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# THE AUTOXIDATION OF ALKYLPYRROLES*

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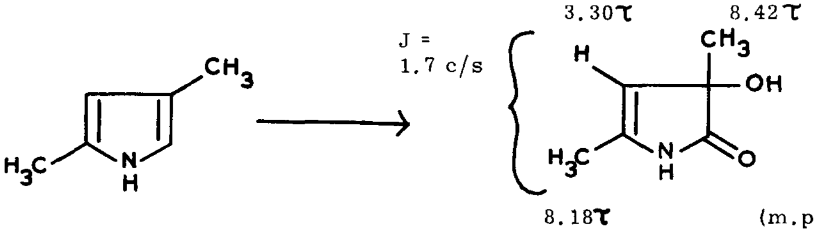
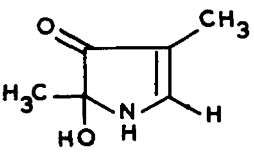
Despite the importance of pyrroles, and their well-known sensitivity to aerial oxidation, relatively little has been accomplished on the assignment of structures to the autoxidation products of simple alkyl derivatives, and the published work is in error (1). Study of the autoxidation of 2,4-dimethyl-, 2,3,4-trimethyl-, and 2,4-dimethyl-3-ethylpyrrole now shows that products of at least three types can be formed in such reactions. Structures (2) were assigned on spectral evidence; NMR chemical shifts (p.p.m. on tau scale) and coupling constants are indicated on the formulae.

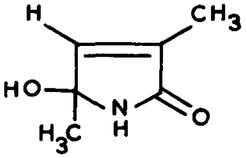


I

II (m.p. 149 - 151°; NMR in $D_2O$)

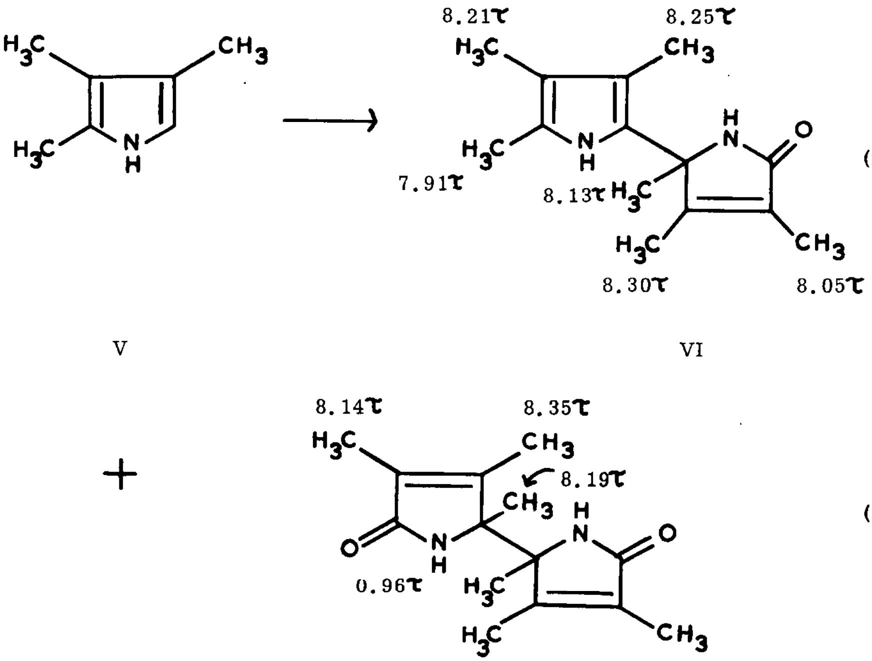


III



IV

2,4-Dimethylpyrrole (I) was oxidised by passing oxygen through a benzene solution of (I), until 1 mole equivalent of the gas was absorbed. The benzene was removed by vacuum distillation, and an ethanol solution of the residue eluted from an alumina column to yield (II). The UV spectrum (in water) showed only a maximum at 204 mμ ( ε 14,150) which supports structure (II) and eliminates the alternatives (III) or (IV), which would satisfy the NMR evidence but should have maxima at higher wave lengths. The IR spectrum of (II) (KBr disc) discloses peaks at 3200 $cm^{-1}$ (s) ( ν bonded OH), 1695 $cm^{-1}$ (s) ( ν C=O), and 1650 $cm^{-1}$ (m) ( ν C=C).



