

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

Anal. Calcd for C₉H₁₁NO₂: 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 C₉H₁₁NO₂: 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 cyclopentylacetone, 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, $\nu_{\text{max}}^{\text{film}}$ 1700 cm⁻¹.

Anal. Calcd for C₉H₁₁NO₂: 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.

(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.

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

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

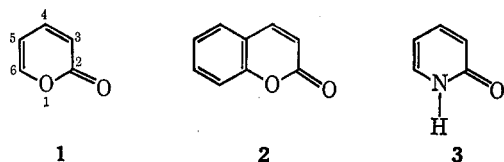
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2-Pyrone (**1**), coumarin (**2**), and 2-pyridone (**3**) were pyrolyzed at 900–1000° in a stream of nitrogen (2–6 mm). The products from **1** are furan (15%), propyne (44%), and allene (4.5%); coumarin gives benzofuran (82%). Products resulting from decarbonylation are isolated from the pyrolysis of 2-pyridone: crotonitrile, isocrotonitrile, pyrrole, and 3-butenitrile. 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) F. Knoller Predoctoral Fellow, 1968–1969.
 (2) Alfred P. Sloan Research Fellow, 1967–1969.
 (3) A. M. Duffield, C. Djerassi, G. Schroll, and S.-O. Lawesson, *Acta Chem. Scand.*, **20**, 361 (1966).
 (4) P. Brown and M. M. Green, *J. Org. Chem.*, **32**, 1681 (1967).
 (5) C. S. Barnes and J. L. Occolowitz, *Aust. J. Chem.*, **17**, 975 (1964).
 (6) W. H. Pirkle, *J. Amer. Chem. Soc.*, **87**, 3022 (1965).
 (7) H. Nakata, Y. Hirata, and A. Tatsumatsu, *Tetrahedron Lett.*, 123 (1965).

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⁺ – CO) ions and the molecular ions of furan, pyrrole, and benzofuran, the (M⁺ – 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

- (8) H. Nakata and A. Tatsumatsu, *ibid.*, 4101 (1967).
 (9) M. M. Bursey and L. R. Dusold, *Chem. Commun.*, 712 (1967).
 (10) W. H. Pirkle and M. Dines, *J. Amer. Chem. Soc.*, **90**, 2318 (1968).
 (11) G. Spiteller and M. Spiteller-Friedmann, *Monatsh. Chem.*, **98**, 1395 (1962).
 (12) W. T. Pike and F. W. McLafferty, *J. Amer. Chem. Soc.*, **89**, 5954 (1967).

reported in 1930; Orlov and Tishchenko pyrolyzed coumarin in the vapor phase through a 2 × 60 cm tinned iron tube, obtaining benzofuran in a 55% yield (based on unrecovered starting material).¹³ We have investigated the pyrolyses of 1–3 in order to compare these reactions with the electron-impact reactions; our results are reported in this article.

Experimental Section

Physical Measurements.—Indices of refraction were determined with a Bausch and Lomb (Abbe) refractometer. Infrared spectra were recorded with a Perkin-Elmer Infracord. Nmr spectra were measured on a Varian A60-A spectrometer, using CDCl₃ or CCl₄ as solvents and TMS as an internal standard. Mass spectra were determined using an Atlas CH4 mass spectrometer equipped with a high-temperature inlet system. All gas chromatographic (glpc) work was carried out with a Hewlett-Packard 5750 research chromatograph with a thermal conductivity detector. The column used was a 12 ft × 0.25 in. copper tube containing 10% Carbowax 20M on Chromosorb W, 60–80 mesh.

Chemicals.—2-Pyrone-5-carboxylic acid, 2-pyridone, and coumarin were obtained from Chemical Procurement Laboratories. Their purities were checked by glpc, nmr spectroscopy, and mass spectrometry. These chemicals were not further purified prior to use. 2-Pyrone was prepared by pyrolysis of 2-pyrone-5-carboxylic acid.¹⁴ The purity was checked by glpc, nmr spectroscopy, and mass spectrometry.

