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Intramolecular [2 + 2] cycloaddition of some 1,*n*-diene-1,1-dicarbonitriles Difference between singlet and triplet reactivity

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Abstract

Intramolecular [2+2] cycloadditions on direct irradiation have been observed with four 1-alkene-1,1-dicarbonitriles bearing an additional C=C bond positioned in Δ^5, Δ^6, or Δ^7within a flexible chain. The cycloadducts formed are the "parallel" regioisomers. These cycloadditions occur by excitation of an intramolecular charge transfer complex formed by the two double bonds. Triplet sensitisation has also been investigated in one case and found also to lead to intramolecular [2 + 2] cycloaddition, however furnishing the "crossed" regioisomer. It appears that the triplet cycloaddition path, other than the singlet one, does not involve an exciplex but rather proceeds in two steps via the most stable triplet 1,4-diradical.

Keywords: Exciplex; Sensitisation; Photoisomerisation; Cycloaddition; Polar olefin

1. Introduction

The photochemistry of directly excited 1-alkene-1,1-dicarbonitriles (1,1-dicyano-1-alkenes, DCNA) bearing additional Δ^5-unsaturation has been extensively investigated. The exclusive reaction found (unless the additional unsaturation formed part of an aromatic ring) was 3,4-C–C bond cleavage to form two allylic moieties which either ended up as separate molecules or recombined resulting in an overall 1,3-migration [1–4]. In the course of our investigations on the photochemistry of DCNA without additional unsaturation [5,6] as well as on the SET-photochemistry of Δ^5-unsaturated DCNA [7–9], we also investigated the behaviour of two directly excited Δ^5-unsaturated DCNA that had not been studied before. Since these systems, besides exhibiting the previously known photoreactivity (vide supra), also showed some unprecedented photochemistry, we report on them and on related systems in the present paper.

2. Experimental

2.1. General aspects and methods

For general aspects and methods, see the previous publications [5,8]. Product distributions were determined by capillary g.l.c. (OV 1701) and 400 MHz ^{1}H NMR analyses of the unseparated reaction mixtures. Molecular structures of new compounds could be unambiguously determined by NMR methods (400 MHz ^{1}H including NOE, COSY, and spin decoupling where appropriate, 100 MHz ^{13}C including BB, DEPT, and C,H-correlation spectroscopy). **3** was prepared by independent synthesis. The regioisomerism of **15** follows both from the oxetane ring carbon and hydrogen chemical shifts and, independently, from an analogy to the literature [10].

2.2. Preparative experiments

2.2.1. 2-Pent-4-enylidene-malononitrile (*1*)

From pent-4-enal [11] and malononitrile according to the general procedure [5]. Liquid, b.p. 54 °C/0.1 mbar. UV (*n*-hexane): λ_{max} (log ε) = 225 nm (4.07); $\varepsilon_{253.7\,nm}$ = 1683. ^{1}H NMR ($CDCl_3$): δ = 2.32 (tddd, J = 2 × 7.1, 6.6, 1.4, 0.8 Hz, 2 H), 2.69 (dt, J = 7.8, 2 × 7.1 Hz, 2 H), 5.10 (dq, J = 16.8, 3 × 1.4 Hz, 1 H), 5.12 (ddt, J = 10.5, 1.4, 2 × 0.8 Hz, 1 H), 5.75 (ddt, J = 16.8, 10.5, 2 × 6.6 Hz, 1 H), 7.31 (t, J = 2 × 7.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ = 30.7 (CH_2), 31.5 (CH_2), 89.5 (C), 110.2 (CN), 111.7 (CN), 116.8 (CH_2), 134.6 (CH), 169.0 (CH).

2.2.2. 2-Allyl-cyclopropane-1,1-dicarbonitrile (*2*), 1,5-hexadiene-3,3-dicarbonitrile (*3*), and 1α,4α-bicyclo[2.2.0]hexane-2,2-dicarbonitrile (*5*)

The solution of 4.0 g (30.3 mmol) **1** in 150 ml acetonitrile was distributed among ten 15 ml quartz tubes under

