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INTERMEDIACY OF FERROCENIUM ION IN OXIDATION OF FERROCENYLDIHYDROPYRIDINE WITH DDQ

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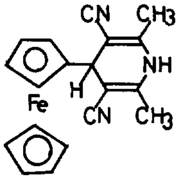
Ferrocene has been known to form charge transfer complex or ionic compound with dichlorodicyanobenzoquinone(DDQ) or chloranil.[1)] Recently we have reported the oxidation of ferrocene with quinones in the presence of aluminium chloride.[2)] On the other hand dihydropyridines have been noted as a model compound of NAD and are known to be oxidized by chloranil or other quinones.[3)] It is of interest to clarify the mode of oxidation of a compound which contains both ferrocene and dihydropyridine nuclei.

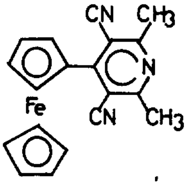
Ferrocenyldihydropyridine(I) was synthesized by the condensation of formylferrocene[4)] with diacetonitrile in acetic acid under nitrogen at 118° for one hour, m.p. 186-7°; Anal. Calcd. for $C_{19}H_{17}FeN_3$ C: 66.45, H: 4.99, N: 12.25, Found. C: 66.36, H: 5.03, N: 12.21; i.r. ν_{max}^{KBr} 3310, 3260, 2200, 1660cm^{-1}; n.m.r. δ(acetone-d_6) 2.11(6H,s), 2.85(1H,s), 4.14, 4.23(10H,s); u.v. λ_{max}^{EtOH}nm(ε): 330(5400), 430(160).

Oxidation of (I) with chloranil in benzene at 80° under nitrogen gave

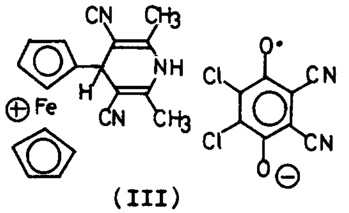
(II), m.p. 211.5-212.5°; Anal. Calcd. for $C_{19}H_{15}FeN_3$ C: 66.88, H: 4.43, N: 12.32, Found. C: 67.00, H: 4.41, N: 12.40; i.r. ν_{max}^{KBr} 2230, 1530cm^{-1}; n.m.r. $\delta(CDCl_3)$ 2.81(6H,s), 4.29(5H,s), 4.65(2H,m), 5.26(2H,m); u.v. λ_{max}^{EtOH} nm(ε) 240(24000), 255(17000), 305(11000), 385(1600), 510(1400).



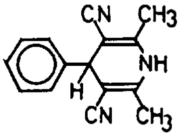
(I)



(II)



(III)

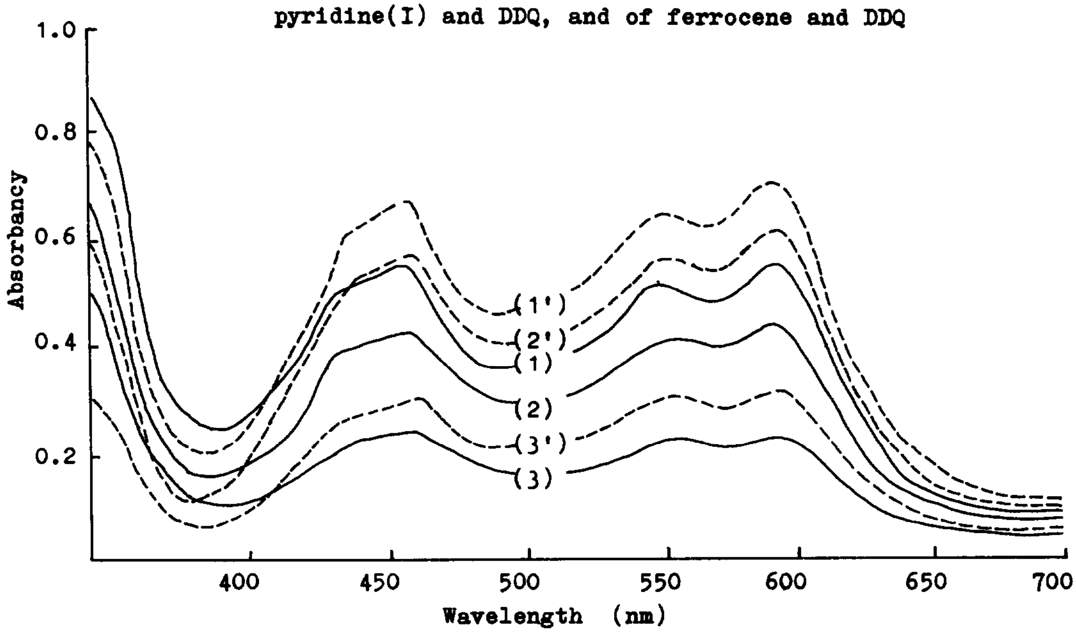


(IV)

