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OXIDATION OF 1-SUBSTITUTED 2,4,6-TRIPHENYLPYRIDINIUM SALTS

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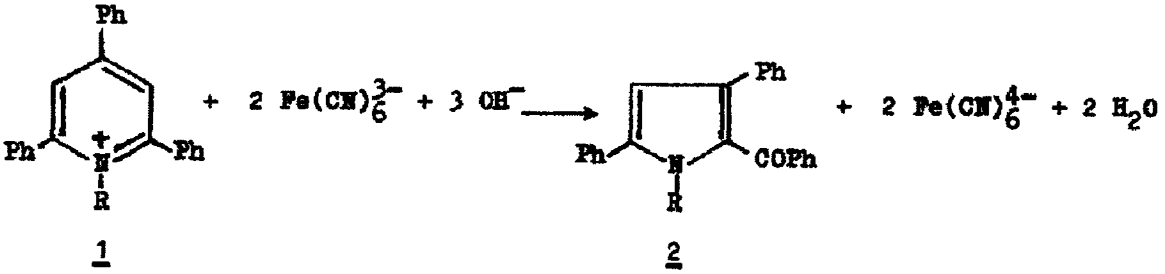
Abstract: During the oxidation of 1,2,4,6-tetrasubstituted pyridinium salts 1 with potassium hexacyanoferrate(III) in alkali medium a contraction of pyridine ring is observed leading to 1,2,3,5-tetrasubstituted pyrroles 2.

It is well known[1,2] that the oxidation of quaternary pyridinium salts possesing at least one unsubstituted alpha position with potassium ferricyanide in alkali proceeds via the corresponding pseudobases to give different 2-,4- or 6--pyridones, respectively. On the other hand, no reports on the interaction of hexacyanoferrate(III) anion with pyridinium cations completely substituted by aryl groups in 2-,4- and 6-positions have been found in the literature. In this communication we wish to report that 1-substituted 2,4,6-triphenylpyridinium cations 1 are easily oxidized to 1-substituted 2-benzoyl-3,5-diphenylpyrroles 2 according to eq.:

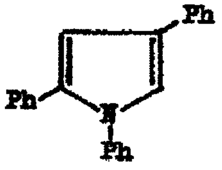


The transformations 1→2 proceed very rapidly at the temperatures 40 to 60°C and the products 2 are isolable without difficulties. As typical example of the experimental procedures the preparation of 2-benzoyl-1,3,5-triphenylpyrrole (2d) is demonstrated: A solution of potassium hexacyanoferrate(III) (3.95 g) and potassium hydroxide (1.0 g) in water (10 ml) was added to a solution of 1,2,4,6--tetraphenylpyridinium tetrafluoroborate (2.36 g) in hot ethanol (80 ml). After five minutes heating chloroform (50 ml) was added, the reaction mixture was filtered and evaporated in vacuum. The residue gave the product 2d (1.5 g) after treatment with water and after filtration. The substance 2d was found to be identical with the product of Friedel-Crafts benzoylation of the known[3] 1,2,4-triphenylpyrrole(3) in accord with the assigned general structure 2 for all further products of the ferricyanide oxidations (see Table).

Table: 1-R-2-Benzoyl-3,5-diphenylpyrroles 2[a)]

	R	Yield,%	mp,°C	^{1}H-NMR ($CDCl_3$, TMS_{int}), δ ppm
2a	Me	71	163-5	3.8(s,3H,CH_3N),6.3(s,1H,HC=),6.9-7.6(m,15H,aromat.
2b	Et	80	100-1	1.17(t,3H,CH_3),4.37(q,2H,CH_2),6.32(s,1H,HC=),6.9-7 (m,15H,aromat.H)
2c	$PhCH_2$	73	165-6	5.63(s,2H,CH_2),6.44(s,1H,HC=),6.8-7.6(m,20H,aromat
2d	Ph	75	177-8[b)]	6.65(s,1H,HC=),7.0-7.75(m,20H,aromat.H)
2e	p-MeC_6H_4	97	200-1	2.28(s,3H,CH_3),6.57(s,1H,HC=),6.9-7.8(m,19H,aromat
2f	p-FC_6H_4	91	190-1	6.58(s,1H,HC=),6.8-7.7(m,19H, aromat.H)

a) All substances exhibit satisfactory elemental analyses and correct IR and M characteristics; b) 13-C-NMR spectrum is in agreement with structure 2d.



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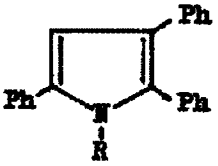

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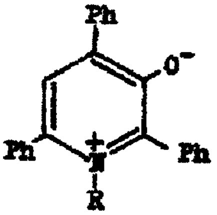

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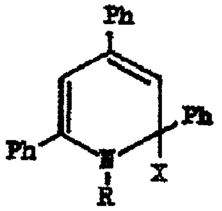

6: X=O_2H

7: X=OFe$(CN)_6$

It is noteworthy that the hydrogen peroxide oxidation of quaternary salts 1 has been recently found[4] to proceed differently giving either pyrrole derivativ 4 or pyridinium betaines 5 via the key-intermediate 6. In our case other dihyd pyridine intermediate 7 might be probably responsible for a change of the reaction path from cations 1 to products 2. Further investigations on the reaction mechanism as well as on the chemical properties of the compounds 2 are in progress and will be published elsewhere.

REFERENCES

1. H. Meislich, Pyridine and Its Derivatives (ed. E. Klinsberg), Part Three, p.596, Interscience Publ., New York, 1962.
2. H. Tieckelmann, ibid.(ed. R. A. Abramovitch), Volume 14, Supplement, Part 3, p.706, Interscience Publ., New York 1974.
3. A. Padwa, R. Gruber and D. Pashayan, J.Org.Chem. 33, 454 (1968).
4. A.R. Katritzky, Ch.A. Ramsden, Z. Zakaria, R.L. Harlow and S.H. Simonsen, J.Chem. Soc., Chem.Commun. 1979, 363.

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