
Photoinduced Electron-transfer Reactions of 1,3,5-Tricyanobenzene with Olefins

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Photoinduced electron-transfer of 1,3,5-tricyanobenzene (**1**) with 2,3-dimethylbut-2-ene leads to a novel annelation to give an indane derivative, while that with 2-methylbut-2-ene or tetrachloroethylene results in substitution at C-1 or C-2 of (**1**), respectively.

Photoinduced electron-transfer reactions between aromatics and olefins have recently attracted interest and numerous novel reactions have been reviewed.¹⁻⁶ However, 1,3,5-tricyanobenzene (**1**) has been little investigated as an electron acceptor—only its photoinduced electron-transfer reactions with aliphatic nitriles⁷ and hexamethyldisilane⁸ have been reported. We expected that the photoinduced electron-transfer reactions of (**1**)–olefin systems would be similar to those of 1,3-dicyanobenzene–olefin systems, studied extensively by Arnold *et al.*⁹ However, it was found that the reaction proceeded in an unexpected way. We report here the first examples of the photoinduced electron-transfer reaction of (**1**) with olefins.

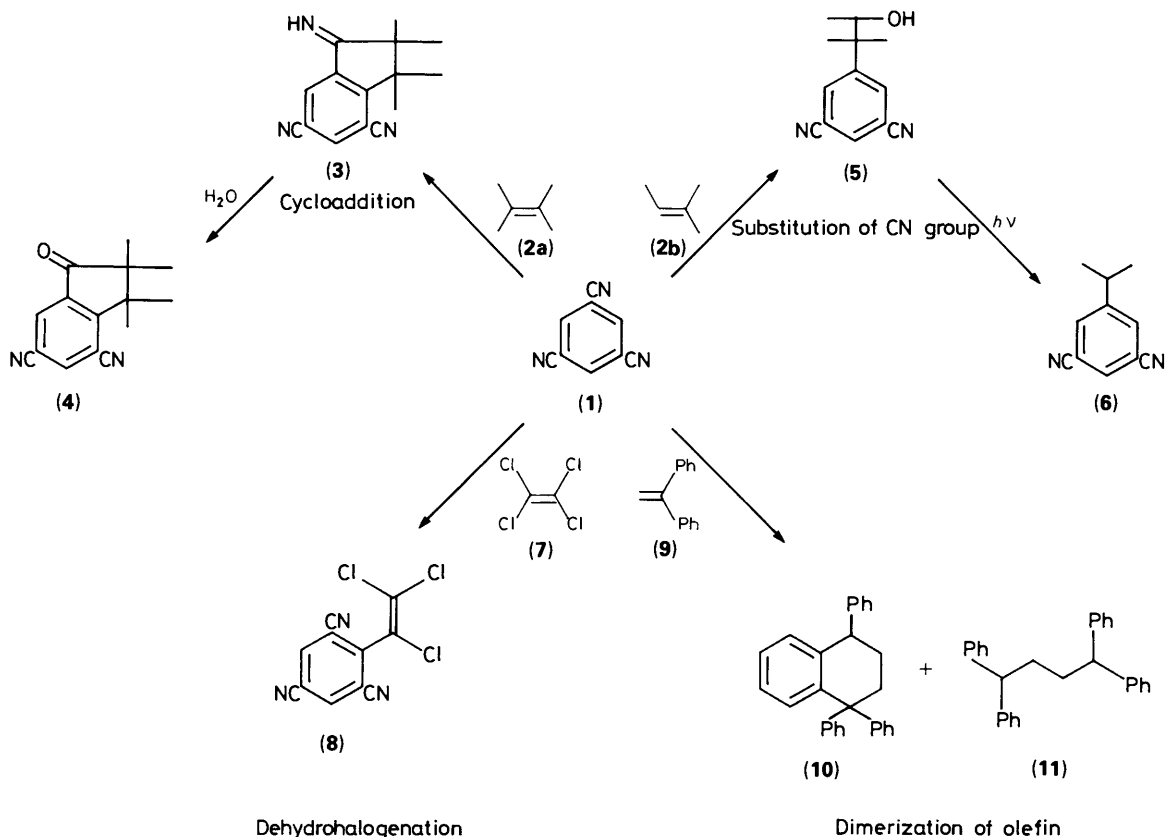
Irradiation of (**1**) (16 mg) in acetonitrile (1 ml) in the presence of 2,3-dimethylbut-2-ene (**2a**) (27 mg) under nitrogen with a medium pressure mercury arc (100 W) for 1 h gave the air-sensitive product (**3**). This was treated with 1M HCl (5 ml) to yield an indanone derivative (**4**), mp 155–157 °C, in 70% yield. The structures of products (**3**) and (**4**) were determined on the basis of spectral data, including accurate mass measurements; the i.r. spectrum of (**4**) was the most informative, with absorptions at 2 220 (CN) and 1 730 cm⁻¹ (C=O). Since the fluorescence of (**1**) was quenched by (**2a**), with a Stern–Volmer constant ($k_q\tau$) of 352 M⁻¹, and since the ΔG value calculated by the Rehm–Weller equation¹⁰ is –116 kJ, the first step of the reaction must be electron-transfer from (**2a**) to (**1**) to give a

radical-ion pair. Coupling of the pair followed by ring formation and proton rearrangement may account for the formation of (**3**) as shown in Scheme 1.

