the reaction subsided and the system had reached room temperature. The reaction mixture was worked up by distillation and trituration with ligroin to give a crystalline solid. The recrystallized product, m.p. 69°, 3.1 g., was obtained in 28% yield. The infrared spectrum of the solid coincided with that of the prepared phenyl sulfoxide. Mixture melting technique gave no depression.

Analysis of the reaction mixture, prior to distillation, by gas chromatography (10-ft. silicone column, 125°, 4 lb. He) showed the presence of *t*-butyl chloride at 3.4 min. and a trace amount of acetone at 3 min. Each of the peaks were raised by successive additions of pure samples. Gas and thin layer chromatography also verified the presence of phenyl sulfide and possibly phenyl tolyl sulfide, but no phenyl sulfone.

Phenyl Sulfide and *t*-Butyl Hypochlorite (B).—A solution of phenyl sulfide (0.054 mole, 10.0 g.) and benzene (150 ml.) was treated exactly the same as in A. The *t*-butyl hypochlorite was added slowly, and the reaction was allowed to proceed for a period of 24 hr. with an ultraviolet light source placed outside of the reaction vessel. The yield of phenyl sulfoxide was 5.15 g., 46%.

Phenyl Sulfide and *t*-Butyl Hypochlorite (C).—The reaction of phenyl sulfide and *t*-butyl hypochlorite was carried out in the dark under a nitrogen atmosphere. The reactants, in the same molar ratio as above but on smaller scale, were placed in a dark room for a period of 30 min. before the addition of the *t*-butyl hypochlorite to the solution of phenyl sulfide in benzene. The *t*-butyl hypochlorite was added and a 4-min. induction period was recorded before the exothermic reaction took place. Thin layer analysis showed the presence of phenyl sulfoxide and phenyl sulfide.

Phenyl Sulfide and Cumyl Peroxide (A).—Phenyl sulfide (0.027 mole, 5.0 g.), cumyl peroxide (0.0135 mole, 3.64 g.), and dry benzene (10 ml.) were placed in a glass ampoule which cooled to −80°, flushed with nitrogen, sealed, and heated at 135° for 8 hr. Thin layer chromatography using a 3% glacial acetic acid, 20% benzene, and ligroin solvent mixture showed the presence of phenyl sulfide and a tar which diffused over the plate. Gas chromatography (5-ft. 5% Carbowax column, 210°, 10 lb. He) indicated the presence of various products, *i.e.* phenyl tolyl sulfide, but the presence of the phenyl sulfoxide or phenyl sulfone was not detected.

Phenyl Sulfide and Cumyl Peroxide (B and C).—The reactants were as stated above in A with a change in reaction conditions. An ultraviolet light source was placed 1 in. from the flask, and the reaction was allowed to proceed for a period of 24 hr. under a nitrogen atmosphere. The analysis of the reaction mixture was carried out as stated above, but neither phenyl sulfoxide nor phenyl sulfone was detected. In reaction C, acetophenone was definitely shown to be present by gas chromatography.

Phenyl Sulfide and Cumyl Hypochlorite.—Phenyl sulfide (0.054 mole, 10.0 g.) was dissolved in benzene (150 ml.) and placed in a flask equipped with a magnetic stirrer and a condenser. The system was flushed with nitrogen. Cumyl hypochlorite (0.054 mole, 9.2 g.) prepared in a manner similar to the *t*-butyl hypochlorite, b.p. 20° (1 mm.), 90% yield, was added and the mixture was irradiated externally. Samples of the reaction mixture were removed after 14 and 24 hr. Gas chromatography (5-ft. 5% Carbowax column, 180–210°, 4–20 lb. He; 10-ft. silicone column, 214–240°, 4–20 lb. He) on two columns showed the presence of a number of products, but the phenyl sulfoxide and phenyl sulfone were not detected. Gas chromatography (10-ft. silicone column, 125°, 10 lb. He) showed the presence of acetophenone at 10.6 min. The size of the acetophenone peak, in comparison with the other products, indicated that it was one of the major products of the reaction. The peak was identified by additions of pure sample as described in previous portions of the experimental section.

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Free-Radical Reactions of Pyrroles

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The free radical resulting from hydrogen atom abstraction from the methyl group of N-methylpyrrole has been shown to dimerize, forming 1,1′-ethylenedipyrrole, and to attack the diene system of N-methylpyrrole, giving 1-methyl-3-(1-pyrrolylmethyl)pyrrole after radical chain transfer. Pyrrole under similar conditions gave 2,2′-(1′-pyrrolinyl)pyrrole. The structure of the latter product indicates that hydrogen atom abstraction occurs at the 2-position of pyrrole and that the pyrrole ring acts as an effective free-radical trap. In addition, the reactivities toward free-radical attack of a number of related compounds have been established and shown to lie in the order N-methylpyrrole > toluene > 4-picoline > benzene for the compounds examined.

