prepared by oximation of the quinone and probably arises from contamination by a small quantity of diazo oxide. It could not be removed by recrystallization. No band appears in this region for any other compound examined.

Region 1667–1538 cm.$^{-1}$. Yates, Ardao, and Fieser[8] have discussed the spectra of *p*-benzoquinones between five and fifteen microns (2000–667 cm.$^{-1}$). They assign absorptions in the 5.97–6.14μ (1675–1629 cm.$^{-1}$) region to the carbonyl stretching vibration and observe that this band is split into two bands in some instances. All of our compounds show a strong band in the range 1645–1626 cm.$^{-1}$ which is probably the carbonyl absorption. In three cases a second weaker band at 1656–1647 cm.$^{-1}$ appears. This band is probably the C=N stretching vibration. The C=N band varies in intensity and position[9] and failure to identify this band in all compounds is not surprising.

Yates *et al.*[8] assign bands in the 6.17–6.49μ (1621–1543 cm.$^{-1}$) region to C=C stretching. All of our compounds show a medium to strong band between 1567 cm.$^{-1}$ and 1550 cm.$^{-1}$ which we assign to the C=C stretching. In the alkyl substituted compounds and in the addition complex an additional band is present at 1608–1600 cm.$^{-1}$.

Region 1538–667 cm.$^{-1}$. Numerous bands occur in this region. The majority cannot be assigned to any definite structural feature. Yates *et al.*[8] observe that quinones with an isolated hydrogen atom on the ring show a medium to strong band in the 10.8–11.4μ (926–877 cm.$^{-1}$) region in the solid state. The same feature is present in our spectra. *p*-Benzoquinone-4-oxime has no band in this region. The same authors report that carbon disulfide solutions of compounds having adjacent hydrogen atoms on the ring show a band at 11.9–12.4μ (840–807 cm.$^{-1}$). They do not report a band in this region in most of their solid state spectra. In the quinone oximes studied all compounds with adjacent hydrogen atoms on the ring show a medium to strong band in the 826–794 cm.$^{-1}$ region. This band is absent in compounds without adjacent hydrogens.

In the region from 769 cm.$^{-1}$ to 667 cm.$^{-1}$ only very shallow, very broad absorptions are present. The spectra are immediately recognizable as nonaromatic in character.

Conclusion. The bands which are characteristic of aromatic structures at 2000 cm.$^{-1}$ to 1660 cm.$^{-1}$, at 1600 cm.$^{-1}$ to 1500 cm.$^{-1}$, and from 1200 cm.$^{-1}$ to 667 cm.$^{-1}$ could not be identified in these compounds. This fact coupled with the presence of the carbonyl absorption and the olefinic absorption together with the close over-all similarity to the spectra of *p*-benzoquinones makes it almost certain that the structure of these compounds in the solid state is quinoid. There appears to be no justification for the assignment of a nitroso phenol structure.

Acknowledgment. The author wishes to express his appreciation to Dr. H. H. Jaffe for a very helpful discussion of this probelm.

CHEMISTRY DEPARTMENT
UNIVERSITY OF GEORGIA
ATHENS, GA.

---

[8] P. Yates, M. A. Ardao, and L. Fieser, *J. Am. Chem. Soc.*, **78**, 650 (1956).

[9] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 1st. Ed., John Wiley and Sons, Inc., New York, 1954, p. 226.

Structures of 4-Nitro- and 5-Nitro-2-propionylpyrroles

THOMAS S. GARDNER, E. WENIS, AND JOHN LEE

Received November 5, 1958

In a previous paper,[1] the structure 5-nitro-2-propionylpyrrole was suggested for the product, m.p. 100–101°, prepared by nitrating 2-propionylpyrrole. The assignment of structure was based on a negative Ehrlich test which usually indicates complete substitution in the α-positions in pyrrole compounds.

It has been pointed out to us by Professor H. J. Anderson[2] that the work of Rinkes[3] and Anderson[4] would indicate that nitration would more likely occur preferentially in the 4- than in the 5-position. Further examination of our product confirms this prediction. Extraction of a sodium carbonate solution of the nitration product with ether[3] yields a larger proportion of a less acidic 4-nitro-2-propionylpyrrole, m.p. 136–137° and on acidification a lesser amount of more acidic 5-nitro-2-propionylpyrrole, m.p. 134–135°. Mixed m.p. of roughly equal proportions, 102–104°.

Both the mono nitro-2-propionylpyrroles fail to give the Ehrlich test given by the parent substance, 2-propionylpyrrole. Similarly, 4-nitro and 5-nitro-2-acetylpyrrole failed to give the Ehrlich test, while the parent substance, 2-acetylpyrrole, gave a positive test.

The assignment of structure above follows Rinkes[3] and is further supported by an absolute proof of structure. Rinkes[3] states that acidity of the nitration products of 2-acetyl- or 2-carboxyethylpyrrole is determined by the proximity of the nitro group to the acidic NH, the closer the group the more acidic the product. However, there does not appear to be any absolute proof to support this reasonable assertion.

---

[1] T. S. Gardner, E. Wenis, and J. Lee, *J. Org. Chem.*, **23**, 823 (1958).

[2] H. J. Anderson, private communication, July 12, 1958.

[3] I. J. Rinkes, *Rec. trav. chim.*, **53**, 1167 (1934).

[4] H. J. Anderson, *Can. J. Chem.*, **35**, 21 (1957).