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argon. These were placed inside a 120 W Rayonet photoreactor equipped with eight low pressure mercury lamps and irradiated for 24 h. Removal of solvent and chromatography over 500 g silica gel with pentane and 2–5% ether furnished consecutively 17.7 mg unidentified mixture, 289.4 mg **3**, 10.6 mg unidentified mixture, 33.0 mg **5**, 7.4 mg unidentified mixture, 263.8 mg **2**, and 318 mg unidentified mixtures. **2**—^{1}H NMR ($CDCl_3$): $\delta = 1.57$ (dd, $J = 8.1, 5.7$ Hz, 1 H), 1.95 (dd, $J = 9.0, 5.7$ Hz, 1 H), 2.08 (ddt, $J = 9.0, 8.1, 2 \times 7.2$ Hz, 1 H), 2.35 (dddt, $J = 15.8, 7.5, 6.2, 2 \times 1.4$ Hz, 1 H), 2.38 (dddt, $J = 15.8, 7.0, 6.2, 2 \times 1.4$ Hz, 1 H), 5.20 (dq, $J = 10.2, 3 \times 1.3$ Hz, 1 H), 5.23 (dq, $J = 17.2, 3 \times 1.5$ Hz, 1 H), 5.87 (ddt, $J = 17.2, 10.2, 2 \times 6.2$ Hz, 1 H). ^{13}C NMR ($CDCl_3$): $\delta = 3.7$ (s), 24.2 (t, $J = 2 \times 169.7$ Hz), 29.8 (d, $J = 167.4$ Hz), 33.5 (t, $J = 2 \times 129$ Hz), 113.6 (s), 115.2 (s), 118.0 (dd, $J = 159.5, 154$ Hz), 132.6 (d, $J = 155.7$ Hz). **3**—^{1}H NMR ($CDCl_3$): $\delta = 2.76$ (dt, $J = 7.2, 2 \times 0.9$ Hz, 2 H), 5.40 (dq, $J = 16.7, 3 \times 0.9$ Hz, 1 H), 5.43 (dq, $J = 10.3, 3 \times 0.9$ Hz, 1 H), 5.60 (m, 1 H), 5.78 (m, 2 H), 5.85 (ddt, $J = 16.7, 10.3, 2 \times 7.2$ Hz, 1 H). ^{13}C NMR ($CDCl_3$): $\delta = 39.6$ (C), 42.5 (CH_2), 113.4 (2 CN), 121.1 (CH_2), 123.2 (CH_2), 127.9 (CH), 128.4 (CH). **5**—^{1}H NMR ($CDCl_3$): $\delta = 2.07$ (dtd, $J = 12.5, 2 \times 7.0, 2.3$ Hz, 1 H, *endo*-5-H), 2.57 (m, 1 H, *exo*-5-H), 2.67 (m, 2 H, 6-H), 2.89 (dd, $J = 13.2, 3.7$ Hz, 1 H, *endo*-3-H), 3.08 (bddddd, $J = 7.9, 7.0, 6.0, 3.7, 2.3$ Hz, 1 H, 4-H), 3.22 (dddd, $J = 13.2, 7.9, 2.0, 1.5$ Hz, 1 H, *exo*-3-H), 3.32 (dtd, $J = 6.0, 2 \times 5.0, 2.0$ Hz, 1-H). ^{13}C NMR ($CDCl_3$): $\delta = 23.4$ (bt, $J = 2 \times 136.8$ Hz, C-6), 27.0 (bt, $J = 2 \times 138$ Hz, C-5), 29.0 (s, C-2), 32.9 (bd, $J = 153$ Hz, C-4), 39.8 (ttd, $J = 2 \times 142.8, 2 \times 8.0, 4.0$ Hz, C-3), 43.6 (d, $J = 154.2$ Hz, C-1), 114.4 (t, $J = 2 \times 4.0$ Hz, CN), 116.7 (dt, $J = 7.6, 2 \times 5.4$ Hz, CN).

2.2.3. 1,5-Hexadiene-3,3-dicarbonitrile (**3**)

Sodium hydride 1.06 g, 55% in mineral oil (Fluka, ca. 24 mmol), was placed in a 250 ml three-necked flask under an atmosphere of dry argon. *n*-Pentane was added in three portions under stirring and each portion removed from the flask by inverse filtration. 10 ml dry tetrahydrofuran was added, followed by the dropwise addition of a solution of 2.0 g (21.7 mmol) ethylidene malononitrile [5] in 50 ml dry tetrahydrofuran with external cooling. After the gas evolution had ceased, 2.65 g (21.9 mmol) allyl bromide was added dropwise. The resulting mixture was refluxed for 2 h, the solvent was evaporated, and the residue was distributed between water and ether. The residue after evaporation of the dried ether phase weighed 0.85 g and contained 50% **3** (^{1}H NMR analysis).