Much research has been done to determine the position of attack of a free radical on organic molecules; these studies have included both addition and abstraction reactions.[2] For example, the benzene aromatics have been studied extensively in terms of addition reactions and to a limited degree in terms of abstraction reactions. In comparison, the free-radical chemistry of heterocyclic aromatics had been investigated only sparsely, with most of this work being done on pyridine. The radical addition and abstraction reactions of pyrrole have been studied to a lesser extent and, therefore, offer a fertile field for investigation.

Most of the free-radical research which has been published on pyrrole has dealt with the reactions of the pyrrole ring under thermal cleavage conditions. In 1958, Jacobsen, Heady, and Dinneen[3] studied the kinetics of the decomposition of N-methylpyrrole to a variety of products in the temperature range 477–745°. These workers suggested no mechanism for the pyrolysis reactions. Subsequent work by Patterson, Brasch, and Drenchko,[4] who repeated the experiments and extended them, implied that the pyrolyses were radical in nature. The latter workers used cycloalkyl pyrroles as illustrated, where $n = 3, 4$, and 5. The cycloalkyl pyrroles were assumed to undergo homolytic thermal cleavage of a carbon to nitrogen bond; resulting radicals were thought to follow these reaction paths (p. 1164). The same type of cleavage occurs with N-butylpyrrole as shown by Jacobsen and Jensen.[5]

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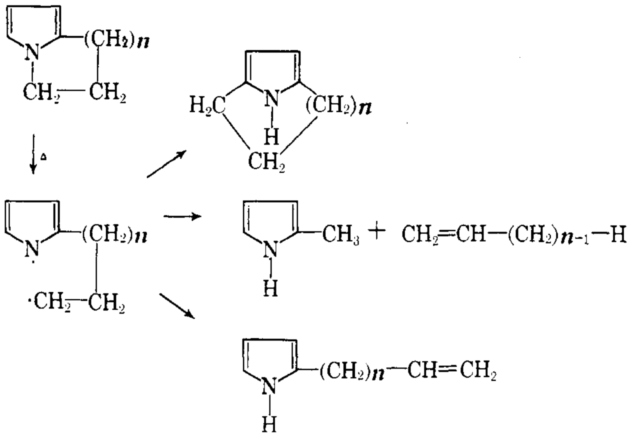
[1] (a) IBM Research Laboratory, San Jose 14, Calif.; (b) from the M.S. thesis of R. J. C., June 1963.

[2] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

[3] I. A. Jacobsen, Jr., H. H. Heady, and G. U. Dinneen, *J. Phys. Chem.*, **62**, 1563 (1958).

[4] J. M. Patterson and P. Drenchko, *J. Org. Chem.*, **27**, 1650 (1962); J. M. Patterson, J. Brasch, and P. Drenchko, *ibid.*, **27**, 1652 (1962).

[5] I. A. Jacobsen, Jr. and H. B. Jensen, *J. Phys. Chem.*, **66**, 1245 (1962).



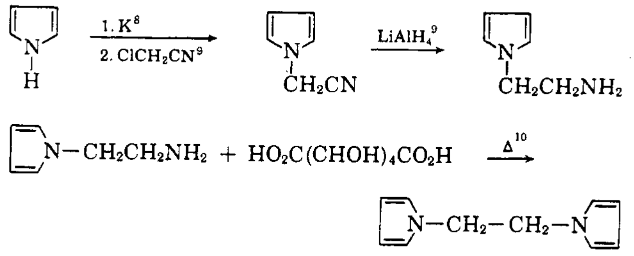
No work dealing with the positions of hydrogen atom abstraction from pyrroles has appeared in the literature, and only one discrete addition reaction has been reported. In 1933, Conant and Chow[6] reported on the reaction of the triphenylmethyl radical with various dienes. Pyrrole was chosen as one of the representative compounds because of its butadiene system. When brought into reaction with the triphenylmethyl radical, an adduct was isolated in 60% yield and by a series of degradative reactions was shown to be 2,5-bis(triphenylmethyl)-3-pyrroline. From the 1,4-addition product isolated, these authors concluded that the reaction was a more sensitive test for the diene character of pyrrole than the familiar Diels–Alder reaction with maleic anhydride, which does not give a normal adduct with pyrrole.

