

Pyrolysis of Pyrrole (1)

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The formation of arenes from various classes of organic compounds by high-temperature pyrolysis is now well established. Alkanes (such as methane (2) and dotriacontane) (3), functional derivatives of alkanes (4), arenes (such as benzene and toluene) (5), thiophene (6) and pyridines (7) are representative of the classes of compounds which have been found to undergo the pyrolytic aromatization reaction.

As part of an investigation of the behavior of organic compounds of natural origin under high-temperature conditions, pyrrole has been pyrolyzed at 850° and the pyrolyzate composition determined. The 850° pyrolysis temperature was selected for the present study because it is close to both the reported cone temperature of the cigarette (880°) (8) and to the temperature reported to be optimum for the production of polynuclear arenes (800°) (8).

While little information is available about the pyrolysis of pyrrole at high temperature, substituted pyrroles have been studied in some detail. At 745° *N*-methylpyrrole gives considerable quantities of tar (40%), isomeric methylpyrroles, pyrrole, and pyridine (9). Other substances found (10) in the pyrolyzate of *N*-methylpyrrole formed at 600-700° include dimethylpyrroles, indoles, benzenes and pyridines.

The pyrolysis of pyrrole at 850° produced hydrogen cyanide in 49% yield. Pyrolysis gases consisted of methane, ethylene, acetylene and ammonia. Other pyrolysis products in order of decreasing abundance included pyridine, benzonitrile, benzene, quinoline, indole, 1- and 2-naphthonitrile, naphthalene, α -picoline, aniline, *o*-tolunitrile, *m*-tolunitrile, 2-cyanopyridine, fluorene, phenanthrene-anthracene mixture, fluoranthene, pyrene, benzfluorene and a mixture of chrysene, triphenylene and benz[*a*]anthracene. Substances which are probable constituents of the pyrolyzate (identifications based upon g.l.p.c. retention times and ultraviolet spectra) include β -picoline, isoquinoline, biphenyl, *o*-phthalonitrile, acenaphthylene, methylpyrene and benzo[*h*]quinoline.

The nitriles listed above along with indole were the major constituents of the polar neutrals. Two additional fractions weighing 0.2 g. and 0.6 g. respectively were

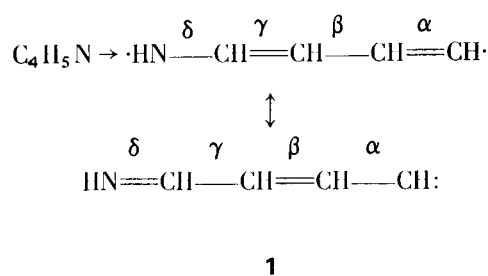
separated by g.l.p.c. and analyzed by spectroscopic methods. The first, which is probably 2-cyanopyrrole, showed N-H and C \equiv N absorption in the infrared. Mass spectral analysis indicated that the fraction was approximately 98% pure. The most abundant fragment *m/e* 65 corresponds to the loss of HCN from the parent ion with *m/e* 92. Further fragmentation of *m/e* 65 (by loss of C₂ diradical or the loss of cyanoacetylene from the parent ion) produces the next most intense fragment, *m/e* 41, C₂H₃N⁺. Fragments with *m/e* 39 and 38 were also observed and are consistent with fragments produced in the mass spectral analysis of pyrrole (11).

The second fraction separated by g.l.p.c. showed N-H and C \equiv N absorption in the infrared, and mass spectral analysis indicated that it consisted of two major components with *m/e* 92 (61%) and *m/e* 128 (29%) and two minor components with *m/e* 129 (7%) and *m/e* 149 (4%). The fragmentation portion of the spectrum contained the same fragment ions recorded above for *m/e* 92 (2-cyanopyrrole). The relative intensities were comparable except that observed for the *m/e* 65 fragment. In the latter mass spectrum the intensity of this ion was about 4 times larger than that observed in the former. Based on the observation that 3-substituted pyrroles usually exhibit longer g.l.p.c. retention times than the 2-substituted pyrroles (12), the compound (*m/e* 92) is tentatively assigned the 3-cyanopyrrole structure.

Since there are fragmentation peaks in the spectrum which correspond to those reported for *p*-dicyanobenzene, molecular ion *m/e* 128 is tentatively identified as *p*- or *m*-dicyanobenzene.

The fragmentation pattern is also consistent for the loss of HCN and (CN)₂ from *m/e* 129. A possible structure which fits the breakdown is dicyanopyridine.

Hurd (13) has pointed out the significance of carbon-heteroatom bond cleavage in the formation of arenes from thiophene and pyridine. The data reported herein on the pyrolysis of pyrrole supports this kind of reaction path. The simultaneous breaking of bonds in the ring and/or the initial rupture of the C-N bond followed by random cleavage of the resulting diradical produces fragments which on recombination give rise to the observed products.