2.2.4. Bicyclo[2.1.1]hexane-5,5-dicarbonitrile (**6**)

A solution of 400 mg (3 mmol) **1** and 183 mg (1 mmol) benzophenone in 50 ml benzene was flushed with argon and placed in a 50 ml solidex glass immersion well irradiation apparatus under an argon atmosphere. The apparatus was cooled with tap water and equipped with magnetic stirring and a concentrically placed 125 W high-pressure mercury lamp (Philips HPK 125). After 2 weeks of irradiation, the solvent was removed, chloroform was added, the solution was filtered, the chloroform was removed from the solution, ether was added, the solution was filtered, and the ether was removed, leaving 290.7 mg residue which according to 400 MHz ^{1}H NMR contained 140 mg benzophenone, 30 mg other aromatic products, 69 mg **1**, 50 mg **6**, and virtually no other material; capillary g.l.c. afforded the product composition (omitting **1** and aromatics) given in Scheme 3. Chromatography of the residue over 70 g silica gel (Merck, 0.04–0.063 mm) with pentane and 2% ether eluted consecutively 126.1 mg benzophenone, 39.7 mg fraction A containing 50% **6** (^{1}H NMR), 100 mg containing various decomposition products but no **6**. Rechromatography of A over 30 g silica gel eluted consecutively 14.1 mg of various material and 17.9 mg **6**. ^{1}H NMR ($CDCl_3$ and C_6D_6, respectively; *endo* designates positions on the same face like the nitrile groups): $\delta = 1, 27/0.12$ (1 H, *exo*-6-H), 1.91/0.86 (2 H, *exo*-2-H and *exo*-3-H), 2.02/1.36 (2 H, *endo*-2-H and *endo*-3-H), 2.49/1.75 (1 H, *endo*-6-H), 3.19/2.00 (2 H, 1-H and 4-H). $J_{H,H}$-values by analysis of an $A_2B_2C_2$DE-system: 9 Hz (*endo*-2-H/*endo*-3-H), 9 Hz (*exo*-2-H/*exo*-3-H), −12 Hz (*endo*-2-H/*exo*-2-H and *endo*-3-H/*exo*-3-H), 3.8 Hz (*endo*-2-H/*exo*-3-H and *endo*-3-H/*exo*-2-H), 0.8 Hz (1-H/*endo*-2-H and 4-H/*endo*-3-H), 0.8 Hz (1-H/*exo*-2-H and 4-H/*exo*-3-H), 2.8 Hz (1-H/*endo*-6-H and 4-H/*endo*-6-H), ±2.5 Hz (*endo*-2-H/*endo*-6-H and *endo*-3-H/*endo*-6-H), ±8.5 Hz (*endo*-6-H/*exo*-6-H), ∼0 Hz (others). ^{13}C NMR ($CDCl_3$): $\delta = 24.3$ (t, $J = 2 \times 138$ Hz, C-2 and C-3), 36.3 (t, $J = 2 \times 140$ Hz, C-6), 37.6 (s, C-5), 50.5 (t, $J = 2 \times 162.9$ Hz, C-1 and C-4), 112.5 (s, CN), 115.8 (s, CN).

2.2.5. 1α,4α-1,3,3-Trimethyl-bicyclo[2.2.0]hexane-2,2-dicarbonitrile (**9**)

The solution of 4.00 g (23 mmol) **7** [8] in 450 ml acetonitrile was flushed with argon, placed in a magnetically stirred quartz apparatus under an argon atmosphere, and irradiated for 20 h in a 120 W Rayonet photoreactor equipped with mercury low-pressure lamps affording predominantly 254 nm light. Evaporation of solvent left a red-brown oil which was separated by chromatography over 400 g silica gel with pentane and 2–20% ether to afford 3.45 g (86%) **8** [8] and 521 mg (13%) crystalline **9**. **9**: MS: $m/z = 174$ (M^+). IR (KBr): 3247 (s), 3227 (s), 3203 (m), 3116 (m), 3017 (s), 2949 (s), 2160 (s), 1533 (m), 1431 (s), 949 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 1.37$ (s, 3 H, 3β-CH_3), 1.41 (s, 3 H, 3α-CH_3), 1.42 (s, 3 H, 1-CH_3), 2.05 (m, 1 H, 5β-H), 2.16–2.27 (m, 2 H, 5α-H and 6α-H), 2.31 (m, 1 H, 4-H), 2.59 (m, 1 H, 6β-H). ^{1}H,^{1}H-NOE enhancements: 1-CH_3/4-H, 1-CH_3/6α-H, 3α-CH_3/4-H, 3β-CH_3/5β-H, 3β-CH_3/6β-H, 4-H/5α-H, 5β-H/6β-H. ^{13}C NMR ($CDCl_3$): $\delta = 17.4$ (t, $J = 2 \times 137$ Hz, C-5), 21.5 (q, $J = 3 \times 127$ Hz, 3β-CH_3), 22.7 (q, $J = 3 \times 126$ Hz, 3α-CH_3), 28.6 (q, $J = 3 \times 128$ Hz, 1-CH_3), 30.9 (t, $J = 2 \times 140$ Hz, C-6), 41.6 (s), 43.0 (s), 45.1 (s), 47.7 (d, $J = 149$ Hz, C-4), 113.3 (CN), 114.0 (CN).

*2.2.6. 2-(2,6-Dimethyl-hept-5-enylidene)-malononitrile (**10**)*

In course of the entire procedure, the temperature was never allowed to exceed 30 °C. To a stirred and cooled slurry of 21 g plaster of Paris in a solution of 10 g (151 mmol) malononitrile, 1 ml piperidine, and 1 ml glacial acetic acid in 150 ml benzene was added dropwise 21 g (150 mmol) 2,6-dimethyl-hept-5-enal [12]. After addition was complete, stirring was continued for 40 min. Filtration, washing the solution with water, drying the solution over magnesium sulfate, filtration, and evaporation of solvent left 27.4 g of an orange-yellow residue which was flash-chromatographed over silica gel in a 35 cm × 8 cm column with dichloromethane to furnish as the first eluted fraction 23.3 g **10**, liquid. UV (*n*-hexane): λ_{max} (log ε) = 223 (4.05), 258 sh (3.28) nm; $\varepsilon_{253.7nm}$ = 2168; ε_{313nm} = 24.5. ^{1}H NMR ($CDCl_3$): δ = 1.12 (d, J = 7.5 Hz, 3 H), 1.35–1.65 (m, 2 H), 1.58 (bs, 3 H), 1.68 (bs, 3 H), 1.97 (q, $J = 3 \times 7.5$ Hz, 2 H), 2.86 (dsext, J = 10.0, 5 × 7.5 Hz, 1 H), 5.00 (bt, $J = 2 \times 7.5$ Hz, 1 H), 7.11 (d, J = 10.0 Hz, 1 H).

