H), a methoxyl singlet at δ 3.63, a broad multiplet at δ 3.15–3.48 (2 H), and three well-resolved multiplets (1 H each) at δ 1.49, 0.77, and 0.29. These spectral properties suggested the 5-carbomethoxy-5-azatricyclo[4.2.0.$0^{2,4}$]oct-7-ene structure (**8**). Although the stereochemistry of **8** was not clearly revealed by the nmr data, the 1α,2α,4α,6α configuration[21] was assigned by analogy to the high degree of stereospecificity observed in the photoinduced electrocyclizations of 2,3-homotropone[21] and homotropilidene.[22] That is to say, it is considered equally likely in the case of **4** that the concerted disrotatory cyclization is also controlled by secondary steric forces operative during the bond reorganization and that exclusive formation of **8** from **10** will occur to the exclusion of the 1β,2α,4α,6β isomer from **11** because of the adverse steric interactions which develop between the two terminal vinyl and the *endo*-cyclopropyl hydrogens in the latter transition state.



The less abundant $C_9H_{11}NO_2$ photoproduct is a colorless liquid which displays intense infrared absorption (film) at 1720, 1630, and 1610 cm^{-1} and ultraviolet

(17) Assignments of the *exo* and *endo* protons at C-8 are founded chiefly on the work of J. G. Traynham, J. S. Dehn, and E. E. Green, *J. Org. Chem.*, **33**, 2587 (1968).

(18) This assumption receives further confirmation from the fact that **4** is produced in a statistically related twofold greater yield than **5**.

(19) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(20) The structurally related ketone 2,3-homotropone is known to be capable of Diels–Alder reactivity: L. A. Paquette and O. Cox, *Chem. Ind.* (London), 1748 (1967).

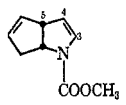
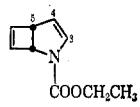
(21) For an explanation of this α and β convention, refer to footnote 24 in L. A. Paquette and O. Cox, *J. Amer. Chem. Soc.*, **89**, 5633 (1967).

(22) W. R. Roth and B. Peltzer, *Ann.*, **685**, 56 (1965).

absorption (ethanol) at 233 nm (ϵ 11,500).[23] In the nmr ($CDCl_3$, 60 MHz), it exhibits a broad doublet centered at δ 6.54 (1 H), a two-proton singlet at δ 5.68, a doublet of doublets (J = 4.5 and 2.5 Hz) centered at δ 5.09, three broad multiplets at δ 4.45–4.9 (1 H), 3.9–4.2 (1 H), and 2.25–3.2 (2 H), and a sharp methoxyl singlet at δ 3.74. These spectral data clearly accommodate structure **9** and not an isomeric 2-azabicyclo[3.3.0]-octadiene, particularly when direct comparison is made with the nmr spectrum of 2-carbethoxy-2-azabicyclo-[3.2.0]hepta-3,6-diene (Table I).

TABLE I

NMR CHEMICAL SHIFT DATA FOR 9 AND 2-CARBETHOXY-2-AZABICYCLO[3.2.0]HEPTA-3,6-DIENE[a]

