

Photo-induced Coupling Reaction of 1, 1-Diphenyl-2, 2-dicyanoethylene with 10-Methyl-9, 10-dihydroacridine

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Abstract: 1, 1-Diphenyl-2, 2-dicyanoethylene reacts with 10-methyl-9, 10-dihydroacridine in deaerated acetonitrile under irradiation with $\lambda > 320$ nm to give the coupling product 1, 1-diphenyl-1-(10'-methyl-9'-acridinyl)-2, 2-dicyanoethane, which has been characterized by X-ray crystallographic, MS and NMR analyses.

Keywords: Photo-induced coupling reaction, 1, 1-diphenyl-2, 2-dicyanoethylene, 10-methyl-9, 10-dihydroacridine, 1, 1-diphenyl-1-(10'-methyl-9'-acridinyl)-2, 2-dicyanoethane.

In a previous communication¹, we reported a novel photo-induced coupling of 9-fluorenylidene malononitrile **1** with the coenzyme NADH model 10-methyl-9, 10-dihydroacridine (AcrH₂) to give 9-dicyanomethyl-9-(10'-methyl-9'-acridinyl)fluorene and proposed a mechanism involving photo-induced electron transfer-proton transfer and radical coupling. This is a scarce mechanism for the reaction of NADH models², which usually takes place by a formal hydride transfer pathway³.

In view of the novelty of the reaction and the interest aroused from mechanistic aspect as well as from possible practical utility, we have extended our investigation to the reaction of 1, 1-diphenyl-2, 2-dicyanoethylene **2** with AcrH₂. Interestingly, a similar coupling product **3** was obtained (**Scheme 1**).

Compound **2** (0.05 mmol) and AcrH₂ (0.06 mmol) were dissolved in dry, deaerated acetonitrile (10 mL) and the solution was allowed to stand under argon at 60 °C with stirring for 24 h in the dark. No reaction occurred. When the above solution in a Pyrex glass tube was continuously irradiated with a 250 W high-pressure mercury lamp for 60 h, the reaction took place. The reaction mixture was worked up by conventional procedure to give a solid product in 18% yield. High resolution mass spectrometry of the product gave the molecular weight 425.1892, in conformity with the molecular formula C₃₀H₂₃N₃ (molecular weight 425.1886), indicating that it was the expected coupling

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product **1**, 1-diphenyl-1-(10'-methyl-9'-acridinyl)-2, 2-dicyanoethane **3** of **2** with AcrH_2 (**Scheme 1**).

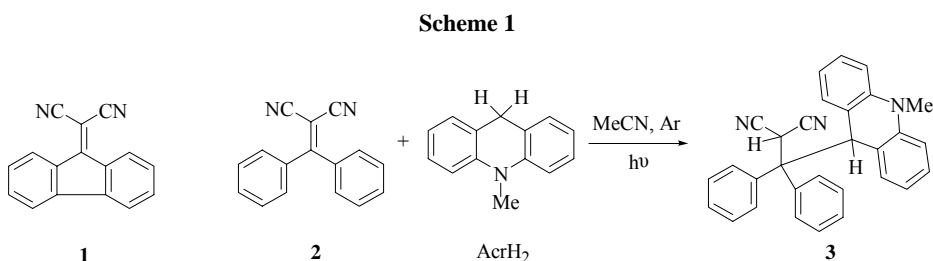
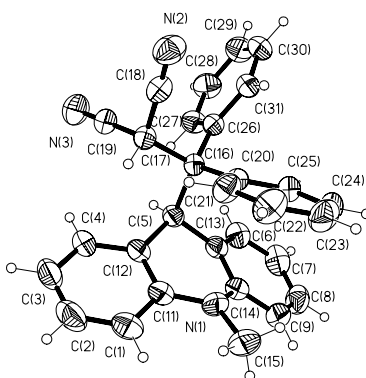


Figure 1 Perspective view of the molecular structure of **3**. The thermal ellipsoids are drawn at the 50% probability level.