Comparisons are quite valuable in the study of particular areas of chemistry and especially in free-radical chemistry. Thus, N-methylpyrrole was one of the compounds chosen for study because of its similarity to toluene. *t*-Butyl peroxide was chosen as the radical source because it would produce the *t*-butoxy radical which should abstract a hydrogen atom from N-methylpyrrole and afford an intermediate free radical similar to the benzyl radical. Pyrrole itself was then considered. The absence of substituent alkyl groups would cause hydrogen atom abstraction to take place from the aromatic ring. The chemistry of the resulting pyrrolyl radical should be influenced by the presence of the nitrogen, and this effect should be evident when the reactions of the pyrrolyl radical are compared to those of the phenyl radical.

The best way of comparing the reactivities of aromatic ring hydrogen atoms with alkyl hydrogen atoms would be by an exact measurement of the rate of free-radical formation by appropriate compounds. To make this comparison, compounds were considered in pairs as follows: benzene and toluene, pyridine and 4-picoline, and pyrrole and N-methylpyrrole. Work was then directed toward obtaining a quantitative measurement of the ease of formation of intermediate free radicals from the above compounds.

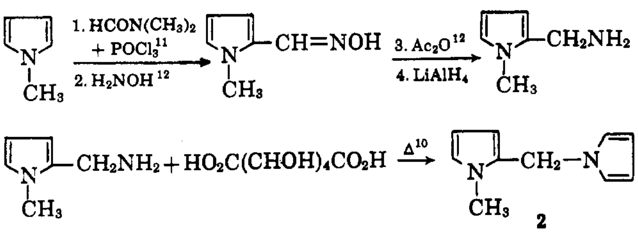
Results

The thermal decomposition of *t*-butyl peroxide in the presence of N-methylpyrrole gave two isomeric products, m.p. 60–61° and 108°. The products were isolated in 0.42% and 0.28% yield, respectively, from the polymeric materials produced in the reaction. The compound having a melting point of 108° was shown to be 1,1′-ethylenedipyrrole (**1**) by comparison with the unequivocally synthesized compound. This compound had been previously prepared by McKeever and coworkers[7] by a multistep synthesis. This started with the reaction of acetylene, cuprous chloride, formaldehyde, and bis(dimethylamino)methane to give an intermediate which, after isomerization with sodium, could be brought into reaction with ethylenediamine to give a compound which upon heating gave the pyrrole. Because of the difficulties involved in using acetylene in the above reaction, a different sequence was employed as described below.



1

The structure of the compound melting at 60–61° was deduced to be 1-methyl-3-(1-pyrrolylmethyl)pyrrole. This compound could not be directly synthesized. Its structure was shown by a comparison of the ultraviolet and infrared spectra of the product in question with those of other pyrroles and the isomeric compound 1-methyl-2-(1-pyrrolylmethyl)pyrrole (**2**). The latter compound was synthesized by the following series of reactions.



2

Several olefin addition reactions were attempted with *t*-butyl peroxide and N-methylpyrrole. In the reaction with 1-octene, no adduct could be found. The reaction was also carried out repeatedly in the presence of 1,3-butadiene with the result that only a polymeric product was found.

t-Butyl peroxide was also thermally decomposed in pyrrole. A free-radical reaction product, m.p. 162.5–163°, was isolated and shown to be 2,2′-(1′-pyrrolinyl)-pyrrole by a comparison with the same compound synthesized in an unequivocal manner. The latter synthesis involved the following steps.

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(6) J. B. Conant and B. F. Chow, *J. Am. Chem. Soc.*, **55**, 3475 (1933).

(7) M. F. Fegley, N. M. Bortnick, and C. H. McKeever, *ibid.*, **79**, 4145 (1957).

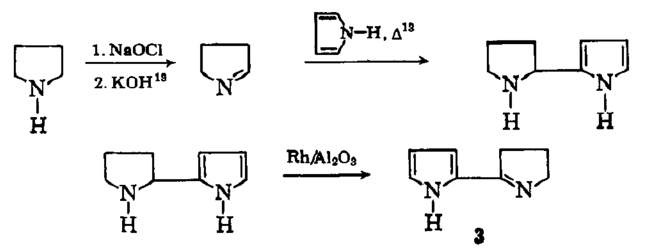
(8) G. R. Clemo and G. R. Ramage, *J. Chem. Soc.*, 49 (1931).

