# Autoxidation of Three 1-Alkylpyrroles

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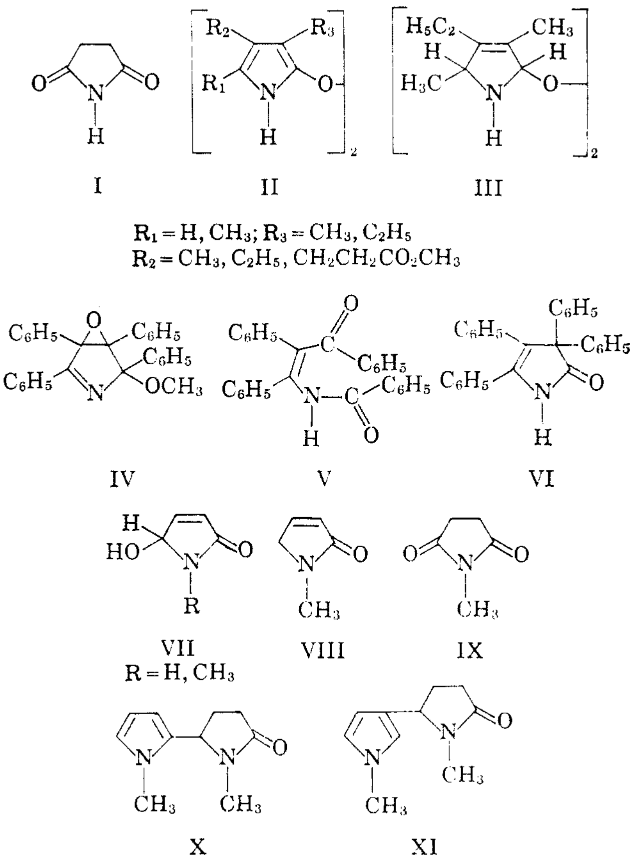
Self-initiated autoxidation of 1-methylpyrrole, 1-isopropylpyrrole, and 1-butylpyrrole formed peroxidic polymers and carbonyl compounds thought to arise from peroxide decomposition. Four of these carbonyl compounds were isolated from 1-methylpyrrole oxidation products and spectral examination detected their homologs in oxidation products of the other two pyrroles. It is suggested that 1-alkylpyrroles react with oxygen by a free-radical peroxy addition process typical of conjugated dienes.

Pyrroles react readily with oxygen to form red-brown tars and promote formation of color, gum, and sludge in petroleum fractions exposed to air.[1] Pyrroles are partly responsible for the rapid deterioration of shale-oil naphtha exposed to air.[2] The present study was undertaken to gain more knowledge about the pyrrole–oxygen reaction.

Although a number of gum-forming reaction paths involving pyrroles have been suggested,[3] the reaction of pyrroles with oxygen has received little attention. Pyrrole oxidation products are usually highly colored, amorphous materials from which only a few compounds have been isolated. Succinimide (I) was found to be a minor product of the air oxidation of pyrrole.[4] Metzger and Fischer[5] proposed peroxide structures, represented by II, for crystalline products which they obtained by exposing solutions of C-substituted pyrroles to air. The validity of such structures in which the peroxide group is attached directly to a $\pi$ system has since been questioned by Seebach,[6] who proposed an allylic structure (III), and reaffirmed by Atkinson and co-workers,[7] who reported the isolation of II ($R_1 = R_2 = R_3 = CH_3$). Photooxidation of 2,3,4,5-tetraphenylpyrrole in methanol led to several interesting products, including IV and V, and to VI in the presence of potassium hydroxide.[8] Under similar conditions, but using water as a solvent, photooxidation of pyrrole and 1-methylpyrrole resulted in products (VII) isomeric with the corresponding succinimides[9,10] (Chart I).

This report describes the autoxidation of 1-methylpyrrole, 1-isopropylpyrrole, and 1-butylpyrrole at 50°. These 1-alkylpyrroles were chosen primarily because they react with oxygen much more slowly than C-alkylpyrroles, thus giving a greater chance of isolating initial reaction products. Also, the autoxidation behavior of 1-alkylpyrroles has apparently not been reported. The oxidation of each pyrrole was studied by measuring the rate at which the pure liquid consumed oxygen at atmospheric pressure. The reactions were periodically sampled and the samples analyzed by infrared and mass spectroscopy.