*2.2.7. 2-(5-Methyl-2-(propen-2-yl)-cyclopentyl)-malononitrile (**11**, 6:1 mixture of stereoisomers)*

By heating of neat **10** at 120 °C for 5 h, quantitative. ^{1}H NMR ($CDCl_3$): major isomer: δ = 1.19 (d, J = 7.5 Hz, 3 H), 1.39 (m, 1 H), 1.53–1.7 (m, 1 H), 1.69 (s, 3 H), 1.72–2.12 (m, 4 H), 2.48 (q, $J = 3 \times 10.0$ Hz, 1 H), 3.81 (d, J = 4.5 Hz, 1 H), 4.82 (bs, 1 H), 4.85 (t, 2×1.2 Hz, 1 H). Minor isomer: δ = 1.22 (d, J = 7.5 Hz, 3 H), 1.80 (s, 3 H), 1.5–2.3 (m, 6 H), 2.70 (m,1 H), 3.52 (d, J = 5.0 Hz, 1 H), 4.95 (bs, 1 H), 5.07 (bs, 1 H).

2.2.8. 1R,4R*,5S*-4,7,7-Trimethyl-bicyclo[3.2.0] heptane-6,6-dicarbonitrile (**12**)*

A solution of 1.0 g (5.3 mmol) **10** in 200 ml *n*-hexane was placed in a 200 ml solidex glass immersion well irradiation apparatus under an argon atmosphere and irradiated as described in Section 2.2.4. After 7 h irradiation, removal of solvent, and crystallisation from *n*-hexane/ether at −23 °C, 900 mg of 96% pure 10 were obtained, m.p. 30–36 °C. ^{1}H NMR ($CDCl_3$): δ = 0.89 (d, J = 7.0 Hz, 3 H, 4-methyl), 1.16 (s, 3 H, *endo*-7-methyl), 1.44 (s, 3 H, *exo*-7-methyl), 1.49 (m, 1 H, *exo*-3-H), 1.67 (m, 2 H, 2-H), 2.08 (ddt, J = 13.5, 12.5, 2×6.5 Hz, 1 H, *endo*-3-H), 2.37 (qddd, 3×7.0, 6.5, 2.5, 1.5 Hz, 1 H, *endo*-4-H), 2.58 (ddd, J = 9.3, 8.2, 1.5 Hz, 1 H, 1-H), 2.76 (dd, J = 8.2, 1.5 Hz, 1 H, 5-H). ^{1}H,^{1}H-NOE enhancements: 0.89/1.67, 0.89/2.37, 0.89/2.76, 1.16/1.44, 1.16/1.67, 1.16/2.08, 1.44/2.58, 2.08/2.37, 2.58/2.76. ^{13}C NMR ($CDCl_3$): δ = 19.5 (q, $J = 3 \times 126$ Hz, 4-CH_3), 21.1 (q, $J = 3 \times 127.2$ Hz, *endo*-7-CH_3), 24.7 (t, 2×130.8 Hz, C-2), 29.7 (q, $J = 3 \times 127.6$ Hz, *exo*-7-CH_3), 33.6 (t, $J = 2 \times 128.8$ Hz, C-3), 36.9 (d, J = 131.8 Hz, C-4), 37.9 and 40.8 (two s, C-6 and C-7), 47.1 (d, J = 139 Hz, C-1), 49.2 (d, J = 149.3 Hz, C-5), 113.1 and 115.3 (two s, two CN).

*2.2.9. (3Z)- and (3E)-4,8-Dimethyl-1,3,7-nonatriene-1, 1-dicarbonitrile (Z-**13** and E-**13**)*