In view of the large quantity of HCN formed, it would appear that cleavage at the γ -position to form $\text{HN}=\text{CH}\cdot$ **2** and the trimethine fragment (13) $\cdot\text{CH}=\text{CH}=\text{CH}\cdot$ **3** is a highly favored process. Rupture at the β -position produces ethylene diradical (acetylene) and $\cdot\text{HN}-\text{CH}=\text{CH}\cdot$ which loses hydrogen to form *azatrimethine* $\cdot\text{N}-\text{CH}=\text{CH}\cdot$ **4**; cleavage at the δ -position gives nitrene $\cdot\text{NH}$ **5** and butadiene diradical **6**; and cleavage at the α -position gives methine $\cdot\text{CH}$: **7** and $\text{HN}=\text{CH}-\text{CH}=\text{CH}\cdot$ which on dehydrogenation gives acrylonitrile diradical, $\text{NC}\cdot-\dot{\text{C}}=\text{CH}$ **8**. Dehydrogenation of **1** gives the cyanotrimethine fragment $\text{NC}-\dot{\text{C}}=\text{CH}-\text{CH}$: **9**.

Interactions of these fragments in various combinations explain how the product observed could have been formed in the pyrolysis. The production of benzene from the trimethine fragment **3** and of naphthalene, quinoline and isoquinoline from the butadiene diradical **6** has been outlined by Hurd (13). Analogously, pyridine can arise by reaction of trimethine **3** with *azatrimethine* **4**, benzonitrile by reaction of trimethine **3** with cyanotrimethine **9** and the isomeric cyanopyrroles by reaction of *aza*-trimethine **4** with acrylonitrile diradical **8**. Reaction of butadiene diradical **6** with ethylene diradical, or with acrylonitrile diradical **8** or with pyrrole, could produce benzene, benzonitrile and indole, respectively.

It is likely that some of the indole arises from an intermolecular diene reaction of pyrrole followed by the elimination of the imine bridge as ammonia. Likewise ring enlargement reactions of carbene or of a methine species **7** with pyrrole or indole may account in part for the production of pyridine and quinoline.

Polynuclear arenes and polynuclear *aza*arenes probably arise from reaction of butadiene diradical **6** with the previously formed cyclic systems described above. Interactions involving a benzyne intermediate may represent an additional pathway to the polynuclear compounds since Fields and Meyerson (14) found that benzyne reacts with benzene to give biphenyl and naphthalene, and with pyridine to give phenylpyridine, quinoline and isoquinoline.

EXPERIMENTAL

Infrared spectra were measured on a Beckman IR 8 spectrophotometer and ultraviolet spectra were measured in cyclohexane using a Perkin-Elmer Model 202 spectrophotometer.

Mass spectra were taken on a Hitachi RMU-6E double focusing mass spectrometer using 70 v. ionizing energy with the inlet system at 200°.

Gas chromatographic analyses were made and retention times were measured on a Beckman Model Gc-4 gas chromatograph using a 6' x 1/8" 20% SE-30 column. Separations were made either on an Aerograph Model A-700 gas chromatograph or on a F and M (Model 720 or Model 810) gas chromatograph using the columns and conditions specified below.

R_f values were obtained from components in the neutral fraction (after separation by column or gas chromatography) using S and S acetylated paper (Grade 2495) and an ethanol:toluene:water (17:4:4) solvent system (15).

Pyrolyses.

The pyrolyses were carried out in a nitrogen atmosphere at 850° using a vertically arranged Vycor reaction tube (94 x 2.5 cm.) containing 18 ml. of Berl Saddles positioned in the hot zone. Heating was accomplished by a Lindberg furnace equipped with a stainless steel liner for heat uniformity and the temperature was regulated to $\pm 5^\circ$ of the indicated value over the volume containing the heat exchanger. The sample was introduced at a constant rate from a syringe mounted on a syringe drive (driven by a Troemner monodrum unit) and swept through the reactor by a stream of dry nitrogen at a flow of 100 ml./minute.

The liquid products were collected in two traps, each of which was cooled in a Dry Ice-chloroform-carbon tetrachloride mixture. Gases which were not condensed by these traps were swept through a trap containing 5% sulfuric acid, collected and examined by infrared spectroscopy using a 100 mm. gas cell. Identifications were based upon comparisons of the absorption bands observed with those reported in the literature (16) and with those obtained from authentic samples.

Pyrolysis of Pyrrole.

In a representative pyrolysis 15.2 g. (44%) of pyrolyzate was obtained from 34.7 g. of pyrrole added to the reactor over 74 minutes. Pyrolyzate gases produced consisted of methane, ethylene, acetylene, hydrogen cyanide and ammonia. Substances in the pyrolyzate with boiling points less than 100° were obtained by distillation using a boiling-water bath. The volatile mixture, separated further by preparative g.l.p.c. and analyzed by infrared spectroscopy, consisted of hydrogen cyanide (13.3 g./mole pyrolyzed) and benzene (0.9 g./mole pyrolyzed) (17). The residue from the distillation was taken up in ether and extracted with 5% hydrochloric acid saturated with sodium chloride. During the extraction, a tarry material deposited which amounted to 57% of the weight of the pyrolyzate (based on the weight of the ether soluble material recovered from the neutral and basic fractions). After drying (magnesium sulfate) and removal of the ether there was obtained 3.3 g. of bases and 2.8 g. of neutrals. In another experiment where the acid extraction time was minimized only small quantities (ca. 1 g.) of tarry material were observed and pyrrole (r.t., i.r.) was recovered from the volatile neutral fraction in 37.4% yield.

