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

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9-Fluorenylidenemalononitrile reacts with 10-methyl-9,10-dihydroacridine in deaerated acetonitrile under irradiation with λ > 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 ($AcrH_2$).[2,3] Previously we[4] 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 $AcrH_2$ gave the reductively debrominated dinitrile *via* an electron transfer mechanism. It was also reported[5,6] that the reduction of 9-fluorenylidenemalononitrile (**1**) with BNAH gave 9-dicyanomethylfluorenide 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 $AcrH_2$.

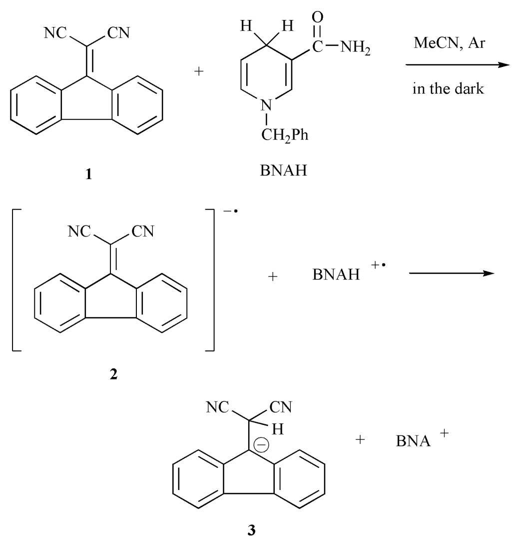
Compound **1** (0.05 mmol) and $AcrH_2$ (0.06 mmol) were dissolved in dry, deaerated acetonitrile (10 ml) and the solution was allowed to stand at 60 °C under argon for 24 h in the dark. No reaction occurred. When the solution in a pyrex glass tube was continuously irradiated with a 250 W high-pressure 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 $C_{30}H_{21}N_3$ (molecular weight 423.1730), which indicated that it was the coupling product **4** of **1** with $AcrH_2$.

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 (sp^3–sp^3) 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 spectroscopy[9] including ^1H–^1H COSY, ^1H–^{13}C COSY and ^1H–^{13}C HMBC.

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 $AcrH_2$ (0.115 mmol) was carried out in oxygen-saturated acetonitrile under



Scheme 1

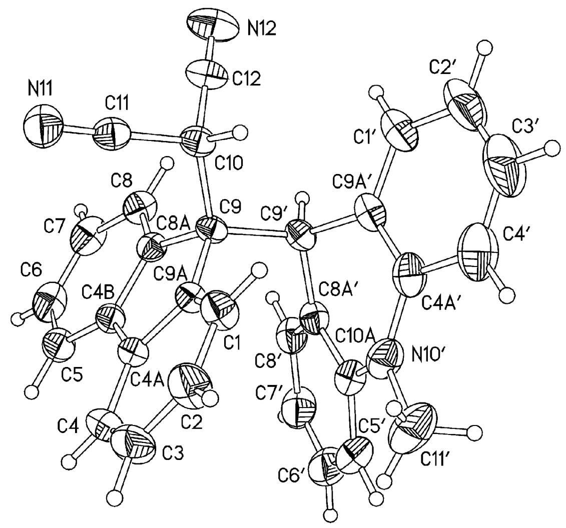


Fig. 1 Perspective view of the molecular structure of **4**. The atoms are drawn at the 30% probability level.

