

Novel photo-induced coupling reaction of 9-fluorenylidene malononitrile with 10-methyl-9,10-dihydroacridine

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Received (in Cambridge, UK) 6th February 2002, Accepted 8th March 2002

First published as an Advance Article on the web 22nd March 2002

9-Fluorenylidene malononitrile reacts with 10-methyl-9,10-dihydroacridine in deaerated acetonitrile under irradiation with $\lambda > 320$ nm to give a coupling product 9-dicyanomethyl-9-(10'-methyl-9'-acridinyl)fluorene, characterized by X-ray crystallographic, MS and NMR analyses.

The mechanism of reduction reaction with 1,4-dihydropyridine derivatives has been of continued interest because of the important role played by the coenzyme nicotinamide adenine dinucleotide (NADH) in biological reduction-oxidation processes.¹ The two most often employed models for NADH in the mechanistic studies are 1-benzyl-1,4-dihydronicotinamide (BNAH) and 10-methyl-9,10-dihydroacridine (AcrH₂).^{2,3} Previously we⁴ reported that the reduction of 2-bromo-1-phenylethylidenemalononitrile with BNAH produced 2-phenyl-1,1-cyclopropanedinitrile apparently *via* a hydride transfer mechanism, while the reduction of the same substrate with AcrH₂ gave the reductively debrominated dinitrile *via* an electron transfer mechanism. It was also reported^{5,6} that the reduction of 9-fluorenylidene malononitrile (**1**) with BNAH gave 9-dicyanomethylfluorene carbanion **3** through the intermediacy of the radical anion **2** (Scheme 1).

In order to gain further insight into the nature and reactivity of NADH model compounds, we have investigated the reaction of **1** with AcrH₂.

Compound **1** (0.05 mmol) and AcrH₂ (0.06 mmol) were dissolved in dry, deaerated acetonitrile (10 ml) and the solution was allowed to stand at 60 °C under argon for 24 h in the dark. No reaction occurred. When the solution in a pyrex glass tube

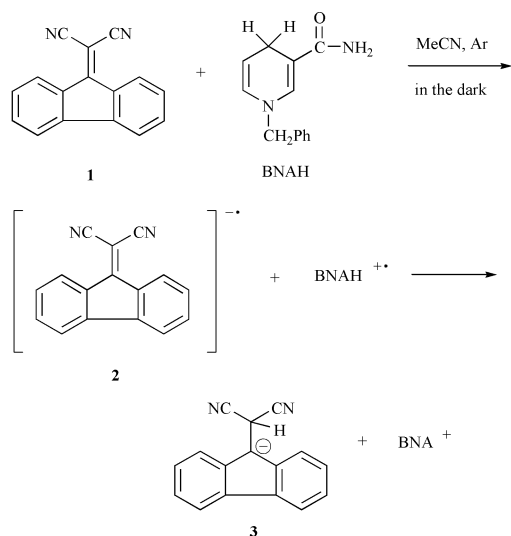
was continuously irradiated with a 250 W high-pressure mercury lamp for 24 h, a reaction took place. The reaction mixture was worked up by a conventional procedure to give a solid product in 70% yield. High resolution mass spectrometry of the product gave molecular weight 423.1729, in conformity with the molecular formula C₃₀H₂₁N₃ (molecular weight 423.1730), which indicated that it was the coupling product **4** of **1** with AcrH₂.

The structure of **4** has been elucidated by single crystal X-ray analysis (Fig. 1).⁷ The molecule is composed of a linkage of 9-dicyanomethylfluorenyl and 10'-methyl-9'-acridinyl moieties at the C9 and C9' positions. The C9–C9' bond length is 1.582 Å, almost 0.04 Å longer than the average length of a normal covalent (sp³–sp³) C–C bond.⁸ The six-membered ring composed of atoms N10', C10A, C8A', C9', C9A' and C4A' is boat-shaped with C9' and N10' as its bow and stern. The bond configuration at the N10' atom is planar as shown by the three bond angles C4A'–N10'–C10A, C4A'–N10'–C11' and C10A–N10'–C11' being all very close to 120°. The structure of **4** was further established by NMR spectroscopy⁹ including ¹H–¹H COSY, ¹H–¹³C COSY and ¹H–¹³C HMB.