CHART I



## Results

Each reaction was characterized by an induction period, during which the originally colorless liquids turned yellow, with no oxygen uptake detected. This period was followed by one of autocatalytic reaction, which gave way to a gradually retarded reaction. The curves obtained by plotting oxygen uptake per mole of pyrrole as a function of reaction time (Figure 1) show that the autocatalytic oxygen consumption rates of 1-methylpyrrole and 1-isopropylpyrrole are comparable and are higher than that of 1-butylpyrrole. During the subsequent retardant periods, the rates are in the order 1-methylpyrrole > 1-butylpyrrole > 1-isopropylpyrrole. The oxygen consumption curve for 2,5-dimethylpyrrole is included only to show the much faster reaction of a C-alkylpyrrole.

Infrared spectra showed a number of characterizable changes which occurred during each of the oxidations. Absorption peaks developed which were characteristic of hydroxy groups (2.9 $\mu$) and carbonyl groups (5.9 $\mu$). Also, sharp peaks developed at 8.0 and 12.5 $\mu$ which

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[1] Y. G. Hendrickson, 134th National Meeting of the American Chemical Society, Boston, Mass., 1959, Preprints, Division of Petroleum Chemistry, Vol. 4, No. 1, p 55; R. B. Thompson, J. A. Chenicek, L. W. Druge, and F. Symon, *Ind. Eng. Chem.*, **43**, 935 (1951).

[2] G. U. Dinneen and W. D. Bickel, *ibid.*, **43**, 1604 (1951).

[3] A. A. Oswald, *J. Chem. Eng. Data*, **6**, 294 (1961).

[4] G. Ciamician and P. Silber, *Chem. Ber.*, **45**, 1842 (1912).

[5] W. Metzger and H. Fischer, *Ann.*, **527**, 1 (1937).

[6] D. Seebach, *Ber.*, **96**, 2723 (1963). This author questioned structure II ($R_1 = R_3 = CH_3$; $R_2 = C_2H_5$) reported by H. Fischer, *et al.*, *Z. Physiol. Chem.*, **212**, 146 (1932).

[7] J. H. Atkinson, R. S. Atkinson, and A. W. Johnson, *J. Chem. Soc.*, 5999 (1964).

[8] H. H. Wasserman and A. Liberles, *J. Am. Chem. Soc.*, **82**, 2086 (1960).

[9] F. Bernheim and J. E. Morgan, *Nature*, **144**, 290 (1939).

[10] P. de Mayo and S. T. Reid, *Chem. Ind.* (London), 1576 (1962).

were attributable to epoxy groups and to peroxy groups.[11,12]

Mass spectra of reaction mixture samples also showed characterizable changes taking place during the autoxidations. As the reactions progressed, mass spectral peaks of increasingly greater mass to charge ratio (*m/e*) appeared. Ions of *m/e*'s corresponding to simple, integral combinations of starting pyrrole and oxygen appeared during the autocatalytic periods. Ions attributed to loss of hydrogen from pyrrole–oxygen compounds appeared later in the reactions, during the autoretardant periods. The maximum *m/e*'s corresponded to compounds containing as many as five starting-pyrrole nuclei.

Appearance-potential studies showed that the following ions were molecular ions: (1) those corresponding to combination of one molecule of alkylpyrrole and one oxygen atom; (2) those from one molecule of alkylpyrrole and two oxygen atoms; and (3) those from two molecules of alkylpyrrole and one oxygen atom. Ions having *m/e*'s other than the above combinations were not sufficiently abundant for meaningful appearance-potential studies. It is probable, however, that ions having weights which could be accounted for by simple combinations of starting pyrrole and oxygen, with or without accompanying hydrogen loss, were indeed molecular ions. Because the spectral evidence indicated that analogous oxidation products were formed in each of the pyrroles, further efforts were devoted to separation and identification of the 1-methylpyrrole oxidation products.