The relationship of the pair, 4-nitro-2-propionylpyrrole [maxima at 247 mμ (log ϵ = 4.16); 300 mμ (log ϵ = 3.89); minimum at 278 mμ (log ϵ = 3.77)] and 4-nitro-2-acetylpyrrole [maxima at 245 mμ (log ϵ = 4.15) and 299 mμ (log ϵ = 3.81); minimum at 278 mμ (log ϵ= 3.80)], is established by the practical superposition of their ultraviolet spectra as is also that of 5-nitro-2-propionylpyrrole [maxima at 240 mμ (log ϵ = 4.03), 3.28 mμ (log ϵ = 4.15); minimum at 265 mμ (log ϵ = 3.38)] and 5-nitro-2-acetylpyrrole [maxima at 239 mμ (log ϵ = 4.00); 328 mμ (log ϵ = 4.11) and minimum at 264 mμ (log ϵ = 3.34)].

The structure of 1-methyl-4-nitro-2-pyrrolecarboxylic acid, m.p. 199–200° has been related to that of 4-nitro-2-acetylpyrrole by Anderson.[4] The synthesis of the ester of this acid by an unequivocal method has been reported.[5] This, on saponification, gave 1-methyl-4-nitro-2-pyrrolecarboxylic acid,[4] m.p. 199–200°. Decarboxylation of this acid gave 1-methyl-3-nitropyrrole,[4] m.p. 63–64°. This represents an absolute proof of the structures of all the nitro-2-acylpyrroles described.

EXPERIMENTAL[6]

4-Nitro-2-propionylpyrrole. The mixed 4-nitro and 5-nitro-2-propionylpyrroles (5.15 g.) previously reported as 5-nitro-2-propionylpyrrole[1] were dissolved in 300 ml. of 10% sodium carbonate solution and extracted ten times with 100 ml. portions of ether. The combined ether extracts were concentrated to a solid and crystallized from boiling water to yield very pale yellow crystals; yield, 2.02 g., m.p. 136–137°.

Anal. Calcd. for $C_7H_8N_2O_3$: C, 50.0; H, 4.8. Found: C, 50.3; H, 4.9.

5-Nitro-2-propionylpyrrole. The sodium carbonate solution after the extraction of the 4-nitro-2-propionylpyrrole was acidified using 10% sulfuric acid solution. The acidified solution was then extracted ten times with ether as previously described and the combined ether extracts concentrated to a solid. The solid residue was crystallized from boiling water to give yellow fibrous needles; yield, 0.975 g., m.p. 134–135°.

Anal. Calcd. for $C_7H_8N_2O_3$: C, 50.0; H, 4.8. Found: C, 50.5; H, 5.1.

A mixed melting point of the separated 4-nitro- and 5-nitro-2-propionylpyrroles was 102–104°. The melting point of the previously reported[1] unseparated isomers was 100–101°.

4-Nitro-2-propionylpyrrole semicarbazone. 4-Nitro-2-propionylpyrrole (3.0 g.), 4.0 g. of sodium acetate, and 4 g. of semicarbazide hydrochloride were dissolved in 100 ml. of warm water. After standing for 20 days, fine yellow needles had separated which were recrystallized from hot water; yield, 2.4 g., m.p. 229–230°.

Anal. Calcd. for $C_8H_{11}N_5O_3$: C, 42.7; H, 4.9. Found: C, 42.8; H, 4.6.

5-Nitro-2-propionylpyrrole semicarbazone. 5-Nitro-2-propionylpyrrole (0.98 g.) was treated with 1.0 g. of sodium acetate and 1.5 g. of semicarbazide hydrochloride in 100 ml. of 25% ethanol water solution. After standing for 20 days the yellow-orange product separated and was recrystallized from hot water; yield, 0.9 g., m.p. 211–212°.

Anal. Calcd. for $C_8H_{11}N_5O_3$: C, 42.7; H, 4.9. Found: C, 42.4; H, 4.7.

A mixed melting point of the 4-nitro- and 5-nitro-2-propionylpyrrole semicarbazones was 203–205°. The previously reported[1] semicarbazone of the unseparated isomers was 203–204°.

Acknowledgment. We are indebted to Dr. Al Steyermark and his associates for the microanalyses and Messrs. A. Motchane and S. Traiman for the ultraviolet spectra.

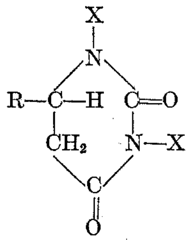
HOFFMANN-LAROCHE, INC.
ROCHE PARK
NUTLEY, N. J.

Chemistry of Hydrouracils. 1,3-Dihalohydrouracils

FRANK B. SLEZAK, ALFRED HIRSCH, LEWIS I. KRIMEN,[1] AND HENRY A. MCELRAVY, JR.

Received November 6, 1958

During the course of investigating the chemical and biological activity of various *N*-halogen compounds, the preparation of a number of heretofore unknown 1,3-dihalohydrouracils became of interest to us.



R = H, CH_3
X = Br, Cl

It was found that the efficiency of the halogenation in an aqueous medium was dependent on the *p*H at which the halogenation was carried out. Chlorination gave fair results (30–40% yield) when the reactions were carried out at a *p*H greater than 7 and gave good results (70–80% yield) when the reaction bath was maintained in the range *p*H 1–3. Bromination, on the other hand, was carried out successfully only at a *p*H greater than 4.

1,3-Dichlorohydrouracil, in concentrations as low as 1 p.p.m., completely inhibited the growth of the test organisms *Erwinia amylovora*, *Xanthomonas phaseoli*, *Micrococcus pyogenes* var. *aureus*, and *Escherichia coli*.[2] 4-Methyl-1,3-dichlorohy-

---

(5) M. J. Weiss, J. S. Webb, and J. M. Smith, *J. Am. Chem. Soc.*, **79**, 1266 (1957).

(6) All melting points are corrected.

(1) Present address: International Minerals and Chemical Corporation, Skokie, Ill.

(2) Biological data by Boyce Thompson Institute for Plant Research, Inc., Yonkers, N. Y.