Compound **4** has no sharp melting point, as it decomposes on heating over 80 °C. It is colourless when pure but discolours upon standing in the air.

m-Dinitrobenzene is a strong electron acceptor and an efficient inhibitor for electron transfer reaction. When *m*-dinitrobenzene (0.05 mmol) was added to the reaction mixture, the yield of **4** was reduced to 30%.

When the reaction of **1** (0.05 mmol) with AcrH₂ (0.115 mmol) was carried out in oxygen-saturated acetonitrile under



Scheme 1

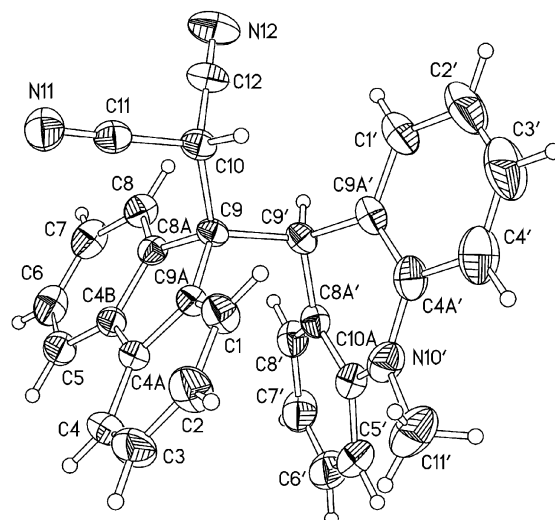
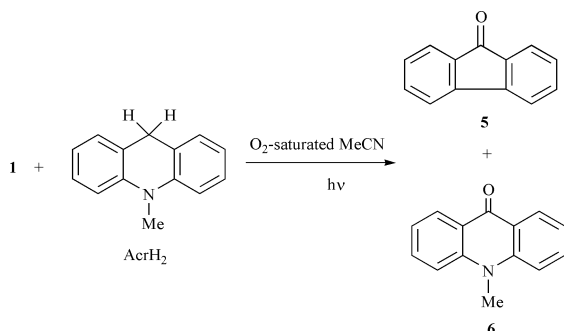


Fig. 1 Perspective view of the molecular structure of **4**. The atoms are drawn at the 30% probability level.

irradiation for 24 h, 9H-fluoren-9-one (**5**) in 72.5% (on the basis of **1**) and 10-methylacridin-9(10H)-one (**6**) in 96.0% (on the basis of AcrH₂) were obtained (Scheme 2). In a control experiment, when a solution of **1** in oxygen-saturated aqueous acetonitrile was irradiated for 24 h, no 9H-fluoren-9-one was obtained.

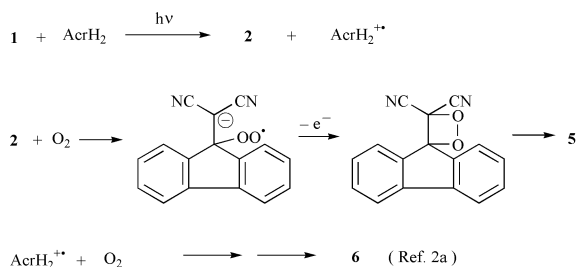


Scheme 2

Fukuzumi *et al.* reported that irradiation of a solution of AcrH₂ in air-saturated acetonitrile with UV light for 25 h produced 10-methylacridin-9(10H)-one and hydrogen peroxide.^{2a} Hoz *et al.* reported that the superoxide radical anion reacted with the activated olefin to give the corresponding ketone through the intermediacy of a peroxide radical anion of the olefin.¹⁰

We have reported that in the reaction of 1,1-diphenyl-2,2-dinitroethylene with BNAH in oxygen-saturated acetonitrile, benzophenone was formed along with 1,1-diphenyl-2,2-dinitroethane.¹¹

In the present case, it is probable that in oxygen saturated acetonitrile electron transfer between AcrH₂ (λ_{max} = 286 nm) and FDCN (λ_{max} = 347 nm) takes place under irradiation to generate the radical cation AcrH₂^{•+} and the radical anion **2**, the latter reacts with oxygen to produce a peroxide radical anion, and the two radical ions then transform to the corresponding ketones, as shown in Scheme 3.