A slurry of 10.5 g plaster of Paris in a solution of 2.41 g (15.8 mmol) citral (5:4 mixture of geranial and neral), 1.15 g (17.4 mmol) malononitrile, and five drops each of glacial acetic acid and piperidine was stirred at room temperature under an argon atmosphere for 3 h. After filtration and washing of the filter cake with 300 ml ether the combined solutions were freed of solvent and the dark-yellow oily residue was chromatographed over 300 g silica gel with pentane and 11% ether to furnish 1.30 g (6.5 mmol) *Z*-13 followed by 1.63 g (9.15 mmol) *E*-**13**. *Z*-**13**: MS: m/z = 200 (M^+). IR (KBr): 2966 (m), 2914 (m), 2224 (s), 1610 (s), 1554 (m), 1439 (m), 1375 (m), 1197 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 309 nm (4.37). ^{1}H NMR ($CDCl_3$): δ = 1.58 (d, J = 1.15 Hz, 3 H, CH_3), 1.69 (q, $J = 3 \times 1.25$ Hz, 3 H, CH_3), 2.08 (d, J = 1.33 Hz, 3 H, 4-CH_3), 2.18 (q, $J = 3 \times 7.27$ Hz, 2 H, 6-H), 2.37 (t, $J = 2 \times 7.31$ Hz, 2 H, 5-H), 5.02 (bt, J = 7.33 Hz, 1 H, 7-H), 6.48 (bd, J = 12.16 Hz, 1 H, 3-H), 7.66 (d, J = 12.18 Hz, 1 H, 2-H). ^{1}H, ^{1}H-NOE enhancements: 2-H/5-H, 3-H/4-CH_3. ^{13}C NMR ($CDCl_3$): δ = 17.2 (CH_3), 25.6 (CH_3), 26.0 (CH_3), 26.7 (C-6), 34.1 (C-5), 80.7 (C-1), 111.7 (CN), 113.9 (CN), 121.8 (CH), 122.3 (CH), 134.3 (C-8), 155.8 (C-2), 164.8 (C-4). *E*-**13**: MS: m/z = 200 (M^+). IR (KBr): 2966 (m), 2930 (m), 2913 (m), 2855 (m), 2224 (s), 1611 (s), 1557 (m), 1440 (m), 1375 (m), 1224 (m), 608 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 309 nm (4.40). ^{1}H NMR ($CDCl_3$): δ = 1.61 (d, J = 1 Hz, 3 H, CH_3), 1.69 (q, $J = 3 \times 1.25$ Hz, 3 H, CH_3), 2.02 (d, J = 1.35 Hz, 3 H, 4-CH_3), 2.23 (m, 2 H, 6-H), 2.34 (bt, $J = 2 \times 7.52$ Hz, 2 H, 5-H), 5.04 (bt, $J = 2 \times 6.96$ Hz, 1 H, 7-H), 6.48 (bd, J = 12.13 Hz, 1 H, 3-H), 7.72 (d, J = 12.18 Hz, 1 H, 2-H). ^{1}H, ^{1}H-NOE enhancements: 2-H/4-CH_3, 3-H/5-H. ^{13}C NMR ($CDCl_3$): δ = 17.7 (CH_3), 18.8 (CH_3), 25.6 (CH_3), 26.1 (C-6), 41.0 (C-5), 81.2 (C-1), 111.7 (CN), 113.9 (CN), 121.4 (CH), 122.1 (CH), 133.4 (C-8), 155.9 (C-2), 165.0 (C-4).

*2.2.10. 1α,5α-4,8,8-Trimethyl-bicyclo[4.2.0]oct-4-ene-7, 7-dicarbonitrile (**14**)*

A solution of 4.0 g (20 mmol) **13** (1:1 *Z*,*E* mixture) in 400 ml acetonitrile was irradiated as described in Section 2.2.1 for 24 h. Evaporation of solvent and chromatography of the residue over silica gel with pentane and 2–10% ether furnished 3.4 g (17 mmol) **14**, colourless, m.p. 57–58 °C. MS: m/z = 200 (M^+). IR (KBr): 2973 (s), 2941 (s), 2240 (s), 1664 (m), 1469 (m), 1445 (m), 1375 (m), 1257 (m), 1159 (m), 1141 (m), 1022 (m), 849 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.29 (s, 3 H, 8β-CH_3), 1.51 (s, 3 H, 8α-CH_3), 1,79 (s, 3 H, 4-CH_3), 1.76–1.83 (m, 2 H, 2-H), 1.97 (m, 1 H, 3-H), 2.02 (m, 1 H, 3-H), 2.14 (bdd, J = 8.9, 7.5 Hz, 1 H, 1-H), 3.38 (bd, J = 8.2 Hz, 1 H, 6-H), 5.43 (m, 1 H, 5-H). ^{1}H,^{1}H-NOE enhancements: 1-H/6-H, 1-H/8α-CH_3, 5-H/6-H, 5-H/4-CH_3, 6-H/8α-CH_3, 8α-CH_3/8β-CH_3. ^{13}C NMR ($CDCl_3$): δ = 20.8 (CH_3), 21.8 (C-2), 24.3 (CH_3), 27.1 (C-3), 27.8 (CH_3), 39.1 (C-6),

40.45 (C-7), 40.52 (C-1), 43.2 (C-8), 114.5 (CN), 114.8 (CN), 115.2 (C-5), 143.5 (C-4).