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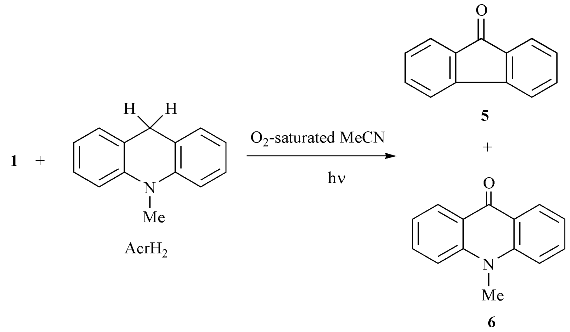
irradiation for 24 h, 9*H*-fluoren-9-one (**5**) in 72.5% (on the basis of **1**) and 10-methylacridin-9(10*H*)-one (**6**) in 96.0% (on the basis of $AcrH_2$) were obtained (Scheme 2). In a control experiment, when a solution of **1** in oxygen-saturated aqueous acetonitrile was irradiated for 24 h, no 9*H*-fluoren-9-one was obtained.

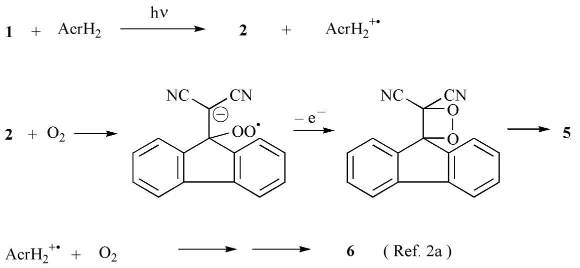


Scheme 2

Fukuzumi *et al*. reported that irradiation of a solution of $AcrH_2$ in air-saturated acetonitrile with UV light for 25 h produced 10-methylacridin-9(10*H*)-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]

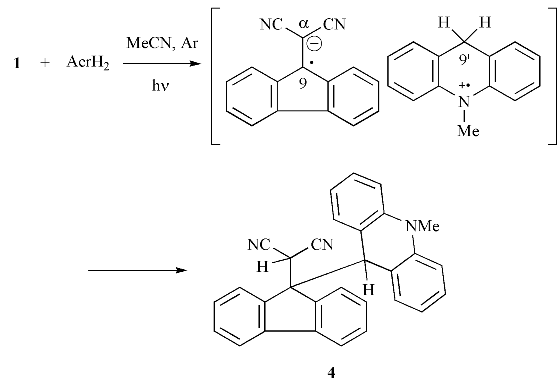
We have reported that in the reaction of 1,1-diphenyl-2,2-dinitroethylene with BNAH in oxygen-saturated acetonitrile, benzophenone was formed along with 1,1-diphenyl-2,2-dinitroethane.[11]

In the present case, it is probable that in oxygen saturated acetonitrile electron transfer between $AcrH_2$ (λ_{max} = 286 nm) and FDCN (λ_{max} = 347 nm) takes place under irradiation to generate the radical cation $AcrH_2^{\cdot+}$ 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 C_9, whereas the spin densities on the C_α and C_9 are 0.195 and 0.246, respectively. Thus, it is conceivable that when the radical ion pair $AcrH_2^{\cdot+}$ and **2** is formed, proton transfer from C_9' of $AcrH_2^{\cdot+}$ to C_α of **2** is followed by radical coupling between C_9 and C_9' to form the product **4** (Scheme 4).



Scheme 4

This provides a rare example of a radical coupling reaction in the reactions of NADH models[13] 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.

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7 *Crystal data* for **4**: $C_{30}H_{21}N_3$, Mr = 423.50, monoclinic, $P2_1/c$, a = 9.7538(5), b = 9.4805(5), c = 24.491(1) Å, β = 95.071(1)°, V = 2255.9(2) Å^3, Z = 4, μ = 0.074 mm^{-1}, θ-range 1.67–25.04°, 3996 independent reflections, refinement on F^2 for 299 parameters, wR (F^2, all refl.) = 0.106, R_1[2281 obs. refl. with $I > 2\sigma(I)$] = 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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9 *Selected spectral data* for **4**. ^{1}H NMR (500 MHz, C_6D_6): 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′); ^{13}C NMR (125.8 MHz, C_6D_6): 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 ^{1}H NMR and ^{13}C NMR spectra were assigned on the basis of ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY and ^{1}H–^{13}C HMBC spectra.

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