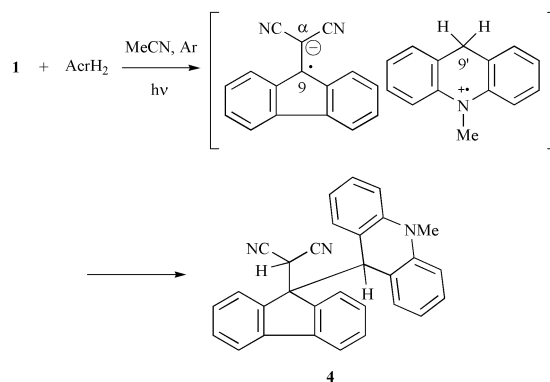


Scheme 3

From the results described above it seems likely that the coupling reaction in deaerated acetonitrile occurs *via* a single electron transfer pathway. According to the quantum mechanics calculation made on 9-fluorenylmalononitrile radical anion (**2**),¹² there are 0.348 units of negative charge on the C_α but little charge on the C₉, whereas the spin densities on the C_α and C₉ are 0.195 and 0.246, respectively. Thus, it is conceivable that when the radical ion pair AcrH₂^{•+} and **2** is formed, proton transfer from C₉' of AcrH₂^{•+} to C_α of **2** is followed by radical coupling between C₉ and C₉' to form the product **4** (Scheme 4).

This provides a rare example of a radical coupling reaction in the reactions of NADH models¹³ since, instead of the usual electron transfer–proton transfer–electron transfer or electron transfer–hydrogen abstraction mechanism, the reaction appears to take place *via* an electron transfer–proton transfer–radical coupling pathway.

This work was supported by National Natural Science Foundation of China (Grant No. 20072036, Grant No.



Scheme 4

29832040) and Special Fund for Doctoral Program from the Ministry of Education of China (Grant No. 98035818).

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- Crystal data for **4**: C₃₀H₂₁N₃, Mr = 423.50, monoclinic, P2₁/c, a = 9.7538(5), b = 9.4805(5), c = 24.491(1) Å, β = 95.071(1)°, V = 2255.9(2) Å³, Z = 4, μ = 0.074 mm⁻¹, θ-range 1.67–25.04°, 3996 independent reflections, refinement on F² for 299 parameters, wR (F², all refl.) = 0.106, R₁[2281 obs. refl. with I > 2σ(I)] = 0.041. CCDC 175312. See <http://www.rsc.org/suppdata/cc/b2/b201239a/> for electronic files in .cif or other electronic format.
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- Selected spectral data for **4**. ¹H NMR (500 MHz, C₆D₆): δ 7.23 (d, J = 7.2 Hz, 2H, H4, H5), 7.04 (d, J = 7.4 Hz, 2H, H1, H8), 6.98 (t, J = 7.2 Hz, 2H, H2, H7), 6.95 (m, 2H, H1', H8'), 6.94 (m, 2H, H3, H6), 6.93 (m, 2H, H3', H6'), 6.62 (t, J = 7.3 Hz, 2H, H2', H7'), 6.27 (d, J = 8.2 Hz, 2H, H4', H5'), 4.94 (s, 1H, H9'), 3.83 (s, 1H, H10), 2.31 (s, 1H, H11'); ¹³C NMR (125.8 MHz, C₆D₆): δ 143.58 (C4A', C10A'), 142.72 (C4A, C4B), 142.14 (C8A, C9A), 130.22 (C1', C8'), 129.53 (C2, C7), 128.67 (C3', C6'), 127.22 (C3, C6), 125.12 (C4, C5), 120.87 (C2', C7'), 120.42 (C1, C8), 119.95 (C8A', C9A'), 112.96 (C4', C5', C11, C12), 59.08 (C9), 49.89 (C9'), 32.83 (C11'), 30.38 (C10). The signals of the ¹H NMR and ¹³C NMR spectra were assigned on the basis of ¹H–¹H COSY, ¹H–¹³C COSY and ¹H–¹³C HMBC spectra.
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