

DIMERIZATION OF 4-METHYLFLAVYLIUM CATION WITH PYRIDINE

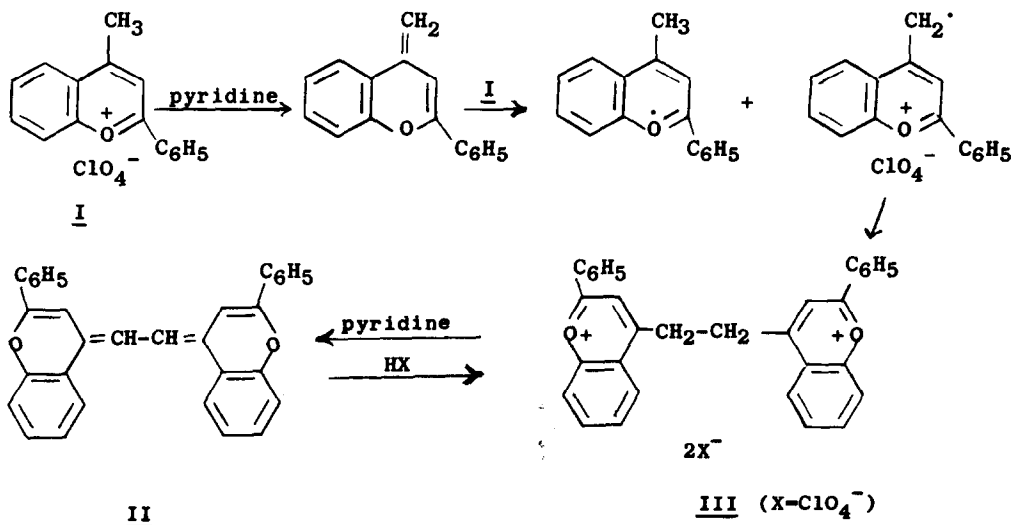
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(Received in USA 27 February 1969; received in UK for publication 29 April 1969)

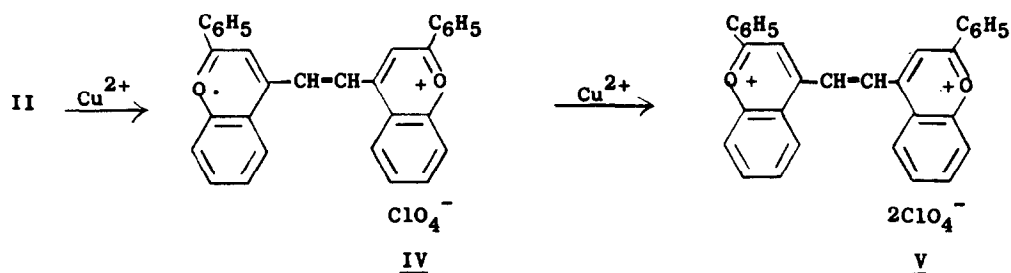
The recent report (1) that 2,4,6-trimethylpyrylium perchlorate and pyridine gave an insoluble methylene base prompts us to publish our results for a similar reaction with 4-methylflavylium perchlorate (I). We have found that brief heating of a solution of I in pyridine gave a dimer of the methylene base which has been assigned structure II: mp 279-280°; mass spectrum M m/e 438, m/e 219, m/e 105, m/e 102, m/e 77 (2). The dimer was shown to have structure II, rather than a structure similar to the dimer of the methylene base of 2,3-dimethylbenzothiazolium salts (3), by the nmr spectrum. II was readily protonated and its 60 Mhz nmr spectrum in CF₃CO₂H showed that the protonated species III (X=CF₃CO⁻) was formed: singlet δ 2.63 (4 H); multiplet δ 6.13 - 7.16 (20 H). Other salts of III are readily prepared from II and strong acids.

It has been established that oxygen is not involved in the formation of II from I and pyridine, since 45-48% yields of II were obtained in the presence and absence of oxygen. We feel that an electron-transfer mechanism will best explain the formation of the dimer, and the following mechanism is proposed. We have not been able to identify the other 50% of the reaction



products which should be formed from the neutral radical. This material shows ir absorption that is identical with a sample of material obtained by the reduction of I with zinc (4), but all evidence indicates that the products from both reactions are mixtures.

Cyclic voltimetric oxidation of II ($5 \times 10^{-4} M$ in benzonitrile) proceeds by two one electron processes to give a relatively stable cation radical (IV) and a di-cation (V): Ref. S.C.E. Pt indicating electrode; $E^1_p = +0.40v$, $E^2_p = 0.57v$ (5). The di-cation V (explodes at 275°) was synthesized in good yield from II and two equivalents of $Cu(ClO_4)_2 \cdot 6H_2O$. Addition of V to a solution of II in benzonitrile gave the deep blue IV which slowly faded on standing. The reactions which have



been described are quite general for flavylum and thiaflavylum derivatives and further work with these compounds will be described at a later date.

Acknowledgement. We are indebted to Dr. J. C. Chang for the determination of half-wave potentials, Mr. D. P. Maier for the determination of the mass spectrum, and Dr. T. H. Regan for the determination of the nmr spectrum.

References

- (1) D. Farcasu and E. Gard, Tetrahedron 24, 4741 (1968).
- (2) All compounds reported in this article gave satisfactory elemental analysis.
- (3) J. Metzger, H. Larive, E. Vincent and R. Dennilauler, J. Chim. Phys. 60, 944 (1963).
- (4) G. A. Reynolds, J. A. VanAllan, and T. H. Regan, J. Org. Chem. 32, 3772 (1967).
- (5) For other reversible redox systems of this type see S. Hunig and G. Ruider, Tetrahedron Letters, 773 (1968).