V

VI

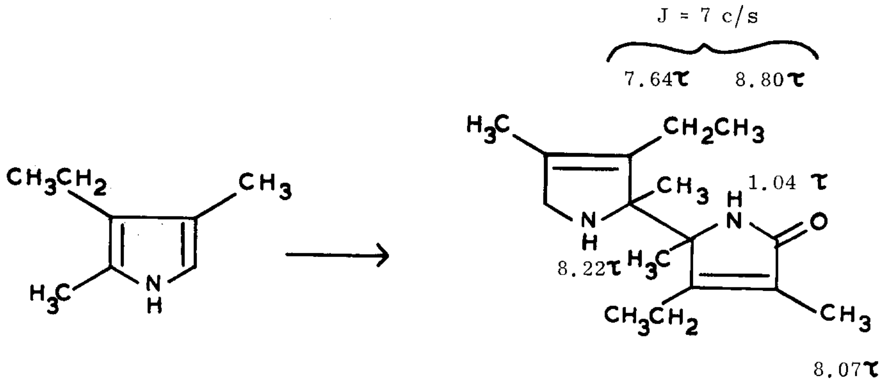
(m.p. 265 - 270°; NMR in $CDCl_3$)

VII

(m.p. 259 - 260°; NMR in $CF_3COOH$)

2,3,4-Trimethylpyrrole (V) in benzene was shaken with oxygen until one mole was absorbed. The pyrrolyl-pyrrolone (VI) formed a crystalline precipitate : the six distinct methyl peaks shown in the NMR spectrum (at 100 Mc/s) (the assignment shown in VI is tentative) show that the pyrrole rings are non-equivalent. Structure (VI) is supported by the IR spectrum : 3320 cm$^{-1}$ (s) and 3260 cm$^{-1}$ (s) ( ν N-H), 1675 cm$^{-1}$ (s) ( ν C=O), and 1605 cm$^{-1}$ (m) ( ν C=C), and by the UV spectrum : λ max 215 mμ ( ε 27,600).

Compound (VII) crystallised from the mother liquors from (VI) after long standing : its structure is shown by the NMR, IR spectrum 3200 cm$^{-1}$ (s) ( ν N-H), 1675 cm$^{-1}$ (s) ( ν C=O), and by the UV spectrum : λ max 214 mμ ( ε 27,200).



VIII

IX

(m.p. = 212 - 214°; NMR in $CF_3COOH$

2,4-Dimethyl-3-ethylpyrrole (VIII) on treatment as for the trimethyl-analogue, gave only the dipyrrolone (IX). The spectral data of (IX) show the expected similarity to (VII). IR spectrum : 3180 cm$^{-1}$ (s) ( ν N-H), 1675 cm$^{-1}$ (s) ( ν C=O). UV spectrum : λ max 216 mμ ( ε 27,000).

Published UV and IR data for pyrroles (e.g. ref. 3) are in good agreement with the above assignments. Bipyrrolones analogous to (VII) and (IX) have recently been synthesised by v. Dobeneck and Brunner (4) and show similar UV characteristics.

Acknowledgement. We thank Professor A. Rieche (Berlin) for his interest in this work.

## References

* Applications of Proton Magnetic Resonance Spectra to Structural Problems Part XXIX; for Part XXVIII, see J.S.G.Cox, C. Fitzmaurice, A. R. Katritzky and G. J. T. Tiddy, J. Chem. Soc. (B) (1967) (in press).

1. W. Metzger and H. Fischer (Liebig's Annalen, **527** (1936) ) carried out reactions (I → II) (V → VII) and (VIII → IX), but assigned product (II) a dihydroxypyrroline structure and (V I) and (IX) dipyrryl peroxide structures. The dipyrryl peroxide structures were apparently accepted by J.H.Atkinson, R.S.Atkinson and A.W. Johnson (J.Chem.Soc., 5999 (1964) ) who obtained the same products.
2. All products gave satisfactory analytical data for C, H, N.
3. H. Plieninger, H. Bauer, A. R. Katritzky and U. Lerch, Liebig's Annalen, **654**, 165 (1962).
4. H. v. Dobeneck and E. Brunner, Hoppe Seyler's Z. physiol. Chem., **340**, 200 (1965).