Four compounds were isolated from 1-methylpyrrole reaction products by gas chromatography. Each compound was a simple combination of oxygen and starting pyrrole as indicated by the appearance-potential study. The compound of lowest molecular weight, 1-methyl-$\Delta^3$-pyrrolin-2-one (VIII), was isolated from a fresh oxidation mixture as a pale yellow liquid. The structure shown is based on the mass spectral molecular ion at *m/e* 97, on infrared absorption indicating amide carbonyl and vinyl groups, and on the nmr spectrum (Chart II). The infrared and nmr spectra compare favorably with those of other 3-pyrrolin-2-ones.[6,7,13] The position of the methylene signal in the nmr spectrum was used to locate the endocyclic double bond.[13c]

A compound formed from one molecule of 1-methylpyrrole and two oxygen atoms, N-methylsuccinimide (IX), was isolated from the pyrrole-free tars. Its identity with authentic material was established by spectral comparison and mixture melting point.

Two compounds of molecular weight 178, equivalent to two molecules of 1-methylpyrrole plus one oxygen atom, were isolated. One, a pale yellow, viscous liquid, was shown to be 5-(1′-methyl-2′-pyrryl)-1-methylpyrrolidin-2-one (X). The other, a pale yellow solid, was identified as 5-(1′-methyl-3′-pyrryl)-1-methylpyrrolidin-2-one (XI). The carbon skeletons of these compounds were established by catalytic hydrogenation,[14] which reduced X to octane, and XI to 3-methylheptane. However, the proof of structures rests on molecular weights and empirical formulas derived from mass spectra, on infrared absorption indicating amide carbonyl group in both compounds, and on the nmr spectra (Chart II). Chemical shifts were assigned by comparison with spectra of 1-methylpyrrole, 1-methylpyrrolidin-2-one,[15] and 2,2′-pyrrolidinylpyrrole.[16]

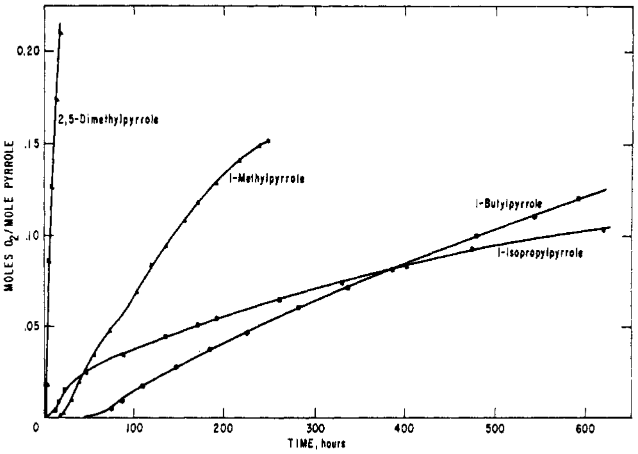
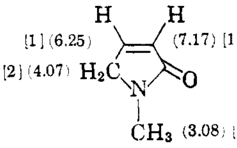
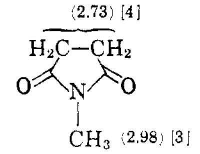


Figure 1.—Consumption of oxygen by pure pyrroles at 50°.

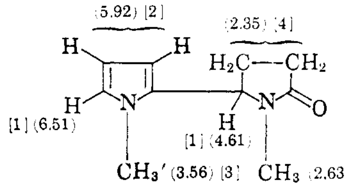
Chart II[a]



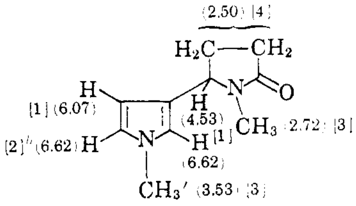
VIII



IX



X



XI

[a] Numbers in parentheses refer to nmr peak positions ($\delta$, parts per million) from tetramethylsilane, measured in deuteriochloroform. Numbers in brackets refer to number of protons in a position, determined by integration. [b] Includes proton at position 2′.

During one oxidation run, the concentrations of the four identified products were measured periodically by gas chromatography. The curves produced by plotting chromatogram peak areas per milligram of reaction mixture with respect to reaction time (Figure 2) show that VIII and IX were the first products detected and that production of the former was dominant during the early, autocatalytic period. Production of IX, X, and XI was of relatively little importance until well into the retardant period, when, at about 80 hr,

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[11] O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *Anal. Chem.*, **23**, 277 (1951).