Pyrolysis Apparatus.—A dry stream of nitrogen is passed over the sample contained in a distilling flask. The nitrogen flow is monitored by a rotometer placed before the distilling flask. The flask is connected by ground glass joints to a 27 × 1 in. (id) hollow quartz tube. A 12-in. Hoskin electric furnace surrounds the tube and is 3–4 in. above the distilling flask. The temperature of the furnace is controlled and read on a Thermolyne Corporation Tempcometer. (The temperature reported is approximately that of the internal portion of the quartz tube in the center of the oven.) A cold finger and/or a variety of gas traps are placed between the quartz tube and a vacuum pump. A manometer and/or McLeod gauge placed before the pump is used to read the pressure of the system. The space between the flask and furnace is heated with Nichrome wire wrapped in asbestos, in order to avoid condensation.

Pyrolysis Procedure.—The distilling flask which contains the sample is cooled in a Dry Ice–2-propanol bath. The system is evacuated and flushed several times with dry nitrogen. The nitrogen flow is adjusted to 0.8–0.9 l./min. The electric furnace is brought to the desired temperature while the coolants are added to the dewar flasks surrounding the traps. The Dry Ice–2-propanol bath is exchanged for a mineral oil or salt (ten parts KNO₃–seven parts NaNO₂) bath to be used to volatilize the sample. The pressure of the system is approximately 2–6 mm during the pyrolysis. Upon completion of the pyrolysis, the system is brought to atmospheric pressure by introduction of dry nitrogen. A chloroform or pyridine solution is made of all trapped materials. These solutions are worked up by vacuum distillation and/or by glpc.

Results

Pyrolysis of 2-Pyrone (1).—The apparatus and procedure described in the previous section were used to pyrolyze 2-pyrone (1). The amount of starting material, oil-bath temperature, and oven temperature used for each of the two pyrolysis runs were as follows: (a) 8.57 g, 125°, 900°; (b) 6.50 g, 120°, 920°.

A pyridine solution of the products from the traps was analyzed by glpc. The per cent yields of the products were determined by comparison of peak areas (by weighing curves) with areas obtained from a standard solution. Yields are reported below on the

basis of theoretical amounts expected from the total amount of starting material used.

The major products from 2-pyrone are furan (15.5% from a and 14.6% from b), propyne (41.2% and 47.6%), and allene (4.1% and 4.8%). No starting material was recovered. Propyne and allene were collected from glpc as a mixture. Propyne was identified in the mixture by comparisons of its retention time and its ir, nmr, and mass spectra with those of propyne. Allene was identified by its characteristic peaks and absorption bands in the mass, ir, and nmr spectra of the mixture: mass spectrum M⁺ *m/e* 40; ir, 1968 cm⁻¹; nmr δ 4.63 (s). The yield of allene is based on integration of the nmr spectrum of the mixture of propyne and allene, in which the ratio was *ca.* ten parts propyne to one part allene.

The nmr spectrum of the mixture of allene and propyne gave no indication of the presence of cyclopropene. An attempt in a separate pyrolysis of 1 to trap any cyclopropene that might have been formed by placing a cooled solution of cyclopentadiene in methylene chloride at the base of the cold finger condenser resulted in no adduct¹⁵ being isolated.

Benzene was identified as a minor component in the pyrolysis products by its retention time and mass spectrum. Minor products with molecular ions at *m/e* 54 and 26 might be 1,3-butadiene and acetylene, respectively.

We also pyrolyzed furan, using the same procedure and apparatus as we used for the pyrolysis of 2-pyrone. Allene and propyne were the major products formed. Hurd and Goldsby had previously pyrolyzed furan and identified propyne as a product; they suspected that allene and cyclopropene were also present.¹⁶ They also observed various amounts of benzene, butadiene, and acetylene. Thus, it appears that the allene and propyne formed in the pyrolysis of 2-pyrone are actually secondary pyrolysis products, coming from furan.