(9) W. Herz, D. S. Raden, and D. R. K. Murty, *J. Org. Chem.*, **21**, 896 (1956).

(10) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., Inc., New York, N. Y., 1956, p. 838.

(11) R. M. Silverstein, E. E. Ryskiewicz, C. Willard, and R. C. Koehler, *J. Org. Chem.*, **20**, 668 (1955).

(12) H. J. Anderson, *Can. J. Chem.*, **37**, 2056 (1959).



Relative reactivities toward the *t*-butoxy radical were determined for benzene, 4-picoline, toluene, and N-methylpyrrole. These were measured indirectly from the relative quantities of *t*-butyl alcohol and acetone produced in each case, as previously outlined by others.[14,15] The reactivities of the compounds examined were found to be as given in Table I.

TABLE I

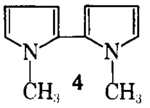
REACTIVITY OF COMPOUNDS TOWARD FREE-RADICAL ATTACKS

Compound	Obsd. *t*-butyl alcohol-acetone	Cor. *t*-butyl alcohol-acetone	Reactivity[a]	Relative reactivity
Toluene	0.743	0.658	0.162	1.00
N-Methylpyrrole	1.69	1.52	0.312	1.93
4-Picoline	0.585	0.473	0.106	0.65
Benzene	0.260	0.206	0.0227	0.14

[a] Corrected for the effect of the chromatography column.

Discussion

The lower melting product of the free-radical reaction of N-methylpyrrole and *t*-butyl peroxide was thought to be 1-methyl-2-(1-pyrrolylmethyl)pyrrole. This compound was synthesized by the series of reactions outlined above. Surprisingly, infrared spectra, thin layer chromatography, and X-ray diffraction patterns showed that the compounds in question were not identical. The infrared spectra showed, however, that the compounds were quite similar in structure. The possible nonbasic free-radical products with formula $C_{10}H_{12}N_2$ containing two pyrrole rings per molecule are as follows.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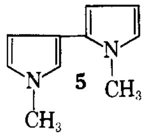
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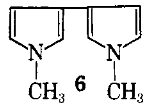
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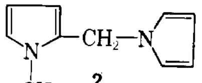
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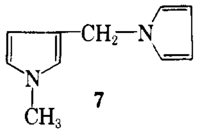
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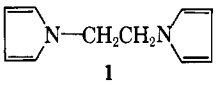
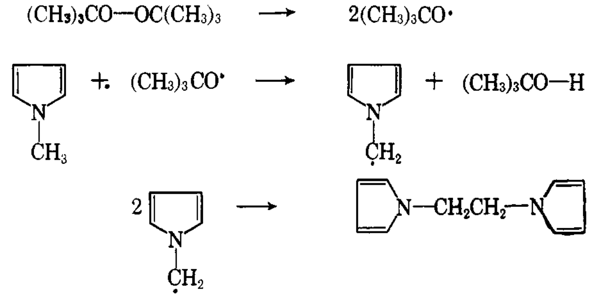

1

The compound shown by structure **1** was available, and readily discounted by a comparison of the infrared spectra. Structures **4–6** contained pyrrole rings which are conjugated with each other. The ultraviolet spectrum of 2,2′-bipyrrole was available and should have resembled the spectra of **4–6** because these structures all contained conjugated pyrrole rings.[16] The additional methyl groups in these structures would be expected to have little or no influence on the spectra of these compounds when compared to the nonmethylated compounds. Ultraviolet spectra were taken of the authentic 1-methyl-2-(1-pyrrolylmethyl)pyrrole (**2**) and of the low melting compound from the radical reaction of N-methylpyrrole. The spectra were virtually identical but not the same, and indicated the presence of two nonconjugated pyrrole rings in each molecule. These structural requirements eliminated structures **4–6**, leaving structure **7** as the only remaining possibility. Thus the identity of the low melting product was deduced to be that represented by structure **7**. The difficulties which would be encountered in the direct synthesis of 1-methyl-2-(1-pyrrolylmethyl)pyrrole (**7**) precluded a more positive means of identification.

Synthesis of the product from the pyrrole–*t*-butyl peroxide reaction was quite straightforward and was described above. It was thought that the dehydrogenation of 2,2′-pyrrolidinylpyrrole would give 2,2′-bipyrrole. If this had occurred, the free-radical product would have to be dehydrogenated to the same product to show that the compounds in question contained the same carbon skeleton. When 2,2′-pyrrolidinylpyrrole was dehydrogenated, it was found that the resulting product was identical with that which formed in the free-radical reaction. It was also shown by Rapoport[17] that the major product of the dehydrogenation of 2,2′-pyrrolidinylpyrrole was 2,2′-(1′-pyrrolinyl)pyrrole (**3**).