[12] O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *ibid.*, **23**, 282 (1951).

[13] (a) J. Plieninger and M. Decker, *Ann.*, **598**, 198 (1956); (b) H. Plieninger, H. Bauer, and A. R. Katritzky, *ibid.*, **654**, 165 (1962); (c) J. Bordner and H. Rapoport, *J. Org. Chem.*, **30**, 3824 (1965).

[14] C. J. Thompson, H. J. Coleman, C. C. Ward, and H. J. Rall, *Anal. Chem.*, **34**, 151 (1962). The furnace temperature employed in the present work has 220°.

[15] Varian NMR Spectra Catalog, Spectrum No. 116.

[16] H. Rapoport and H. Castagnoli, *J. Am. Chem. Soc.*, **84**, 2178 (1962).

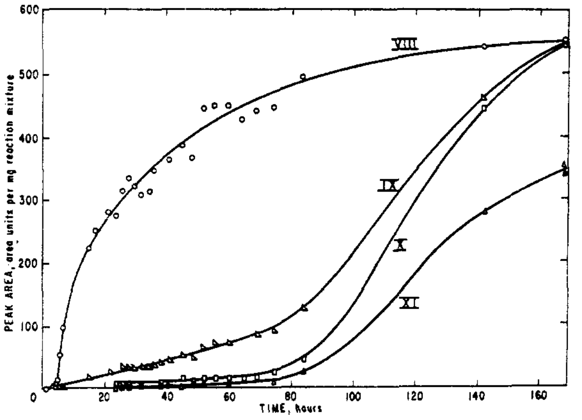

Figure 2.—Development of products VIII, IX, X, and XI during oxidation of 1-methylpyrrole.

the curves for these compounds show a concurrent rise while the curve for VIII tends to flatten out. This suggests that an initially important process leading to VIII is diverted in some manner to production of the other compounds.

Gas chromatographic analysis of the reaction mixture after absorption of 0.12 moles of oxygen per mole of 1-methylpyrrole showed that about one-tenth of the charge had reacted. Of this converted pyrrole, about 5% was accounted for by VIII, 15% by IX, 30% by X, and 20% by XI. These products, however, account for only about 30% of the oxygen absorbed and it was therefore concluded that more highly oxygenated, thermally labile species, such as peroxides, were formed in the reaction.

Evidence of peroxide formation was provided by examination of freshly formed 1-alkylpyrrole oxidation products. The pyrroles were treated with pressurized oxygen, degassed, diluted with pentane, and the solutions tested with aqueous potassium iodide solution. In each case, release of iodine at the liquid interface indicated that peroxides were present. By this test, peroxides were detected in very lightly oxidized samples, indicating that they are among the earliest reaction products. Pentane-insoluble tars deposited from heavily oxidized samples also released iodine from potassium iodide solution, but both the tars and pentane solutions lost this ability after aging at room temperature. However, the tars retained some peroxide character for several weeks, shown by their reaction to release iodine from hydriodic acid. Thus, labile peroxides are apparently formed in the initial stages of these reactions and continued oxidation leads to the formation of relatively stable peroxidic polymers.

About 70% of the pentane-insoluble tar from 1-methylpyrrole oxidation was soluble in water. The water-soluble extract was a red-brown, peroxidic semisolid with an elemental composition approximating that of a copolymer of 2 moles of oxygen with 3 moles of methylpyrrole. However, the molecular weight of 220 was too low for such a copolymer. Gas chromatographic separation of this material gave mainly compounds IX, X, and XI. The water-insoluble portion of the tar gave no peroxide test. It was a dark brown solid, soluble in methanol or acetone, with a molecular weight of 420. The infrared spectrum showed absorption for carbonyl, methyl or methylene, and vinyl or pyrrole ring groups. Elemental analysis showed that it contained the equivalent of one oxygen atom per methylpyrrole unit.