When (I) was treated with DDQ in acetonitrile at room temperature, the formation of anion radical of DDQ was demonstrated by visible absorption spectra, shown in Fig.1. The visible absorption spectra of ionic compound of ferrocene and DDQ$^{1)}$ are also shown. The similarity in shapes of the curves of ionic compound of (I) and DDQ and that of ferrocene and DDQ reveals that ionic bonding is formed between ferrocene nucleus of (I) and DDQ as shown in (III). When phenyldihydropyridine(IV) was treated in the same procedure as in the case of (I), visible absorption spectrum was not detected. This fact rejects the possibility of the formation of bonding between dihydropyridine nucleus in (I) and DDQ.

After (I) was treated with equimolar amount of DDQ in acetonitrile, the change of visible spectrum of the ionic compound was checked with time intervals as shown in Fig.2, from which it can be speculated that the ionic compound gradually changed to (II) and dichlorodicyanohydroquinone. These experiments support the intermediacy of the ionic compound in the oxidation reaction of (I) with DDQ. The intermediacy of the ionic compound could not be observed if benzene was used instead of acetonitrile. This is in accord with the speculation that benzene prevents formation of the ionic compound of (I) and DDQ. The compound (I) also could not form the ionic compound with DDQ in the same condition as in Fig.1 and 2.

Fig.1 Visible absorption spectra of the ionic compound of 3,5-dicyano-2,6-dimethyl-4-ferrocenyl-1,4-dihydropyridine(I) and DDQ, and of ferrocene and DDQ



——— absorption of mixture, (I) and DDQ

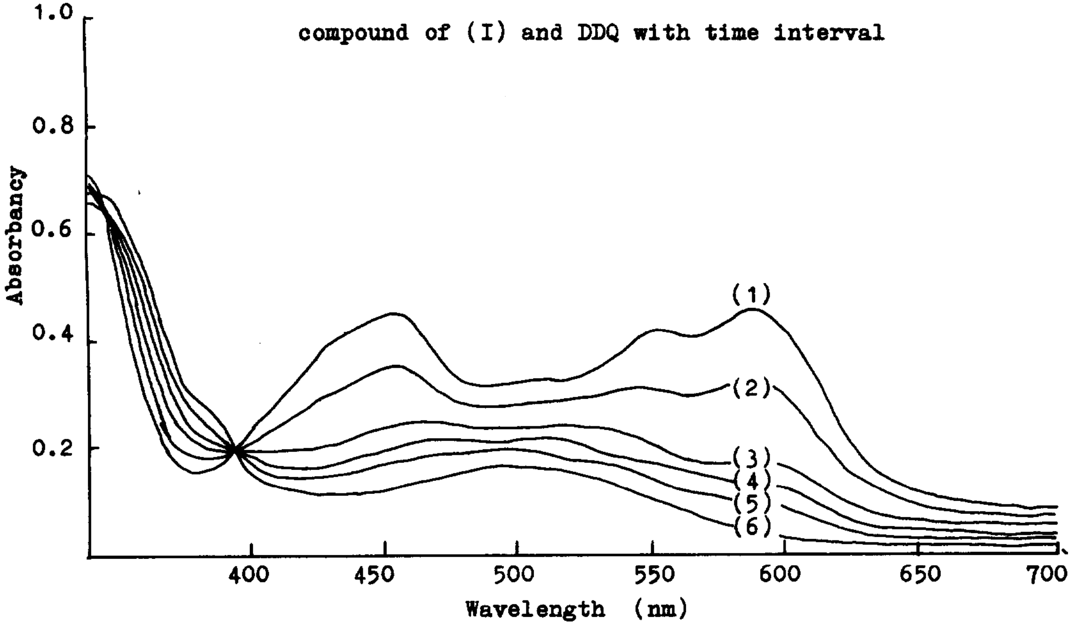
----- absorption of mixture, ferrocene and DDQ

The concentration of (I) or ferrocene in each mixture was 10^{-4}mol/l.

Ratio of (I) (or ferrocene) to DDQ:

(1) or (1') 1 : 2, (2) or (2') 1 : 1, (3) or (3') 1 : 0.5.

Fig.2 Change of visible absorption spectrum of the ionic compound of (I) and DDQ with time interval



(I); 10^{-4}mol/l, DDQ; 10^{-4}mol/l

(1), 0 hr (2), 1 hr (3), 3 hr (4), 5 hr (5), 7 hr (6), 44 hr

References

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