The structure of **3** was elucidated by single crystal X-ray analysis (**Figure 1**)⁴. The molecule is composed of a linkage between dicyanomethyl-diphenylmethyl and 10'-methyl-9'-acridinyl moieties at the C-5 and C-16 positions. The bond length of C-5–C-16 is 1.608 Å, almost 0.06 Å longer than the average length for a normal covalent C–C bond⁵. The structure of **3** was further established by NMR spectroscopy including ¹H-¹H COSY, ¹H-¹³C COSY⁶.

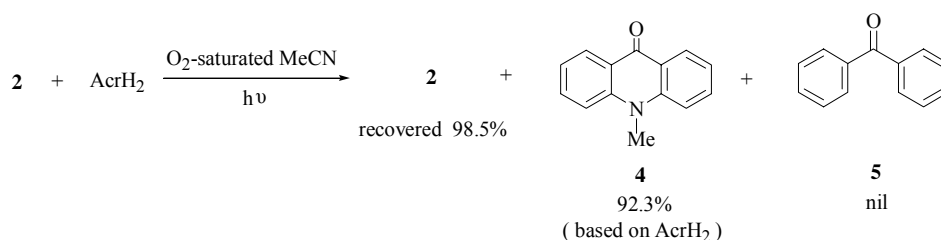
Compound **3** has no sharp melting point, as it decomposes on heating above 78°C. It is colourless when pure but discolours upon standing in air.

When the reaction of **2** (0.05 mmol) with AcrH_2 (0.10 mmol) was conducted in oxygen-saturated acetonitrile (8 mL) under irradiation with a 250 W mercury lamp for 60 h, 10-methyl-9(10H)-acridinone **4** was obtained in 92.3% yield (based on AcrH_2), while **2** was recovered (98.5%) without the formation of benzophenone **5** (**Scheme 2**). The formation of **3** and **4** can be rationalized by the following scheme (**Scheme 3**)¹.

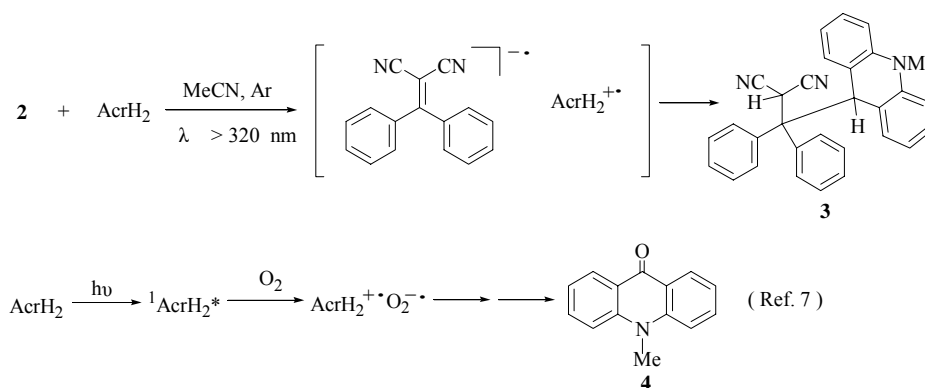
It is noteworthy that the yield of **3** from the reaction of **2** with AcrH_2 in deaerated acetonitrile was quite low and that no benzophenone was obtained from the reaction in oxygen-saturated acetonitrile, in contrast with the results obtained from the reaction of **1** with AcrH_2 in oxygen-saturated acetonitrile wherein 9H-fluoren-9-one was obtained in

72.5% yield (based on **1**) and **4** was obtained in 96.0% yield (based on AcrH₂)¹. The reported oxidation potential of ¹AcrH₂* is E_{ox}⁰ = -3.1 V⁷, and the reduction potentials of **1** and **2** are -0.68 V, -0.83 V vs. Ag/AgCl⁸, respectively. Electron transfer from ¹AcrH₂* to both **1** and **2** are exergonic. It appears, therefore, necessary to seek an explanation for the remarkable difference in reactivity between **1** and **2** in their reactions with AcrH₂.