## Discussion

Autocatalytic raction with oxygen, as shown by the S-shaped curves in Figure 1, has been reported for many organic compounds and the free-radical nature of the reaction is well established in most cases.[17] Peroxides are usually detected in the products, their decomposition leading to the formation of carbonyl or hydroxy compounds structurally similar to the starting material. Observation of these characteristics in the autoxidation of 1-alkylpyrroles suggests that these pyrroles also react with oxygen by a free-radical process.

Comparing the autoxidation products of these pyrroles with those of conjugated dienes and with alkyl aromatic systems indicates that the pyrroles more nearly resemble the dienes in their reactivity toward oxygen. Conjugated dienes usually react readily with oxygen and do so mainly through peroxy addition to the double-bond system to form peroxidic polymers and their carbonyl decomposition products.[17] This result is also observed in the nonphotoinitiated autoxidation of furans[18] which are heteroaromatics chemically similar to the pyrroles. By comparison, oxidation of alkylbenzenes leads mainly to monomeric aralkyl hydroperoxides by attack on the alkyl group.[19] Furthermore, the oxidation rate of isopropylbenzene by virtue of the easily abstracted tertiary benzylic hydrogen atom is considerably higher than that of toluene. This is not the relationship observed for 1-isopropyl- and 1-methylpyrrole, which suggests that hydrogen abstraction is not the dominant feature in the oxidation of 1-alkylpyrroles and that addition processes should be considered.

There is evidence that pyrroles exhibit diene character in the presence of radicals. This was first demonstrated by Conant and Chow,[20] who isolated the 1,4-addition product in 60% yield from the reaction of triphenylmethyl radicals and pyrrole. The diene behavior of both pyrrole and 1-methylpyrrole in the presence of *t*-butoxy radicals has also been reported.[21] Competitive reactions of phenyl radicals with carbon tetrachloride solutions of olefins and aromatic compounds[22] show that 1-methylpyrrole is little more susceptible to hydrogen abstraction than toluene. However, our calculations, based on Bridger and Russell's data, indicate that 1-methylpyrrole has reactivity toward radical addition approaching that of 2,5-dimethyl-2,4-hexadiene and greater than that of a number of monoolefins.

It is therefore plausible to characterize the oxidation of 1-alkylpyrroles as a process in which products are formed mainly by radical addition. Such a process is postulated in the reaction sequence give in Scheme I.

Reactions 1, 2, and 3 of Scheme I are those generally proposed for chain autoxidation. Reactions of the resulting peroxy radicals with the substrate lead to peroxide formation and autocatalytic oxygen uptake.

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[17] C. Walling, "Free Radicals in Solution," 1st ed, John Wiley and Sons, New York, N. Y., 1957.

[18] G. O. Schenk, *Ber.*, **B77**, 661 (1944).

[19] G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

[20] J. B. Conant and B. F. Chow, *ibid.*, **55**, 3475 (1933).

[21] R. J. Gritter and R. J. Chriss, *J. Org. Chem.*, **29**, 1163 (1964).

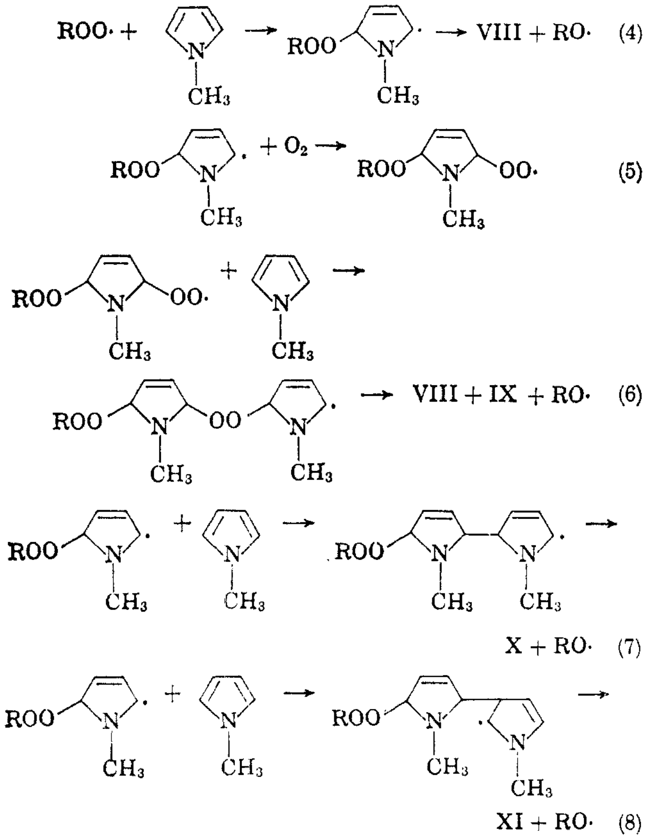
[22] R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