Similar irradiation of (**1**) (100 mg) and 2-methylbut-2-ene (**2b**) (1 ml) in acetonitrile for 100 h gave little product. However, in the presence of water (250 μ l) the reaction proceeded smoothly over 10 h to give the substitution products (**5**), m.p. 100–101 °C and (**6**), mp 69–71 °C, in 36 and 6% yields, respectively. No annelation products were detected. Since (**5**) was converted into (**6**) quantitatively upon irradiation, (**6**) must be a secondary product of (**5**). Similar photoinduced C–C bond cleavage of phenethyl ethers has already been reported.¹¹ The Stern–Volmer constant of fluorescence quenching of (**1**) by (**2b**) is 256 M⁻¹, and an electron-transfer reaction similar to that with (**2a**) has been deduced ($\Delta G = -56$ kJ). However, the substitution at C-1 is unusual for a coupling within the radical ion pair, since a radical or a radical cation should attack the radical anion at the position having the highest spin density; this is the C-2 position in the radical anion of (**1**).^{7,8}

When D₂O was used in place of H₂O, no deuterium was incorporated on the aromatic ring of (**5**). This result precludes a proton-transfer mechanism, such as that observed for 1,3-dicyanobenzene–olefin systems.⁹

On the other hand, we found that trimethylsilyl or benzyl radical attacked not only C-2 but also C-1, though the former



Scheme 1. Photoreaction of 1,3,5-tricyanobenzene with olefins.

was predominant.^{8,12} These results lead us to suppose that the alkyl radical produced by the reaction of the radical cation and water may attack both C-1 and C-2 of the radical anion of (1) to give anionic intermediates (a) and (b), respectively, as shown in Scheme 2. Loss of cyanide from (a) may give the desired product (5), while loss of hydroxide anion accompanied by bond cleavage may regenerate the starting materials. The latter process may result in the quenching of the photoreactions.

Similar irradiation of (1) (16 mg) in acetonitrile (1 ml) in the presence of tetrachloroethylene (7) (48 mg) gave the substitution product (8) in 50% yield. In this case substitution occurred at C-2 in accord with the previous results.^{7,8} The Stern–Volmer constant of fluorescence quenching was 85 M^{-1} and the calculated ΔG was -22 kJ ; an electron-transfer mechanism was again suggested. We assume that in this case the first step of the reaction, *i.e.* coupling of the radical cation–anion pair, must occur at C-2 of the radical anion of (1), in accord with the higher frontier electron densities in the radical anion; loss of HCl then gives (8).

A similar photochemical electron-transfer reaction of 1,1-diphenylethylene (9) with (1) gave the dimers (10) and (11) in 44 and 10% yields, respectively. This result is similar to that for the dicyanoanthracene–(9) system reported previously.¹³

In sharp contrast with the dicyanobenzene–olefin systems reported by Arnold *et al.*,⁹ proton-transfer from the radical cation to the radical anion followed by coupling of the resulting radicals has never been observed in (1)–olefin systems.