Scheme 2



Scheme 3



The primary cause for the different reactivities of **1** and **2** is related to the different bonding characteristics of their structures. While **1** is planar, **2** is nonplanar due to the steric interaction between the two phenyl groups. Theoretical calculation (DFT) indicates a dihedral angle of about 72 ° between the two phenyl rings⁹. When **1** accepts one electron from ¹AcrH₂^{*}, the resulting radical anion contains a fluorenyl radical anion moiety, in which the spin and charge are delocalized over the fluorenyl system with stabilization by the conjugation interaction effect. In contrast, when **2** accepts an electron, the resulting radical anion cannot be stabilized by the two phenyl rings as effectively as by the fluorenyl system. A density-functional theoretical study indicates that the electron affinity of **1** is larger than that of **2** by about 10 Kcal/mol⁹. Therefore, the electron transfer from ¹AcrH₂^{*} to **1** should proceed more readily than that from ¹AcrH₂^{*} to **2**, and hence a high yield of the coupling product results. In oxygen-saturated acetonitrile solution, AcrH₂ can undergo photo-induced electron transfer with oxygen and subsequent oxidation of the resulting radical cation (AcrH₂⁺) to produce **4**⁷, while **2** remains intact due to the competition by oxygen for electron transfer from AcrH₂ (the reported reduction potential of O₂ is -0.86 V⁷).

In addition, planar **1** can approach AcrH₂ more closely for electron transfer while the nonplanar **2** can not be in a close contact with ¹AcrH₂* for effective electron transfer.

The present work provides another example of a novel radical coupling reaction for the NADH models.

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References and Notes

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4. *Crystal data* for **3**: C₃₀H₂₃N₃, *Mr* = 425.51, monoclinic, *P*2₁/*n*, *a* = 11.8806(11), *b* = 14.1864(14), *c* = 13.6027(13) Å, *β* = 97.721(2)°, *V* = 2271.9(4) Å³, *Z* = 4, *μ* = 0.074 mm⁻¹, *θ*-range 2.08–28.04°, 5474 independent reflections, refinement on *F*² for 299 parameters, *wR* (*F*², all refl.) = 0.136, *R*₁[2281 obs. refl. with *I* > 2σ(*I*)] = 0.044.
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6. *Selected spectral data* for **3**. ¹H NMR (500 MHz, C₆D₆): δppm 7.79 (m, 2H, H-22, H-30), 7.72 (m, 2H, H-24, H-28), 7.18 (m, 2H, H-4, H-6), 7.16 (m, 2H, H-23, H-29), 6.92 (m, 2H, H-21, H-31), 6.63 (m, 2H, H-2, H-8), 6.59 (m, 2H, H-3, H-7), 6.32 (m, 2H, H-25, H-27), 6.16 (m, 2H, H-1, H-9), 5.51 (s, 1H, H-5), 4.34 (s, 1H, H-17), 1.97 (s, 3H, H-15); ¹³C NMR (125 MHz, C₆D₆): δppm 144.66 (C-11, C-14), 137.68 (C-20, C-26), 131.69 (C-24, C-28), 131.15 (C-4, C-6), 129.79 (C-22, C-30), 129.17 (C-23, C-29), 126.50 (C-2, C-8), 121.41 (C-21, C-31), 120.71 (C-3, C-7), 119.72 (C-12, C-13), 114.21 (C-18, C-19), 113.33 (C-25, C-27), 112.83 (C-1, C-9), 60.41 (C-16), 47.92 (C-5), 34.88 (C-17), 32.88 (C-15). The signals of the ¹H NMR and ¹³C NMR spectra were assigned on the basis of ¹H-¹H COSY, ¹H-¹³C COSY.
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8. The reduction potentials were determined by cyclic voltammetry measurements, which were performed at 50 mV/s on CV-27 Voltammograph at 298 K in acetonitrile containing 0.1 mol/L Bu₄NClO₄ as a supporting electrolyte using Ag/AgCl electrode as a reference electrode.
9. Absolute energetics, optimized geometries, and harmonic vibrational frequencies were computed using density functional theory B3LYP. The 6-31G** and 6-311++G** basis sets were used for the geometry optimization and single point energy calculations, respectively.

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