Discussion of Free-Radical Products

From a consideration of the two dimeric products formed, 1,1′-ethylenedipyrrole (**1**) and 1-methyl-3-(1-pyrrolylmethyl)pyrrole (**7**), it has been adequately demonstrated that the *t*-butoxy radical abstracts a hydrogen atom from the methyl group of N-methylpyrrole. This radical may then dimerize to give 1,1′-ethylenedipyrrole, a reaction similar to that which occurs when a hydrogen atom is abstracted from the alkyl group of toluene giving dibenzyl as a product. It can be inferred that the benzyl radical and the pyrrolylmethyl radical are stabilized in like manner by resonance forms involving their respective aromatic nuclei. In addition, they should both be nucleophilic in nature.[18]



The unexpected product of the *t*-butyl peroxide and N-methylpyrrole reaction, *i.e.*, 1-methyl-3-(1-pyrrolylmethyl)pyrrole (**7**), was quite interesting in view of the fact that N-methylpyrrole was alkylated in the 3-position. This is probable mechanism for its formation.

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(13) D. W. Fuhlhage and C. A. VanderWerf, *J. Am. Chem. Soc.*, **80**, 6249 (1958).

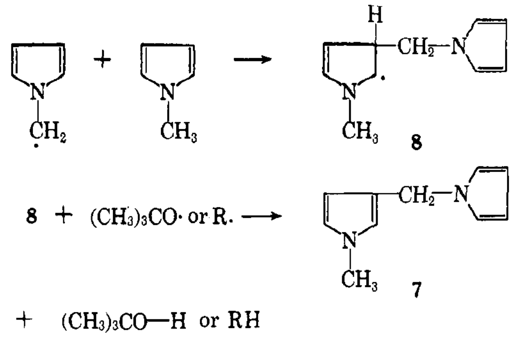
(14) K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1446 (1960).

(15) E. L. Patmore and R. J. Gritter, *J. Org. Chem.*, **27**, 4196 (1962).

(16) H. Rapoport and K. Holden, *J. Am. Chem. Soc.*, **84**, 635 (1962).

(17) H. Rapoport and N. Castagnoli, *ibid.*, **84**, 2178 (1962).

(18) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Inc., New York, N. Y., 1960, p. 66.



Roberts[19] has performed LCAO-MO calculations on pyrrole and has arrived at the following charge distributions: position 1 = +0.32, position 2 = −0.10, and position 3 = −0.06. From these values it is readily apparent that C-2 is much preferred as the position of attack by an electrophilic radical. Attack on the 3-position, as shown by the product, indicated that the pyrrolymethyl radical was nucleophilic in nature, as would be predicted.

Another interesting observation can be made concerning the reactivity of the butadiene system of pyrrole toward free-radical attack. The lack of reaction of 1-octene with *t*-butyl peroxide and N-methylpyrrole showed that the pyrrolylmethyl radical did not have sufficient reactivity to add to simple olefins typified by 1-octene. The 3-alkylated product which was isolated indicated that the pyrrole molecule was a more reactive species toward free-radical attack than an ordinary olefin.[6]

The product of the reaction of pyrrole with *t*-butyl peroxide further substantiated the proposition that the pyrrole ring is a reactive diene when in the presence of free radicals. The 2,2′-(1′-pyrrolinyl)pyrrole isolated established the fact that the *t*-butoxy radical abstracted a hydrogen atom from the 2-position of pyrrole. The resulting radical then attacked the diene system of pyrrole and gave an intermediate radical which probably chain terminated as above.

The outstanding feature of this reaction was the position of attack by the pyrrolyl radical. Attack by this radical on the pyrrole ring occurred at the 2-position and suggested an electrophilic type of radical as opposed to the nucleophilic radical implied by the 3-attack of the pyrrolylmethyl radical in the previously described reaction. This similarity to the electrophilic phenyl radical[18] adequately demonstrates that the pyrrolyl radical is electrophilic in nature.