Pyrolysis of Coumarin (2).—For two pyrolysis runs on coumarin (2), 15 g of starting material was used each time. The oven temperature was 930° and a salt-bath temperature of 180° was used to volatilize the coumarin. The products were removed from the traps with chloroform and separated by vacuum distillation. From the first run, 4.0 g of coumarin was recovered, and benzofuran (86.2%, based on unrecovered starting material) was the only pyrolysis product isolated. In the second run, 3.2 g of coumarin was recovered, and the yield of benzofuran, based on unrecovered starting material, was 78.0%. The benzofuran was identified by its ir spectrum,¹⁷ its index of refraction [*n*^{25D} 1.5650 (lit.¹⁸ *n*^{25D} 1.565)], and its mass spectrum (M⁺ *m/e* 118; *m/e* 90 and 89).

Pyrolysis of 2-Pyridone (3).—When 2-pyridone (3) was heated to 170–210° to volatilize it, a crust slowly formed which began to inhibit volatilization. For this reason, the pyrolyses were terminated before completion. A mass spectrum identical with the mass

(15) K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.*, **82**, 6375 (1960).

(16) C. D. Hurd and A. R. Goldsby, *ibid.*, **54**, 2530 (1932).

(17) "Sadtler Standard IR Spectra," Sadtler Research Laboratories, Philadelphia, Pa., Spectrum No. 3739.

(18) "Handbook of Chemistry and Physics," 47th ed, The Chemical Rubber Co., Cleveland, Ohio, 1966.

(13) N. A. Orlov and V. V. Tishchenko, *J. Russ. Phys.-Chem. Soc.*, **62**, 2243 (1930); *Chem. Abstr.*, **25**, 3994⁶ (1931).

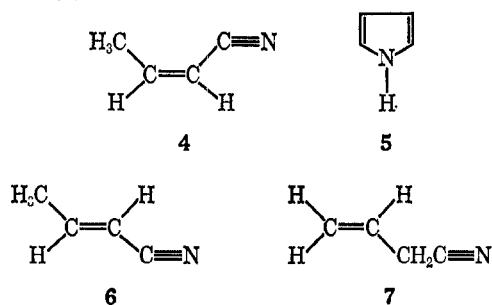
(14) H. E. Zimmerman, G. L. Grunewald, and R. M. Paufer, *Org. Syn.*, **46**, 101 (1966).

spectrum of 2-pyridone was obtained from the residue. The nmr spectrum of that part of the residue which is soluble in deuteriochloroform showed it to be 2-pyridone. The 2-pyridone was extracted from the residue with chloroform. Approximately 0.5% insoluble polymer remained, which could be heated to 280° without melting.

The conditions used for three pyrolysis runs were as follows (amount of starting material, amount of recovered starting material, oven temperature, salt-bath temperature): (c) 15.0 g, 5.2 g, 960°, 170°; (d) 15.0 g, 4.6 g, 1000°, 210°; (e) 10.0 g, 2.7 g, 1000–1020°, 180°.

A chloroform solution of the pyrolysis products was vacuum distilled; 1.44 g of pyrolysate was obtained from c, 0.93 g from d, and 0.55 g from e. The distillate was further separated by glpc. The glpc trace showed four major and at least four minor components. The major components were labeled A–D in the order in which they were eluted. A and D could be resolved on glpc, but B and C overlapped.

Component A was identified as isocrotonitrile (4). A molecular ion peak is found in the mass spectrum of A at m/e 67. Its ir and nmr spectra agree with published spectra.^{19,20} The ir, nmr, and mass spectra and retention time of component D are identical with those of pyrrole (5).



