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PHOTOSENSITIZED (SET) CONVERSION OF 2'-HYDROXYCHALCONES TO FLAVONOIDS A PROBABLE BIOGENETIC PATHWAY

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Abstract: 2'-Hydroxychalcones undergo transformation to flavonoids by photoinduced single electron transfer processes.

Chalcones are widely distributed in plants[1] and it is also believed to serve as biosynthetic precursors to all other class of flavonoids and isoflavonoids[2]. There have been several attempts made to rationalize 2'-hydroxychalcones as true intermediates in the biosynthesis of flavonoids[3]. Light induced single electron transfer in molecular complexes of multiple component has been implicated as the primary step in photosynthesis[4]. In view of mounting importance of photoinduced SET reactions in organic chemistry[5] and our own continuing interest[6], led us to report a model biomimetic transformation of chalcones **1a-b**, to flavonoids *via* single electron transfer processes utilizing excited 9,10-dicyanoanthracene as electron acceptor.

Photolysis of a solution of **1a-b** (2.54×10^{-4} **M**) and DCA (7.05×10^{-4} **M**) in methanol at 405 nm (450-W Hanovia medium pressure lamp, $CuSO_4$: NH_3 solution filter, 40-45h, pyrex tubes, practically all light absorbed by DCA only) in nitrogen atmosphere, using Applied Photophysics Annular Photoreactor gave flavone (**3a-b**), flavonone (**4a-b**) and methyl ether of flavonol (**5a-b**)[7]. Similar irradiation in benzene did not show any products. The quantum efficiency[8] of **1a-b** disappearance (ϕdis) in methanol was estimated to be $\approx 10^{-4}$. The ϕdis in CH_3CN: H_2O (9:1) was slightly improved over methanol.

The fluorescence of DCA (λexcit = 430 nm) was efficiently quenched by **1a**. The value of K_{SV} (3.20×10^{10} $M^{-1}S^{-1}$) was obtained from the least square slope of fluorescence quenching Stern-Volmer plot taking singlet life time 19.6 ns for DCA[9]. The present result could be rationalised by considering initial electron transfer (SCHEME 1) from **1a** to excited singlet state of DCA generating **2a** probably *via* exciplex formation[10]. Electrochemical transformation of **1a** to flavonoids, reported recently[11], substantiates our findings.

Photolysis of **1a** (Uranium yellow filter, $\lambda \geq 365$ nm) in methanol gave only **4a** in poor yield. Matsushima et al[12] have also reported the photocyclisation of **1a** to flavonones in poor efficiency in acetonitrile, ethanol and several other solvents. The reaction mechanism was discussed[12] in terms of enolization. The conversion of 2'-hydroxychalcones to various flavonoids have also been effected by several oxidants[13]. This model biomimetic approach of photoinduced SET conversion of 2'-hydroxychalcones to flavonoids appears to be interesting observation. Further detailed study using a molecular complex is in progress.

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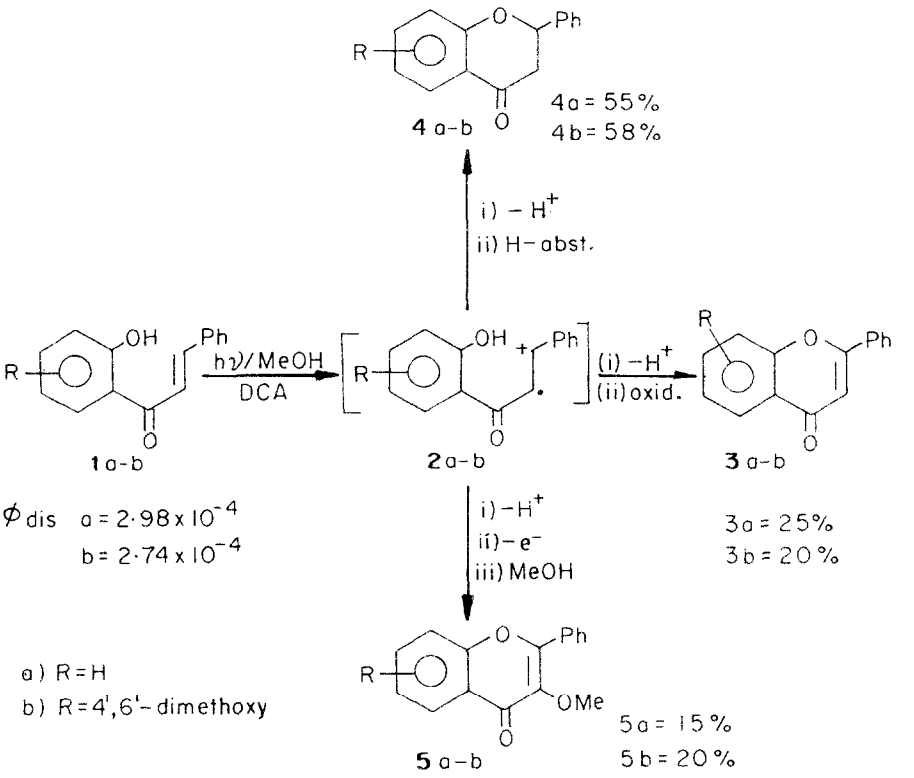
SCHEME -I