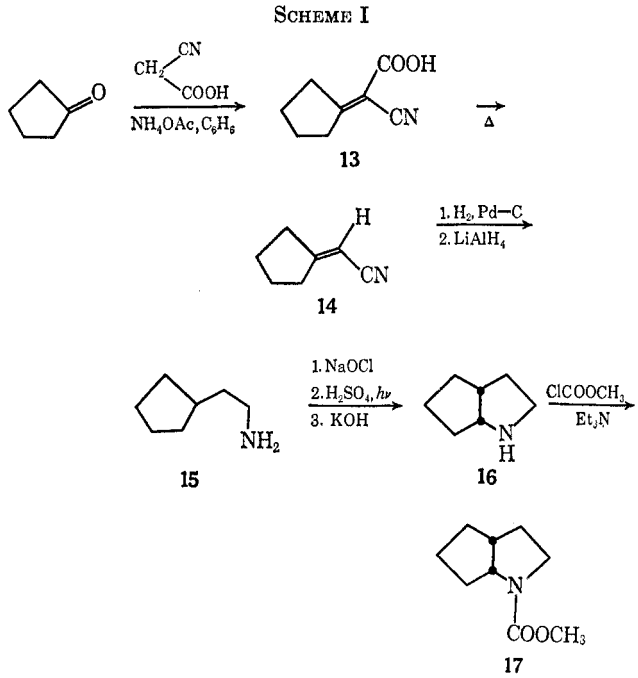



Proton	9	12
H-1	4.74	4.88
H-3	6.54	6.56
H-4	5.09	5.18
H-5	3.9–4.2	3.88

[a] In parts per million (δ) ($CDCl_3$). The values for **12** are taken from ref 23a.

Chemical confirmation of this assignment was derived from catalytic hydrogenation of **9**, which proceeded with the uptake of 2 mol of hydrogen to give 2-carbomethoxy-2-azabicyclo[3.3.0]octane (**17**). The unequivocal independent synthesis of **17** is shown in Scheme I.

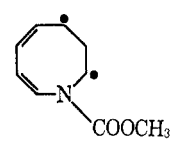
SCHEME I



Cyclization of cyclopentylethylamine (**15**) to *cis*-2-azabicyclo[3.3.0]nonane (**16**) was effected by means of the Hofmann–Löffler–Freytag reaction.[24] In 1966, Schmitz and Murawski reported the first successful cyclization of a primary amine by this method.[25] These workers contended that the undesirable disproportionation of primary chloramines which occurs in weakly acidic solution is the result of a reaction between a protonated and an unprotonated species. The recommendation was made that concentrated sulfuric acid rather than the usual 80–85% variety be employed to prevent this side reaction. In the case of **15**, however, the use of concentrated sulfuric acid and ferrous ammonium sulfate resulted only in tar formation, whereas the milder conditions and light afforded **16** in 30% yield.

Because photochemically induced vinylcyclopropane rearrangements of the type involved in the conversion of **4** into **9** have been only infrequently encountered,[26] we considered it imperative to demonstrate that **9** did not arise by an extraneous thermal process. This is seen from the following facts: (a) **4**, **5**, and **8** are entirely stable to the vpc conditions used to monitor the progress of the photoreaction; (b) both **8** and **9** are seen to be present (nmr and tlc analysis) in the crude photolysate prior to any exposure to elevated temperatures.

With regard to the multiplicity of the photorearrangement of **4**, the inability of acetone to sensitize the reaction denotes that, under the conditions of direct irradiation, $\pi \rightarrow \pi^*$ singlet states are involved. It is interesting and perhaps significant that [1,3] sigmatropic rearrangement of the internal cyclopropyl bond in **4** to give **18** can compete effectively with cyclobutene-



18

ring formation (*i.e.*, **8**), particularly since analogous products do not result from 2,3-homotropone[21] or homotropilidene,[22] but only from their dihydro counterparts.[26]

Experimental Section[27]

Reaction of Cycloheptatriene with Methyl Azidoformate.—A 7% solution of methyl azidoformate in cycloheptatriene in a thick-walled sealed tube was immersed in an oil bath preheated to 127–128°, where it was maintained for 4 hr. Removal of excess hydrocarbon *in vacuo* followed by preparative-scale gas chromatography (5 ft × 0.25 in. Al column packed with 20% SE-30 on 60–80 mesh Chromosorb W) and molecular distillation permitted separation of three fractions.

The first substance to be eluted was 2,3-homo-1H-azepine **4**.

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.16; H, 6.74; N, 8.48.

The second component was 4,5-homo-1H-azepine **5**.

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.84. Found: C, 65.60; H, 7.11; N, 8.26.

On the basis of infrared and nmr spectra, the third fraction was seen to contain a mixture of cycloheptatrienyl urethanes, which were not further characterized.