The order found in the relative reactivities of N-methylpyrrole, toluene, 4-picoline, and benzene is in agreement with that predicted, if one considers that the electron availability from the aromatic ring will determine the stability of the resulting radical in the transition state. N-Methylpyrrole is considered to be "superaromatic" and as such would form a very stable radical.[20] Toluene behaves as a moderately reactive aromatic compound and would, therefore, be expected to give a moderately stable radical. 4-Picoline, next in order, resembles an alkylated nitrobenzene in its reactions. This compound is relatively deficient in electron availability and would be expected to give a relatively unstable radical. This, indeed, was found to be the case. The phenyl radical resulting from the hydrogen atom abstraction on benzene is one of the most unstable radicals known and would be expected to fall last in the above order.[2]

Experimental

Reagents.—The following reagents were used without further purification: acetic anhydride (Baker and Adamson reagent grade), alumina (Woelm), lithium aluminum hydride (Metal Hydrides, Inc.), mucic acid (Matheson Coleman and Bell), 1,3-butadiene (The Matheson Co.), and chloroacetonitrile (Eastman Kodak Co., White Label).

The following reagents were distilled before use through a 14-in. column equipped with a tantalum-wire spiral: *t*-butyl peroxide (Lucidol Corp., b.p. 45° at 68 mm., $n^{20}\text{D}$ 1.3892), pyrrolidine (Matheson Coleman and Bell, b.p. 88°), 4-picoline (Reilly Tar and Chemical Co., b.p. 143°, $n^{20}\text{D}$ 1.5062), xylene (Fisher Scientific Co., b.p. 140–142°), 1-octene (Matheson Coleman and Bell, b.p. 120°, $n^{20}\text{D}$ 1.4140), and toluene (Matheson Coleman and Bell, b.p. 110°, $n^{20}\text{D}$ 1.4970).

N-Methylpyrrole (Ansul Chemical Co.) and pyrrole (Ansul Chemical Co.) were dried for 4 hr. over potassium hydroxide and were distilled through a Podbielniak concentric tube column (Model No. 2208). Immediately before use, the N-methylpyrrole (b.p. 113.5–114°, $n^{20}\text{D}$ 1.4885) and pyrrole (b.p. 130°, $n^{20}\text{D}$ 1.5091) were redistilled through an 18-in. column fitted with a tantalum-wire spiral.

Free-Radical Reactions. N-Methylpyrrole and *t*-Butyl Peroxide Reactions.—N-Methylpyrrole (1.9 moles, 157.3 g.) and *t*-butyl peroxide (0.13 mole, 19.04 g.) were treated in a glass-lined stainless steel bomb for 8 hr. at 150° in a nitrogen atmosphere. The reaction mixture was distilled through a 14-in. column equipped with a tantalum-wire spiral to give a residue (13.9 g.). One-gram portions of the residue were chromatographed on 30-g. portions of basic alumina (activity grade I). Elution with benzene–pentane solvent mixtures gave two white crystalline products, m.p. 60–61° (shown to be 1,1′-ethylenepyrrole) and 108° (deduced to be 1-methyl-3-(1-pyrrolylmethyl)pyrrole), the lower melting compound being eluted first.

Anal. Calcd. for $C_{10}H_{12}N_2$: C, 74.97; H, 7.54; N, 17.49. Found (m.p. 60–61°): C, 74.80; H, 7.44; N, 17.56. Found (m.p. 108°): C, 75.11; H, 7.56; N, 17.47.

Because of the extremely small yields (0.7% based on conversion), the reaction was repeated using (a) N-methylpyrrole (1.9 moles, 148.1 g.) and *t*-butyl peroxide (0.19 mole, 27.70 g.), (b) N-methylpyrrole (1.7 moles) and peroxide (0.17 mole), and (c) N-methylpyrrole (1.1 moles) and peroxide (0.12 mole). The isolation of the products from the other three reactions was accomplished in the same manner. The yields were virtually the same in all cases, 0.42% and 0.28%, respectively.

N-Methylpyrrole, *t*-Butyl Peroxide and 1-Octene Reaction.—N-Methylpyrrole (1.9 moles, 149.3 g.), 1-octene (0.13 mole, 14.26 g.), and 5 ml. (0.03 mole) of *t*-butyl peroxide were treated as above to give a 7.0 g. residue. No product could be separated by chromatography which corresponded to the expected product.

N-Methylpyrrole, *t*-Butyl Peroxide, and 1,3-Butadiene Reactions.—The three reactants were treated in the same ratio and way as above. A residue (12.42 g.) was formed which was hydrogenated and chromatographed, but no product could be separated. When repeated with twice the amount of butadiene, polymeric material resulted.