Scheme I

$$RH \longrightarrow R\cdot \quad (1)$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \quad (2)$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \quad (3)$$



In reactions 4, 6, 7, and 8, the identified products are shown to result from radical addition, followed by scission of bonds between oxygen atoms in growing peroxide chains. These products have in common the attachment of oxygen to the carbon atoms adjacent to nitrogen. Because these $\alpha$-carbon atoms occupy the regions of highest electron density in the pyrrole ring, they should be most attractive to the electrophilic peroxy radicals. Reactions 4, 5, and 6 sum up these observations. The competing reactions represented by eq 7 and 8 reflect a similar polar influence on the course of the reaction, since X is formed in preference to XI (Figure 2).

Inspection of models of the 1-alkylpyrroles and the proposed radical intermediates indicates that bulky alkyl groups attached to the nitrogen atoms could interfere with the approach of these radicals to the $\alpha$ positions. Thus, the observed differences in oxidation rates may be due to steric hindrance of addition at electronically preferred positions.

## Experimental Section

**Materials.**—Pyrroles were obtained from American Petroleum Institute Research Project 52. Purities in mole per cent estimated from freezing-point data were as follows: 1-methylpyrrole, 99.5%; 1-butylpyrrole, 99.5%; 1-isopropylpyrrole, 98.5%. Each pyrrole sample was stored in a break-seal ampoule under its own vapor prior to use. Oxygen was taken from commercial cylinders and was passed through magnesium perchlorate and sodium hydroxide absorbers to remove water and carbon dioxide.

**Oxidation Apparatus and Procedure.**—The oxidation system consisted of a reaction vessel and a gas manifold. The reaction vessels were made from 100-ml, flat-bottom flasks, each having a central break-seal neck with a side arm below the seal and a capillary neck stoppered with a silicone rubber plug. A glass-encased magnetic stirring bar was placed in each vessel during fabrication. The gas manifold was made of heavy-walled glass capillary tubing, connecting a gas buret assembly, the reaction vessel, the oxygen source, and vacuum. In a typical run, a pyrrole (35–40 ml) was vapor transferred into a weighed reaction vessel through the side arm, which was attached to the vacuum system by a short length of rubber tubing. The pyrrole was frozen with liquid nitrogen, the sidearm sealed off near the neck with a flame, and the vessel, contents, and side arm were weighed when the sample reached room temperature. A glass-encased iron slug was placed in the neck and the vessel was flame sealed to the manifold and surrounded by a water bath regulated to 50 ± 0.1°. The stirring bar in the vessel was activated, the system was evacuated and filled with oxygen three times, and oxygen was admitted to the sample by breaking the seal with the magnetically manipulated slug. Oxygen consumption was measured at constant pressure by manually adjusting the mercury level in the gas buret. The reaction mixture was sampled by inserting a hypodermic needle through the silicone rubber plug of the capillary side arm and withdrawing 0.2–0.3 ml of liquid with a syringe. Oxygen consumption rates were not noticeably affected by the light in the laboratory or by oxygen pressure variations in the range 350–620 mm. Stirring rates were maintained well above those at which any decrease in oxygen consumption rates could be detected.

For more rapid formation of oxidation products, samples of pyrroles in Pyrex containers were exposed to 100-psig oxygen pressure in a steel pressure bomb at 50°.