*2.2.11. 3-But-3-enyl-2,2-dimethyl-oxetane-4, 4-dicarbonitrile (**15**)*

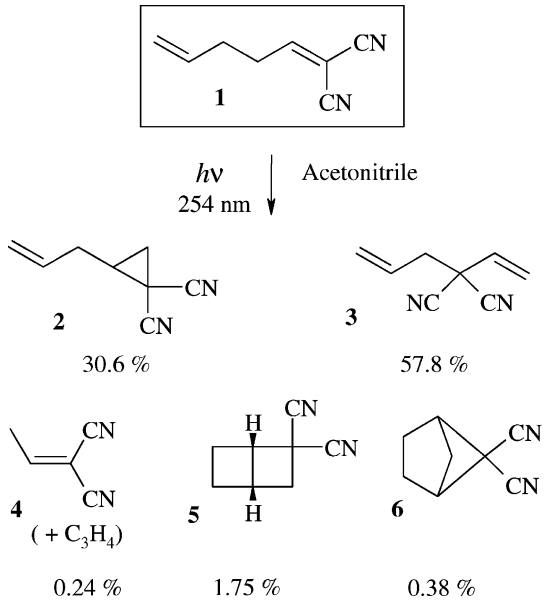
A solution of 500 mg (3.78 mmol) **1** in 50 ml acetone was irradiated as described in Section 2.2.1 for 28.5 h. Removal of solvent and short-path distillation at 0.01 mbar up to 150 °C bath temperature furnished 181 mg distillate which was chromatographed over 70 g silica gel with dichloromethane. 152.4 mg **15** was eluted as the first fraction. ^{1}H NMR ($CDCl_3$): $\delta = 1.48$ (s, 3 H), 1.55 (s, 3 H), 1.84 (dtd, $J = 14.0, 2 \times 7.0, 6.3$ Hz, 1 H, 1′-H), 2.02 (ddt, $J = 14.0, 9.2, 2 \times 6.5$ Hz, 1 H, 1′-H), 2.10 (m, 2 H), 3.34 (dd, $J = 9.2, 6.3$ Hz, 1 H, 3-H), 5.09 (bd, $J = 10$ Hz, 1 H, *E*-4′-H), 5.11 (bd, $J = 17$ Hz, 1 H, *Z*-4′-H), 5.74 (ddt, $J = 17, 10, 2 \times 7.0$ Hz, 1 H, 3′-H). ^{13}C NMR ($CDCl_3$): $\delta = 23.3$ (q, $J = 3 \times 127$ Hz, CH_3), 25.9 (t, 2×126 Hz, C-1′), 30.6 (t, 2×125 Hz, C-2′), 30.9 (q, $J = 3 \times 127$ Hz, CH_3), 53.9 (d, $J = 141$ Hz, C-3), 65.0 (s, C-4), 89.8 (s, C-2), 112.7 (s, CN), 114.2 (s, CN), 117.5 (dd, $J = 158, 153$ Hz, C-4′), 135.6 (d, $J = 152$ Hz, C-3′).

2.3. Analytical irradiations

These were carried to only partial conversions. Thus, the determination of the dependence of the ratio [**15**]/[**6**] on [**1**] in acetone was carried to conversions of **1** of 1.3–10%.

3. Results and discussion

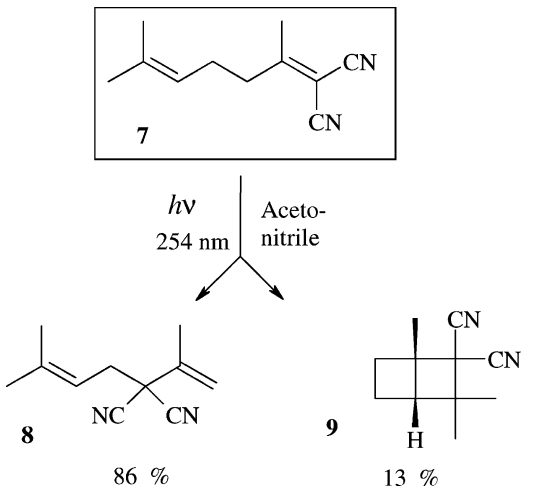
The DCNA **1** on direct irradiation with 254 nm in acetonitrile was found to furnish the product distribution shown in Scheme 1. Of these products, **2** represents the typical photoreactivity of directly excited DCNA bearing no additional C=C bonds, [5,6] **3** and **4** represent the typical photoreactivity of directly excited Δ^5-unsaturated DCNA as it was known previous to our work, [1–4] while intramolecular [2 + 2] cycloadducts like **5** and **6** had hitherto not been observed on direct irradiation of DCNA. The DCNA **7**, which differs from **1** by bearing three additional methyl groups, was found to furnish under the same conditions predominantly the analogue of **3**, viz. **8** [8], (Scheme 2); an expected result [1–4]. **7** was found to differ from **1** by not forming the analogue of **2** in a significant amount; an expected result as well [5,6]. Surprisingly, however, **7** furnished besides **8** as much as 13% **9**; this was much higher a relative amount than the 1.75% at which the analogous **5** had been formed. Switching from Δ^5- to Δ^6-unsaturation greatly enhanced the tendency towards this mode of reaction. Thus, the DCNA **10** on direct irradiation in *n*-hexane with 254 nm formed as much as 67% of the intramolecular [2 + 2] cycloadduct **12** (Scheme 3). **10** is thermally labile by readily undergoing intramolecular ene addition to furnish **11** (two stereoisomers, 6:1, of undetermined configuration [13]) at elevated temperatures, [13,14]



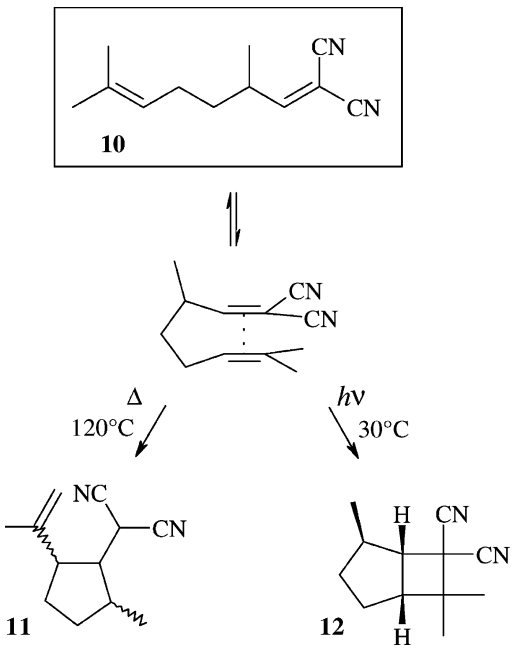
Scheme 1.

but it is stable at 30 °C at which the irradiations were carried out. **13**, at last, featuring Δ^7-unsaturation, on direct irradiation furnished the intramolecular [2 + 2] cycloadduct **14** in 85% isolated yield (Scheme 4).