Photoisomerization of 4.—A solution of 2.33 g of a mixture of **4** and **5** in a ratio of *ca.* 3:1 in 450 ml of ether was irradiated under nitrogen for 2.5 hr with a 200-W Hanovia lamp in a standard

(23) Such ultraviolet absorption is characteristic of the enamide chromophore: (a) L. A. Paquette and J. H. Barrett, *J. Amer. Chem. Soc.*, **88**, 1718 (1966); (b) R. H. Mazur, *J. Org. Chem.*, **26**, 1289 (1961).

(24) M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).

(25) E. Schmitz and D. Murawski, *Chem. Ber.*, **99**, 1493 (1966).

(26) L. A. Paquette, G. V. Meehan, and R. F. Eizember, *Tetrahedron Lett.*, 995, 999 (1969).

(27) The microanalyses were determined by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The nmr spectra were determined with Varian A-60 or HA-100 spectrometers. Infrared spectra were obtained with a Perkin-Elmer 237 Infracord spectrometer and ultraviolet measurements were made with a Cary Model 14 recording spectrometer. Melting points are corrected while boiling points are uncorrected.

quartz immersion vessel. The progress of the reaction was monitored at 0.5-hr intervals by vpc (160°, 12 ft × 0.25 in. Al column packed with 10% SE-30 on 60–80 mesh Chromosorb G). Solvent removal afforded 2.25 g of orange oil. Preparative-scale thick layer chromatography allowed the separation and isolation of photoproducts **8** and **9** from unchanged **5**. Final purification was achieved by preparative vpc on the above column and molecular distillation.

The major phosoisomer was identified as 5-carbomethoxy-5-aza-1α,2α,4α,6α-tricyclo[4.2.0.0^{2,4}]oct-7-ene (**8**).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.34; H, 6.71; N, 8.30.

The minor photoisomer was identified as 2-carbomethoxy-2-azabicyclo[3.3.0]octa-3,6-diene (**9**).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.07; H, 6.66; N, 8.30.

Cyclopentylethylamine (15).—This amine was prepared by a modification of the procedure of Protiva, *et al.*[28] Heating a solution of 50 g (0.59 mol) of cyclopentanone, 50 g (0.59 mol) of cyanoacetic acid, and 2 g of ammonium acetate in 50 ml of benzene for 7 hr at a bath temperature of 155° with continuous removal of water gave 84 g (94.4%) of **13**, mp 129–133° dec, from water (lit.[28] mp 125–128°). Decarboxylation of 40 g (0.265 mol) of unrecrystallized **13** at 180° gave 21.8 g (77.8%) of **14** as a clear, colorless liquid, bp 82–85° (14 mm), which, when hydrogenated in 150 ml of methanol over 5% palladium on charcoal, afforded 18.3 g (83%) of cyclopentylacetonitrile, bp 91–92.5° (26 mm) [lit.[28] bp 88° (27 mm)]. Reduction of 10.93 g (0.10 mol) of this nitrile with 4.42 g (0.116 mol) of lithium aluminum hydride in 200 ml of anhydrous ether yielded 10.75 g (95%) of **15**, bp 83–84° (45 mm).

***cis*-2-Azabicyclo[3.3.0]nonane (16).**—A 3.77-g sample (33.3 mequiv) of **15** was added to 40 ml of a stirred, ice-cold, 0.82 *M* sodium hypochlorite solution (32.8 mequiv), and the mixture immediately became cloudy. After an additional 15 min, the stirring was stopped and two layers separated. A drop of the upper layer gave a positive test for N-chloramine with sodium iodide. This mixture was extracted with pentane (four 25-ml portions), the pentane extract was added dropwise during 15 min with stirring to 40 ml of cold 80% sulfuric acid, and the whole was stirred vigorously for an additional 15 min. The opalescent acid layer was separated and irradiated in a quartz tube with a bank of nine 15-W germicidal lamps for 10 min. At this point, the solution gave a negative sodium iodide test. It was poured onto 200 g of ice and, with ice cooling, the solution was rendered highly alkaline by the addition of potassium hydroxide pellets at such a rate that the temperature never rose above 20°.