**Analytical Instruments[23] and Procedures.**—Mass spectra were obtained with a Consolidated 21-103C mass spectrometer equipped with a high-temperature inlet. Infrared spectra were obtained with a Perkin-Elmer 21 spectrophotometer equipped with sodium chloride optics and a Perkin-Elmer 521 grating spectrophotometer. Liquids were analyzed either neat or in chloroform solution. Solids were analyzed in chloroform solution, in KBr pellets or as thin layers between salt plates. The nmr spectra of oxidation products were obtained with a Varian A-60 spectrometer; samples were irradiated in $CDCl_3$ solution and chemical shifts were determined with respect to internal tetramethylsilane. Gas chromatograms were obtained with a Barber-Colman Model 61-C chromatograph equipped with a flame-ionization detector and with an Aerograph Model A-700 chromatograph which was also used for trapping of individual compounds.

The saturated hydrocarbons from catalytic hydrogenation of X and XI were separated on a 0.25 in. diameter × 25 ft column, packed with 30% tricresylphosphate on firebrick, operated at 100° and at 20-psig helium pressure. The hydrocarbons were identified by their retention times, which were 17.0 (3-methylheptane) and 19.7 min (octane), identical with retention times of the pure reference hydrocarbons.

The column used to monitor the development of oxidation products (Figure 2) and for quantitative analysis of the final reaction mixture was $^1/_8$ in. diameter × 10 ft long, packed with 15% Carbowax 20 M on Gas-Chrom-P support. Operating conditions were as follows: column temperature, 200°; helium flow rate, 75 ml/min. Retention times were 4.5 (VIII), 7.0 (IX), 45 (X), and 55 min (XI). Because the flame-ionization detector used in this experiment responds differently to carbon atoms in different chemical environments, peak areas represented in Figure 2 were corrected for each compound, based on response data published by Sternberg and co-workers.[24]

**Procedures for Separation of 1-Methylpyrrole Oxidation Products.**—Compound VIII was isolated for identification from freshly prepared bomb-oxidation products. The unreacted 1-methylpyrrole was distilled from the reaction mixture at *ca.* $10^{-6}$ torr and VIII was isolated from the undistilled product by gas chromatography on a $^3/_8$ in. × 20 ft aluminum column packed with 15% Carbowax 20 M on acid- and base-washed diatomaceous earth. Compounds IX, X, and XI were isolated in the same

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[23] Reference to specific brands or models of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

[24] J. C. Sternberg, W. S. Gallaway, and D. T. L. Jones, in "Gas Chromatography," N. Brenner, J. E. Callen, and M. D. Weiss, Ed., Academic Press, Inc., New York, N. Y., 1962, p 265.

manner from aged reaction mixtures accumulated from the rate studies.

**1-Methyl-Δ$^3$-pyrrolin-2-one (VIII)** was obtained as a clear liquid with a faint yellow tinge which darkened on standing in air. The infrared spectrum (CDCl$_3$) showed principal bands at 5.97 (NC=O), 6.26, 6.32, 10.0, and 10.3 μ. The mass spectrum showed the molecular ion at *m/e* 97 and the major fragment ion at *m/e* 68. The empirical formula, $C_5H_7NO$, was derived from intensities of isotope peaks at *m/e* 98 and 99 relative to *m/e* 97 = 100[25] (Table I).

TABLE I

| | *m/e* | | |
|---|---|---|---|
| | 97 | 98 | 99 |
| Theory, $C_4H_3NO_2$ | 100 | 4.83 | 0.49 |
| Theory, $C_5H_7NO$ | 100 | 5.94 | 0.35 |
| Theory, $C_6H_{11}N$ | 100 | 7.04 | 0.21 |
| Found, VIII | 100 | 6.17 | 0.41 |

**N-Methylsuccinimide (IX)** was obtained as colorless needle crystals, recrystallized from cyclohexane: mp 66°; mmp 66° (lit.[26] mp 66°). The infrared spectrum (CHCl$_3$) showed principal bands at 3.31, 5.88 (NC=O), 7.22, 7.71, 7.81, and 8.97 μ. The mass spectrum showed the molecular ion at *m/e* 113 and major fragement ions at 85 and 84. The empirical formula, $C_5H_7NO_2$, was derived from the intensities of isotope peaks at *m/e* 114 and 115 relative to *m/e* 113 = 100 (Table II).