The volatile substances (volatile neutrals) were removed from the neutral fraction by collecting material boiling up to 44° at 0.15 mm. The neutral fraction residue was further separated into

polar neutrals, aliphatics and aromatics by solvent partitioning (18), first between cyclohexane and 90% methanol-water, and then between cyclohexane and nitromethane.

Identification of Constituents in Pyrolyzate Fractions.

Identifications are based on comparisons of g.l.p.c. retention times (r.t.) and/or ultraviolet spectra (u.v.) and/or infrared spectra (i.r.) and/or R_f values with those obtained from authentic samples. Estimation of relative abundances of constituents (17) are based on area percent values obtained from g.l.p.c.

Bases.

Separations were made on a 12' x 3/8" 20% Apiezon L column heated at 50° for 4 minutes and then programmed at 10°/minute to 250°. Constituents obtained (identified by r.t., u.v., i.r.) were pyridine (3.7 g.), α -picoline (0.2 g.), aniline (0.08 g.) and quinoline (0.6 g.). β -Picoline (0.1 g., r.t., u.v., i.r.) was identified in the fraction but was impure since the infrared spectrum showed several additional bands to those found in the spectrum from an authentic sample. Probable constituents were isoquinoline (0.3 g., r.t., u.v.) and benzo[h]quinoline (0.01 g., r.t., u.v.). On the basis of g.l.p.c. retention times, the isomeric lutidines and isomeric vinylpyridines are not present in detectable amounts.

Volatile Neutrals, Polar Neutrals and Polynuclear Aromatic Hydrocarbons.

The volatile neutrals were separated by preparative g.l.p.c. using a 20' x 3/8" 20% SE-30 column heated at 125° for 8 minutes and then programmed at 4°/minute to 250°. The polar neutrals were separated by using a 20' x 3/8" 20% Apiezon W column heated at 125° for 8 minutes and then programmed 4°/minute to 250°. The polynuclear aromatic hydrocarbons were separated on an 8' x 3/8" 30% SE-30 column heated to 150° and then programmed at 6°/minute to 280°. Constituents identified by r.t., u.v., i.r. were benzonitrile (1.1 g.), *o*-tolunitrile (0.06 g.), *m*-tolunitrile, 2-cyanopyridine (r.t., i.r.), naphthalene (0.3 g.), indole (0.5 g.), 2-naphthonitrile (0.3 g.) and 1-naphthonitrile (0.4 g.). Those identified by r.t., u.v. and R_f were fluorene (0.05 g.), phenanthrene-anthracene (0.1 g.), fluoranthene (0.04 g.), pyrene (0.03 g.), benzfluorene (0.05 g.), and a mixture of chrysene, triphenylene and benz[a]anthracene (0.09 g.).

Probable constituents of the fraction (based upon r.t. and u.v.) include biphenyl (0.01 g.), *o*-phthalonitrile (0.07 g.), acenaphthylene (0.1 g.) and methylpyrene (0.04 g.).

Additional components of the polar neutral fraction were examined by u.v., i.r. and mass spectrometry.

The component (0.2 g.) appearing just before indole in the g.l.p.c. separation showed the following properties: u.v. max (cyclohexane) 241, 246, 252 μ ; i.r. (carbon tetrachloride) 3475 (pyrrole N-H) 3330 brd. and 2230 cm^{-1} (CN); mass spectrum m/e (rel. intensity) 92 (100), 65 (19), 41 (15), 64 (10), 38 (10), 39 (8). The mass spectrum showed 1.5% mass 118 as an impurity.

The major peak (0.6 g.) appearing immediately after indole in

the g.l.p.c. separation gave a positive Ehrlich test and exhibited the following properties: u.v. max (cyclohexane) 209, 216 sh., 222 sh., 231 sh., 236 sh., 247, 272 and 301 μ sh.; i.r. (carbon tetrachloride) 3480 (pyrrole NH), 3300 brd., 2230 cm^{-1} (CN); mass spectrum (parent ions only) m/e (rel. intensity) 92 (100), 117 (1), 128 (47), 129 (12), and 149 (4). Parent ion assignments were verified by using low-voltage scans. The mass spectrum showed the following fragmentation pattern: m/e (rel. intensity) 149 (4), 129 (12), 128 (47), 106 (5), 101 (13), 93 (7), 92 (100), 76 (4), 75 (5), 65 (78), 64 (13), 51 (4), 50 (6), 41 (12), 39 (4), 38 (10). On the basis of the fragmentation patterns and relative intensities of the parent ions, the following structures are assigned and percentages in the fraction are estimated: mass 92, cyanopyrrole (61%); mass 117, indole (1%); mass 128, *m*- or *p*-dicyanobenzene (29%); mass 129, a dicyanopyridine (7%) and mass 149 (4%).

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Received May 8, 1968

Lexington, Kentucky 40506