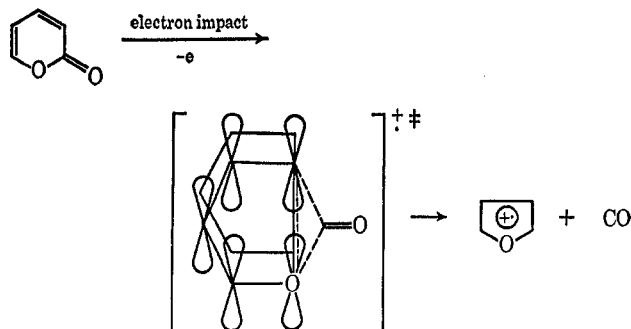
The mass spectra of the overlapping components B and C show molecular ions at m/e 67. The nmr and ir spectra of the mixture can be interpreted in terms of A 1.3 (B) to 1 (C) mixture of crotonitrile (6) and 3-butenitrile (7).^{20–22} Approximately a 15% yield of the C_4H_5N isomers was obtained from the first pyrolysis (c), based on unrecovered starting material.

Discussion

The electronic relationships among electron-impact and pyrolytic decomposition reactions are of current interest. Recently, Dougherty has extended the perturbation molecular orbital (PMO) method to cover radical cations in order to examine these relationships on this basis.^{23,24} If a normal metastable is observed for reaction of an odd-electron ion, the reaction occurs from a low-lying doublet state; mass spectrometric electrocyclic reactions exhibiting normal metastable peaks should be analogous to thermal processes.²³ Dougherty has shown that five-orbital transition states will be preferred for electrocyclic reactions in this class, especially if the system contains an oxygen heteroatom;

also, heteronuclear five-electron, five-orbital cyclic conjugated systems could be aromatic.²³ However, analogies with thermal processes will break down for reactions in the mass spectrometer which occur from rearranged molecular ions not accessible at modestly high thermal energies.²³

The metastables from decarbonylation of the molecular ions of 1–3 are broad and flat-topped with $[m^*]/[M^+]$ intensity ratios on the order of 1:2100 at 70 eV from the Atlas CH4. The $[m^*]/[M^+ - CO]$ intensity ratios are approximately 1:1600 in the mass spectra of 1 and 2, and 1:550 in the mass spectrum of 3. If the electron-impact decarbonylations are electrocyclic reactions, the transition state might be expected to be stabilized by aromaticity of the following heteronuclear five-electron, five-orbital cyclic homoconjugated system, especially if the transition state resembles products.



We have examined the pyrolytic process for 2-pyrone in order to make the comparison of the pyrolytic decarbonylation with the electron-impact decarbonylation. We have shown that from the pyrolytic decarbonylation of 2-pyrone we isolate furan. Likewise, coumarin decarbonylates to benzofuran. In the case of 2-pyridone, however, formation of isomeric products with the ring opening competes with expulsion of carbon monoxide to pyrrole.

Our data indicate that there are similarities between electron-impact and pyrolytic reactions of 2-pyrone, as might be predicted; CO is expelled. However, the pyrolysis product with formula C_4H_4O is furan, whereas the structure of the C_4H_4O radical cation has been described as other than furanlike.¹⁰ Perhaps this difference is due to the fact that (1) the expulsion of carbon monoxide from the molecular ion is not an electrolytic process; (2) a rearranged molecular ion of structure inaccessible at the thermal energies of the pyrolysis occurs; (3) furan is actually a secondary pyrolysis product formed from the reaction of an initially formed, less stable C_4H_4O isomer; (4) an unexpected factor prevails. Reason 1 seems to have been implicitly used by most of the proponents of the non-furanlike structures for $C_4H_4O^+$ from 2-pyrone, to explain their findings. Our data do not allow us to reach a definitive conclusion regarding these factors.

Registry No.—1, 504-31-4; 2, 91-64-5; 3, 142-08-5.

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(19) Reference 17, Spectrum No. 11914.

(20) G. S. Reddy, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, **83**, 1300 (1961).

(21) "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 56.

(22) Reference 17, Spectra No. 11902 and 9727.

(23) R. C. Dougherty, *J. Amer. Chem. Soc.*, **90**, 5780 (1968).

(24) R. C. Dougherty, *ibid.*, **90**, 5788 (1968).