TABLE II

| | *m/e* | | |
|---|---|---|---|
| | 113 | 114 | 115 |
| Theory, $C_4H_3NO_3$ | 100 | 4.87 | 0.70 |
| Theory, $C_5H_7NO_2$ | 100 | 5.98 | 0.55 |
| Theory, $C_6H_{11}NO$ | 100 | 7.08 | 0.42 |
| Found, IX | 100 | 5.95 | 0.59 |

**1-Methyl-5-(1′-methyl-2′-pyrryl)-pyrrolidin-2-one (X)** was obtained as a viscous liquid having a pale-yellow color which darkened on standing in air. The infrared spectrum (CHCl$_3$,) showed principal bands at 3.39, 5.92, 6.65–7.20, 8.73, 9.00, 9.16, 9.48, and 10.6 μ. The mass spectrum showed the molecular ion at *m/e* 178 and the major fragment ion at 121. The empirical formula, $C_{10}H_{14}N_2O$, for this compound and for XI was derived from mass spectra in the same manner as described above (Table III).

TABLE III

| | *m/e* | | |
|---|---|---|---|
| | 178 | 179 | 180 |
| Theory, $C_9H_{10}N_2O_2$ | 100 | 9.98 | 1.25 |
| Theory, $C_{10}H_{14}N_2O$ | 100 | 11.83 | 0.84 |
| Theory, $C_{11}H_{14}O_2$ | 100 | 12.19 | 1.08 |
| Theory, $C_{11}H_{18}N_2$ | 100 | 12.94 | 0.77 |
| Found, X | 100 | 11.94 | 0.86 |
| Found, XI | 100 | 11.86 | 0.83 |

**1-Methyl-5-(1′-methyl-3′-pyrryl)-pyrrolidin-2-one (XI)** was obtained as a pale-yellow solid which melted in the range 73–75°. The infrared spectrum (CHCl$_3$) was essentially the same as that of X above. In the mass spectrum, the molecular ion and major fragment ion were at the same locations as for X and the isotope peak ratios led to the same empirical formula. However, the intensity of the *m/e* 177 peak relative to that of the parent peak was 92%, as contrasted to 26% for X. The reason for this much more facile loss of a hydrogen atom from XI is not apparent.

**Peroxide Detection.**—Each of the 1-alkylpyrroles was both lightly and heavily oxidized under pressure by the bomb-oxidation method described under oxidation procedures. The reaction products were degassed at reduced pressure, diluted with 8–10 volumes of pentane, and 5 ml of the pentane solution was added slowly to a test tube containing 2 ml of 0.5 *N* potassium iodide, 1 drop of glacial acetic acid, and 2 drops of starch indicator. In each case, iodine was released at the liquid interface. The color was dispelled by agitation of the contents of the tube, attributed to the rapid reaction of iodine with the pyrrole ring. After 3 days at 5°, the pentane solutions lost this ability to release iodine. Pentane dilution of heavily oxidized pyrroles precipitated red-brown tars, which after trituration with pentane to remove unreacted pyrrole, were tested by immersing a small portion on the end of a glass rod in acidified potsssium iodide-starch solution. Each of the tars released iodine when fresh, but lost this ability after 1 week's aging at room temperature. The aged tars were further tested by mixing a small amount of each tar with a few drops of concentrated hydriodic acid in a test tube, diluting with a few milliliters of water, and adding starch indicator. The starch–iodine color was observed in every test.

The pentane-insoluble tar (15.60 g) from 1-methylpyrrole was extracted at room temperature with five successive 30-ml portions of water, the combined extracts were filtered, and water was removed by lyophilization to give 11.20 g (71.8%) of red-brown syrup, mol wt 220 (osmometer, acetone). This water-soluble tar released iodine from hydriodic acid but not from potassium iodide. The water-insoluble tar was a dark brown solid, mol wt 420 (osmometer, acetone), which did not release iodine from hydriodic acid.

**Registry No.**—VIII, 13950-21-5; IX, 1121-07-9; X, 13950-22-6; XI, 13950-23-7; 1-methylpyrrole, 96-54-8; 1-isopropylpyrrole, 7057-97-8; 1-butylpyrrole, 589-33-3.

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[25] J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, The Netherlands, 1960, p 486.

[26] I. M. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. 3, p 509.