The tendency among **1**, **7**, and **10** in their propensities to form the [2+2] cycloadducts is paralleled by their absorption properties. The absorption spectrum of **1** in *n*-hexane above 200 nm is virtually indistinguishable from the absorption spectra of DCNA that are devoid of further unsaturation, [5] featuring one single band, $\lambda_{max} = 225$ nm ($\log \varepsilon = 4.07$), and no absorption above 270 nm. The absorption spectra of **7** and **10** in *n*-hexane, while showing the same main band like **1**, however show in addition a second absorption at longer wavelengths, i.e. for **7**: 256 nm (sh; $\log \varepsilon = 3.73$, tailing to ca. 295 nm); for **10**: 258 nm (sh; $\log \varepsilon = 3.28$, tailing to ca. 330 nm). In contrast to the main bands which remain almost

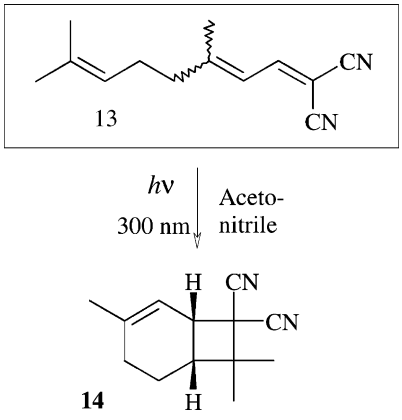


Scheme 2.



Scheme 3.

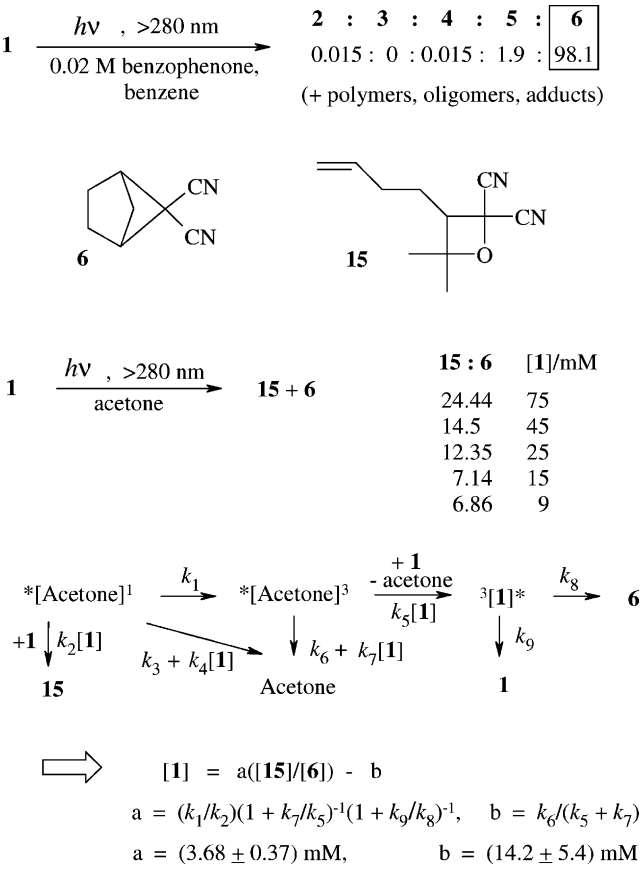
unchanged upon a change of the solvent from *n*-hexane to acetonitrile, [5] the extra band for **7** experienced a strong bathochromic shift: λ_{max} (acetonitrile) = 312 nm ($\log \varepsilon$ = 2.00) [8]. These extra bands indicate that in cases **7** and **10** closed conformations entailing the formation of intramolecular CT complexes between the two C=C bonds coexist with the stretched conformations. They thus suggest that the enhanced propensity to form the [2 + 2] cycloadducts in cases **7** and **10** may be due to these CT complexes. When **7** was irradiated in acetonitrile with >280 nm (i.e. largely into the CT band) rather than with 254 nm, the ratio [**9**]/[**8**] increased from 0.15 to 0.53. When **10** was irradiated in *n*-hexane with >280 nm (i.e. largely into the CT band) rather than with 254 nm, the relative amount of **12** among the photoproducts rose from 67 to >86%. Hence, the CT complexes are converted on irradiation to **9** and **12**, respectively.