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References

1. *J.B. Harborne* **Comparative Biochemistry of Flavonoids**, *Academic Press, New York, p. 78 (1967).*
2. *J.H. Grisebach* **Recent Advances in Phytochemistry**, *T.J. Mabry, R.E. Alston and V.C. Runeckles, Ed. Appeleton - century - crofts, New York, p. 379 (1978).*
3. *(a) V. Weiss and J.M. Edwards* **The Biosynthesis of Aromatic Compounds**, *John Wiley and Sons, New York, p. 472 (1980). (b) V.T. Ramakrishnan and J. Kagan,* **J. Org. Chem.**, **35**, *2898 (1970).*
4. *(a) S.G. Boxer and G.L. Closs,* **J. Am. Chem. Soc.**, **98**, *5406 (1976). (b) M.J. Pellin, K.J. Kaufman and M.R. Wasielewski,* **Nature** *(London),* **278**, *54 (1979). (c) J.Fajer, M.S. Davis, A. Forman, V.V. Klimov, E. Dolan and B. Ke,* **J. Am. Chem. Soc.**, **102**, *713 (1980). (d) R.R. Bucks, and S.G. Boxer, ibid,* **104**, *340 (1982) and references therein.*
5. *(a) M.A. Fox,* **Advances in Photochemistry**, *John Wiley & Sons,* **13**, *p. 237 (1986). (b) S.L. Mattes and S. Farid,* **Organic Photochemistry**, *A. Padwa, Ed.,* **6**, *p. 233 (1983).*
6. *(a) G. Pandey, A. Krishna and J.M. Rao,* **Tetrahedron Letters**, **27**, *4075 (1986). (b) G. Pandey G. Kumaraswamy and A. Krishna,* **Tetrahedron Letters**, **28**, *000 (1987).*
7. *Yields were estimated by HPLC (Column C_8 reverse phase, eluent MeOH:H_2O 70:30), based on the loss of chalcones.*
8. *Intensity of photons at 405 nm was measured by Uranyl oxalate actinometry.*
9. *S.L. Mattes and S. Farid,* **J. Am. Chem. Soc.**, 105, *1386 (1983).*
10. *We could not observe any exciplex emission of* **1a**/*DCA mixture.*
11. *Z. Saniconis and I. Tabakovic* **Tetrahedron Letters**, **27**, *407 (1986).*
12. *R. Matsushima and I. Hirao,* **Bull. Chem. Soc.**, *Japan,* **53**, *518 (1980).*
13. *(a) K. Kurosawa,* **Bull. Chem. Soc.**, *Japan,* **42**, *1456 (1969). (b) K. Kurosawa and J. Higuchi,* **Bull. Chem. Soc.**, *Japan,* **45**, *1132 (1972). (c) A. Kasahara, T. Izumi, and M. Ooshima,* **Bull. Chem. Soc.**, *Japan,* **47**, *2526 (1974). (d) J.A. Donnelly and H.J. Doran,* **Tetrahedron**, **31**, *1565 (1975) and references therein.*

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