Experimental

Selected Photochemical Reactions and Selected Spectral Data

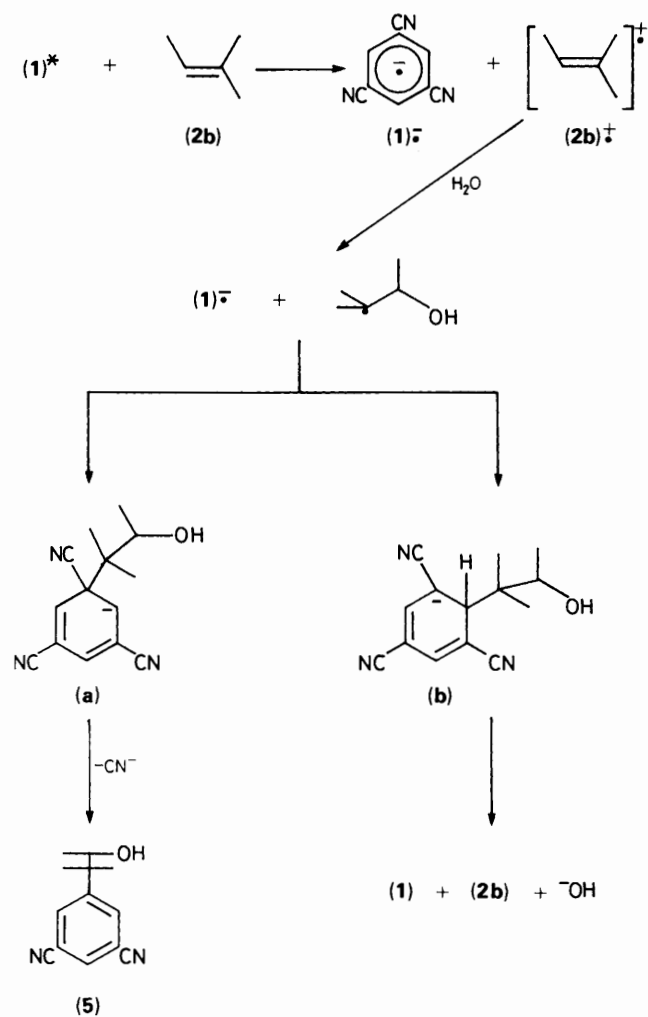
for New Compounds.—A solution of (1) (16 mg) and 2,3-dimethylbut-2-ene (2a) (27 mg) in acetonitrile (1 ml) under nitrogen was irradiated externally by means of a medium pressure mercury lamp (100 W) for 1 h. To the reaction mixture was added 1 M HCl (5 ml) and the mixture allowed to stand for 6 h. After removal of the solvent *in vacuo*, tlc of the residue on silica gel (Merk 60 PF₂₅₄) with CHCl₃ as eluant gave (1) (11.4 mg, corresponding to a conversion of 28%) and (4) (4.9 mg, 70%). For isolation of the intermediate (3), a solution of (1) (50 mg) and (2a) (81 mg) in acetonitrile (10 ml) was irradiated externally by means of a medium pressure mercury lamp (100 W) under nitrogen for 10 h. After removal of the solvent *in vacuo*, preparative gc (OV-17 10% on Chromosorb, 170 °C) of the residue gave pure (3). Compound (3) is easily hydrolysed on silica gel chromatography to give (4).

Compound (3); δ_{H} (CDCl₃; 270 MHz) 9.65 (1 H, br), 8.32 (1 H, br), 8.01 (1 H, d, *J* 1.5 Hz), 1.39 (6 H, s), and 1.10 (6 H, s); *m/z* (70 eV) 237 (*M*⁺, 18), 222 (100), and 207 (15%) (Found: *M*⁺, 237.1261. C₁₅H₁₅N₃ requires *M*, 237.1264).

Compound (4); δ_{H} (CDCl₃; 270 MHz) 8.19 (1 H, d, *J* 1.5 Hz), 8.12 (1 H, d, *J* 1.5 Hz), 1.47 (6 H, s), and 1.13 (6 H, s); ν_{max} (KBr) 1 730 (C=O) and 2 220 cm⁻¹ (CN); *m/z* (70 eV) 237 (*M*⁺, 28) and 223 (100%) (Found: *M*⁺, 238.1132. C₁₅H₁₄N₂O requires *M*, 238.1105).

Compound (5); δ_{H} (CDCl₃; 270 MHz) 7.93 (2 H, d, *J* 1.5 Hz), 7.80 (1 H, t, *J* 1.5 Hz), 3.84 (1 H, dt, *J* 4.4 and 6.2 Hz), 1.43 (1 H, d, *J* 4.7 Hz), 1.364 (3 H, s), 1.361 (3 H, s), and 1.04 (3 H, d, *J* 6.2 Hz); *m/z* (70 eV) 170 (*M*⁺ – CH₃CHO, 100), 155 (27), and 142 (12%).

Compound (6); δ_{H} (CDCl₃; 270 MHz) 7.77 (1 H, t, *J* 1.5 Hz), 7.74 (2 H, d, *J* 1.5 Hz), 3.02 (1 H, sept, *J* 7.0 Hz), and 1.30 (6 H, d, *J* 7.0 Hz); *m/z* (70 eV) 170 (*M*⁺, 18), 155 (100), and 128 (18%).



Scheme 2.

Compound (8); $\delta_{\text{H}}(\text{CDCl}_3; 270 \text{ MHz})$ 8.24 (s); m/z (70 eV) 285 (32), 283 (98), 281 (M^+ , 100), 250 (11), 248 (64), 246 (98), 213 (30), 211 (91), 176 (12), and 149 (17%).

Acknowledgements

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