The alkaline solution was then decanted from the precipitated salts and extracted with ether (six 100-ml portions). The combined organic layers were dried and evaporated and the residue was distilled to give 1.26 g (29.4%) of **16** as a clear, colorless liquid, bp 82–85° (44 mm).[29]

2-Carbomethoxy-2-azabicyclo[3.3.0]octane (17). A. Hydrogenation of 9.—A solution of 80 mg of **9** in 15 ml of anhydrous THF was hydrogenated over Adams catalyst at 50 psig. Filtration followed by solvent removal gave 84 mg of pale yellow oil. Isolation of purified product (82%) by preparative vpc gave a colorless liquid, ν_{max}^{film} 1700 cm^{-1}.

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.71; H, 9.14; N, 8.21.

B. Carbomethoxylation of 16.—A solution of 933 mg (9.88 mmol) of methyl chloroformate in 10 ml of dry ether was added dropwise to a stirred, ice-cold solution of 1.095 g (9.85 mmol) of **16** and 1.196 g (11.82 mmol) of triethylamine in 25 ml of the same solvent. After completion of the addition, the stirred mixture was allowed to warm to room temperature during 1 hr. Water (10 ml) was added and the ether layer was separated, dried, and evaporated. A small sample of this material, when purified by preparative vpc, was identical in all respects with the sample prepared above.

Registry No.—**4**, 22140-42-7; **5**, 22140-43-8; **8**, 22139-35-1; **9**, 22139-36-2; **12**, 20628-99-3; **14**, 5732-88-7; **15**, 5763-55-3; **16**, 2030-37-7; **17**, 22139-39-5.

(28) M. Protiva, V. Mychajlyszyn, and J. O. Jilek, *Chem. Listy*, **49**, 1045 (1955); *Chem. Abstr.*, **50**, 3476 (1956).

(29) H. Booth, F. E. King, K. G. Mason, J. Parrick, and R. L. St. D. Whitehead [*J. Chem. Soc.*, 1050 (1959)] have reported the preparation of **16**, bp 161° (764 mm). We have been unsuccessful in repeating that portion of their scheme which involves the reductive cyclization of ethyl 2-hydroxyiminocyclopentylacetate.

Pyrolysis of 2-Pyrone, Coumarin, and 2-Pyridone

D. A. BRENT,[1] J. D. HRIBAR, AND D. C. DEJONGH[2]

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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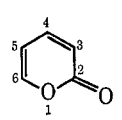
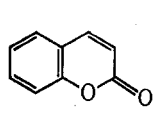
2-Pyrone (**1**), coumarin (**2**), and 2-pyridone (**3**) were pyrolyzed at 900–1000° in a stream of nitrogen (2–6 mm). The products from **1** are furan (15%), propyne (44%), and allene (4.5%); coumarin gives benzofuran (82%). Products resulting from decarbonylation are isolated from the pyrolysis of 2-pyridone: crotononitrile, isocrotononitrile, pyrrole, and 3-butenenitrile. These results are compared with the mass spectra of **1–3** and discussed in terms of possible electronic relationships between the electron-impact and pyrolytic reactions.

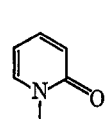
Mass spectrometric reactions of 2-pyrone (**1**), coumarin (**2**), and 2-pyridone (**3**) have received considerable attention.[3-12] In particular, the assignments



1



2



3

of structure to the cations formed by decarbonylation of the molecular ions from **1–3** have been controversial. Since similarities are found between the fragmentations of these ($M\cdot^+ - CO$) ions and the molecular ions of furan, pyrrole, and benzofuran, the ($M\cdot^+ - CO$) ions from **1–3** have been assigned furan- and pyrrolelike structures.[5,7,8,11] Other data have been interpreted to be inconsistent with these assignments.[6,9,10,12]

While the electron-impact reactions of **1–3** have received considerable attention, their pyrolytic reactions have been neglected. One pyrolysis study was

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(2) Alfred P. Sloan Research Fellow, 1967–1969.

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