Pyrrole and *t*-Butyl Peroxide Reactions.—Pyrrole (2.3 moles, 152.3 g.) and 5 ml. (0.03 mole) of *t*-butyl peroxide were treated in a glass liner in a stainless steel container for 8 hr. at 150° in a nitrogen atmosphere. Vacuum distillation of the reaction mixture left a residue (2.5 g.). The residue was chromatographed on basic alumina (activity grade I) using a number of solvent systems. No separation could be effected although the product became somewhat less viscous. Steam distillation gave a white crystalline compound (2.0 g., 80% yield based on the 2.5 g. of product, m.p. 162°). The product, subsequently shown to be 2,2′-(1′-pyrrolinyl)pyrrole, was sublimed at 110° at atmospheric pressure after which the melting point was raised to 163.5–164°.

Anal. Calcd. for $C_8H_{10}N_2$: C, 71.60; H, 7.51; N, 20.87. Found: C, 71.71; H, 7.54; N, 20.78.

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(19) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1961, p. 80.

(20) H. Gilman and E. B. Towne, *Rec. trav. chim.*, **51**, 1054 (1932).

The reaction was rerun under the same conditions using pyrrole (4.3 moles, 291.0 g.) and 25 ml. (0.15 mole) of *t*-butyl peroxide. Vacuum distillation left a crude residue (4.2 g.). The crude product was purified by steam distillation followed by double sublimation to give the same product. Minimum yield based on the per cent conversion to products (4.2 g.) was 75%.

Synthesis of 1,1′-Ethylenedipyrrole

Potassium pyrrole was prepared in quantitative yield[8] and treated with chloroacetonitrile in xylene to give the nitrile.[9] Reduction with lithium aluminum hydride[9] and isolation by the method of Amundsen and Nelson[21] gave the corresponding amine.

Preparation of 1,1′-Ethylenedipyrrole.[10]—Mucic acid (0.0055 mole, 1.2 g.) was neutralized with 1-(2-aminoethyl)pyrrole (0.0055 mole, 0.60 g.) dissolved in distilled water (3 ml.). The resulting solution was evaporated to dryness over a steam bath and allowed to stand for 24 hr. The salt was powdered and subjected to red heat until no more distillate was obtained. The remains were broken up and boiled in benzene (50 ml.). The benzene solution was washed several times with dilute sulfuric acid (6 *M*) and evaporated to dryness leaving a residue (0.5 g.). The residue was chromatographed using the procedure previously described for the isolation of the higher melting (m.p. 108°) product of the N-methylpyrrole and *t*-butyl peroxide reaction. Approximately 10 mg. (1.27%) of 1,1′-ethylenedipyrrole was isolated, m.p. 107.5–108°, lit.[7] m.p. 107.5–108°. The crystal structure appeared to be in the shape of a parallelogram. The infrared spectrum matched perfectly with that of the compound (m.p. 108°) isolated from the free-radical reaction.

Synthesis of 1-Methyl-2-(1-pyrrolylmethyl)pyrrole

1-Methyl-2-pyrrolecarboxaldehyde was prepared as reported[11] and its oxime immediately was prepared by the method of Anderson.[12] Hydride reduction and isolation as above[21] or reduction with sodium in ethanol (40% yield)[22] gave 1-methyl-2-(aminomethyl)pyrrole. The highly unstable amine was treated with phenyl thioisocyanate to give a thiourea, m.p. 143–144°, which was recrystallized from absolute ethanol.

Anal. Calcd. for $C_{13}H_{15}N_3S$: S, 13.07. Found: S, 12.90.

Preparation of 1-Methyl-2-(1-pyrrolylmethyl)pyrrole.—Preparation and isolation was accomplished by the sequence used for 1,1′-ethylenedipyrrole.[10] Mucic acid (0.0107 mole, 2.25 g.) was neutralized with 1-methyl-2-(aminomethyl)pyrrole (0.0213 mole, 2.35 g.) dissolved in distilled water (5 ml.). Pyrolysis of the salt gave 0.160 g. (9%) of the desired compound (m.p. 71–72°). The infrared spectrum differed from that of the compound melting at 60–61° which was isolated from the free-radical reaction of N-methylpyrrole. An X-ray diffraction pattern confirmed the nonidentity of the two compounds. The ultraviolet spectra were virtually identical and indicated that both compounds possessed the same type of conjugation. Ultraviolet absorption in 95% ethanol showed 1-methyl-2-(1-pyrrolylmethyl)pyrrole, λ_{max} 218 mμ (ϵ 13,000); product of free-radical reaction (m.p. 60–61°), λ 217 mμ (ϵ 13,600); and 2,2′-bipyrrole, λ 282 mμ (ϵ 16,700) and 277 (17,300). No elemental analysis could be obtained for the compound because of its extremely short shelf life, although thin layer chromatography indicated that the product was pure.