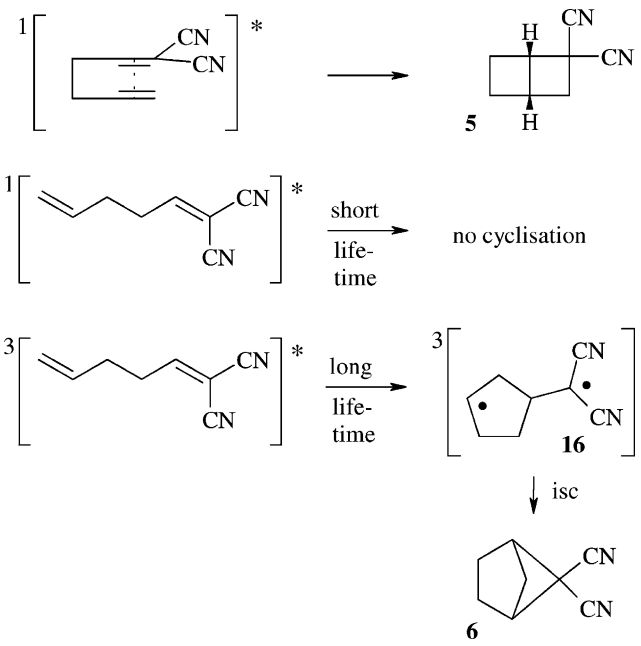
Scheme 4.

The photochemistry based on direct excitation of intramolecular CT complexes, formed by the DCNA moiety and substituted phenyl moieties in several 4-phenyl-DCNA, has been studied before [15]. Instead of [2 + 2] cycloaddition, the prevailing reaction in these cases was formation of a five-membered ring triggered by an attack of the C-2 atom of the DCNA moiety on the phenyl ring.

The photochemistry of **1** on direct irradiation, displayed in Scheme 1, is due to the first excited singlet state of **1** [5]. When **1** was irradiated with >280 nm (where **1** does not absorb light) in the presence of benzophenone, i.e. under conditions of sensibilisation by triplet benzophenone, it gave rise to an entirely different product spectrum (Scheme 5) which must be due to the triplet state of **1**. **6** is now a main product, accounting for 98% of the non-polymeric material formed from **1**, in analogy to an earlier finding obtained with another Δ^5-unsaturated DCNA [4]. The small amount (0.38%) of **6** found on direct irradiation of **1** (Scheme 1) may well be due to triplet **1** which is probably formed in about 1% from the first excited singlet of **1** [5]. Irradiation of **1** in acetone with >280 nm, i.e. under conditions where only acetone absorbs light, furnished, besides material of higher molecular weight, **15** and **6** (Scheme 5). The ratio [**15**]/[**6**] increased with [**1**] (Scheme 5). This indicates that two different excited states of acetone must be involved, the



Scheme 5.



Scheme 6.

first one giving rise to **15** and the second one giving rise to **6**, and that the first one must be the precursor to the second one. Since the excited state of acetone directly populated by light of >280 nm is the lowest exited singlet ($^1n\pi^*$), lower to which in energy is only one further excited state, viz. the triplet $^3n\pi^*$, one may conclude that **6** is formed by sensitation of **1** by acetone in its $^3n\pi^*$state, whereas the oxetane **15** is formed by addition of **1** to acetone in its $^1n\pi^*$ state. The latter result is in line with an analogous conclusion obtained in case of the related oxetane formation from acetone and 1,2-dicyanoethylene [16,17]. The corresponding reaction scheme, displayed in Scheme 5, predicts a linear increase of the ratio [**15**]/[**6**] with [**1**] (Scheme 5) which is in agreement with observation. The principal cause for the strongly different propensities of the first excited singlet states of benzophenone and acetone to form oxetanes of type **15** is the difference in their lifetimes (benzophenone in benzene: 30 ps [18], acetone, neat liquid: 1.7 ns [19]).

While the [2 + 2] cycloaddition of ^{1}[1]*, yielding **5**, involves the intramolecular singlet exciplex, the [2 + 2] cycloaddition of ^{3}[1]* obviously does not involve the analogous triplet exciplex since it does not lead to **5** but to **6**. Instead, ^{3}[1]*, the triplet DCNA chromophore of which resembles a 1,2-diradical, ring-closes preferentially to **16** (Scheme 6) which is the energetically most stable of four potentially accessible triplet 1,4-diradicals and which on intersystem crossing collapses to **1** and/or to **6**. In our view, this is another illustration of the notorious reluctance of photochemical systems to form triplet exciplexes [20,21]. ^{1}[1]*, if formed in its open conformation, cannot follow the analogous path like ^{3}[1]* since its lifetime is too short [5,6] to allow the necessary change of conformation during its lifetime.

4. Conclusion

Those 1-alkene-1,1-dicarbonitriles (1,1-dicyano-1-alkenes, DCNA) that bear an additional Δ^5-, Δ^6-, or Δ^7-C=C bond and show an absorption band due to an intramolecular CT complex between the two double bonds, on irradiation of this band pass into the "linear" intramolecular [2 + 2] cycloadducts like **5**, **9**, and **12**. On irradiation of their main absorption band, appearing at shorter wavelengths relative to the CT band, they preferentially form no [2 + 2] cycloadducts but rearrangement products. On triplet sensitisation of **1**, the "crossed" intramolecular [2 + 2] cycloadduct **6** which is isomeric to **5** is formed as the main monomeric product. The formation of **6**, in contrast to that of **5**, appears not to involve an exciplex but rather a ring closure of triplet-**1** to the most favourable triplet 1,4-diradical, viz. **16**, which on intersystem crossing collapses to **6**.

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