Synthesis of 2,2′-(1′-Pyrrolinyl)pyrrole

Preparation of 2,2′-Pyrrolidinylpyrrole.—This compound was prepared by the method of Fuhlhage and VanderWerf[13] with the modification that the sodium hypochlorite used was prepared by the reaction of sodium carbonate on 70% calcium hypochlorite (Pittchlor). This sequence gave 7.0 g. of 2,2′-pyrrolidinylpyrrole, m.p. 85°, lit.[13] m.p. 84–86°, in 20% yield.

Preparation of 2,2′-(1′-Pyrrolinyl)pyrrole.—A mixture of 2,2′-pyrrolidinylpyrrole (0.0585 mole, 0.796 g.), 5% rhodium on alumina (0.786 g.), and cumene (20 ml.) were placed in a flask with a reflux condenser and magnetic stirrer. The mixture was heated under reflux with vigorous stirring under a stream of nitrogen for 12 hr. The resulting mixture was poured into a chromatography column containing 30 g. of neutral alumina (activity grade III). Elution with benzene–chloroform (3:1) gave 0.64 g. (82%) of the desired compound melting at 163–164° after sublimation (110°). The reported[17] m.p. is 162–163°. The infrared showed strong C=N bands at 1630 cm.$^{-1}$. The ultraviolet spectrum (95% ethanol) of the prepared compound gave λ 279 mμ (ϵ 16,500).

Determination of the Relative Reactivities

Each of the compounds used in this determination was distilled through a 14-in. column fitted with a tantalum-wire spiral immediately before use. Purity was established by gas chromatographic analysis.

The following procedure was used for each compound studied. A standard solution of *t*-butyl peroxide in benzene was prepared (7.64% *t*-butyl peroxide by weight). A standard amount (5 ml.) of this solution and the individual compound was pipeted into a Pyrex ampoule. The sample was cooled in a chloroform–carbon tetrachloride–Dry Ice-cooling bath, flushed with nitrogen, and sealed. The sample was placed in an oil bath at 150 ± 0.2° for approximately 12 hr., which corresponds to at least 99% decomposition of the peroxide. At the end of this time the sample was removed, allowed to cool, and placed in the Dry Ice mixture. After solidification was complete, the sample was removed, its seal was broken, and its warmed contents were analyzed by gas chromatography. The ratio of *t*-butyl alcohol to acetone was obtained by determining the ratio of counts of the alcohol and acetone peaks from the chromatogram obtained using a recorder equipped with a Disc-Integrator. The concentration of the compound was calculated from the known weights and from the density at 150°.

It was observed that experimentally determined values for alcohol to acetone ratios resulting from an analysis of known ratios did not correspond exactly to the calculated values. The magnitude of the variation depended upon the nature of the chromatography column and upon the nature of the mixture in which the alcohol and acetone were found. The following procedure was used for each compound studied, to determine the effect of the compound and column on the ratios determined above. From the molar ratio of alcohol to acetone observed, the gram ratio was calculated. A known ratio was prepared corresponding exactly to the observed ratio. A portion of this prepared ratio was added to benzene such that the alcohol–acetone portion of the mixture comprised approximately 7% of the total solution by weight. To the solution of benzene, alcohol, and acetone was added an equal volume of the appropriate compound. A sample of the final solution was transferred to a Pyrex ampoule and the ampoule was cooled, sealed, heated, and analyzed in exactly the same manner as previously described. The results of the ratio determinations are summarized in Table I.

Gas Chromatography Conditions.—The gas chromatographic unit (Aerograph Master A-100, Wilkens Instrument and Research, Inc., Walnut Creek, Calif.) was equipped with a Leeds and Northrup recorder (S-60,000) with a Disc-Integrator (Model K-3, Disc Instrument Co.). The gas chromatographic unit was operated under the following conditions: Ucon polyethylene-glycol column, 1-mv. recorder range, 7.5-lb./in.^{2} helium pressure, 200-ma. filament current, and 103–105° temperature oven.

Determination of Volume Change of Samples with Temperature.—The volume expansions with temperature (20–150°) of the compounds used in this study were determined by an extrapolation of the results of the work of Patmore and Gritter[15] whose values were determined in the range 25 to 135°. Patmore[15] found 12% average expansion; extrapolation gave 14%.

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