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The photochemistry of an 1,1-dicyano-3-oxa-1-alkene and of its 3-aza analogue

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Abstract

The photoreactions of two 3-alkoxy-1,1,-dicyano-1-alkenes, viz. 2-(2,2-dimethyl-tetrahydrofuran-3-ylidene)-malononitrile (**1**) and 2-(2-methoxy-2-methyl-propylidene)-malononitrile (**6**), and of the analogue of **1** bearing methylamino in place of oxygen, **8**, on direct irradiation has been investigated. Compounds **1** and **6** rearrange to 2-alkoxy-1,1-dicyano-cyclopropanes via 1,2-migration of methyl followed by ring closure. The cyclopropanes are thermally unstable but when the irradiation of **1** was carried out in methanol, the product **4** resulting from ring opening addition of methanol to the cyclopropane was obtained in high yield. In contrast to **1**, **8** was photostable due to efficient intramolecular quenching of the excited dicyanoalkene chromophore by the tertiary amine nitrogen atom. A 1,3-transposition product of **1**, 3-isopropylidene-tetrahydrofuran-2,2-dicarbonitrile (**3**), is formed as a by-product of **4**. Its probable mode of formation is discussed.

Keywords: Photoisomerization; 1,2-Shift; Cyclopropane; Intramolecular quenching

1. Introduction

1,1-Dicyano-1-alkenes (DCNA) devoid of further unsaturation and of heteroatoms undergo an "olefin-to-cyclopropane-photorerarrangement" (OCPR) upon direct excitation with light of 253.7 nm wavelength as pictured in Scheme 1 [1]. OCPR proceeds via the cationic mechanism shown in Scheme 1 and, therefore, proceeds efficiently if the substituents R^3 and R^4 left behind on atom C-3 after departure of the migrating group R^2 can stabilize a positive charge on C-3. Thus, if R^3 and R^4 are varied from hydrogen to alkyl, the efficiency of OCPR increases dramatically [1].

Alkoxy placed directly on carbonium is known to be a very much better stabilizer for the positive charge than alkyl, which would suggest that 3-alkoxy-substituted DCNA underwent particularly efficient OCPR furnishing 2-alkoxy-1,1-dicyano-cyclopropanes (Scheme 1, R^3 = RO); dialkylamino should be even better than alkoxy. Unfortunately, 2-alkoxy-1,1-dicyano-cyclopropanes are thermally quite unstable and polymerize readily; [2] they thus might frustrate attempts to isolate them. On the other hand, they are known to undergo ready ring cleavage with alcohols at ambient temperature to furnish cleanly 3,3-dialkoxy-1,1-dicyano-propanes (Scheme 2) [2,3]. With this in mind, we investigated the photochemical behavior of two 3-alkoxy- and one 3-dialkylamino-DCNA.

2. Experimental

2.1. General aspects

For general methods, see the accompanying paper [4]. Irradiations used low-pressure mercury lamps and quartz equipment opaque below 200 nm. Given the UV–VIS absorption spectra of DCNA, the principal exciting wavelength was, therefore, 253.7 nm. The molecular constitutions and configurations of all new compounds followed unambiguously from NMR experiments (400 MHz ^{1}H NMR including NOE where appropriate, 100 MHz ^{13}C NMR BB-, DEPT-, and CH-correlation).

2.2. 2-(2,2-Dimethyl-tetrahydrofuran-3-ylidene)-malononitrile (1)

From 2,2-dimethyl-tetrahydrofuran-3-one [5] and malononitrile according to the standard procedure [6]. Purification of the crude product by distillation, bp 80 °C/0.13 mbar: mp 34–37 °C (from ether at −70 °C). UV (*n*-hexane): λ_{max} (log ε) = 235 nm (4.07); $\varepsilon_{253.7\,nm}$ = 6285. ^{1}H NMR ($CDCl_3$): δ = 1.54 (s, 6H), 3.13 (t, $J = 2 \times 6.5$ Hz, 2H),

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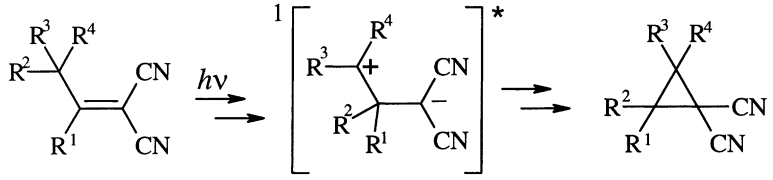
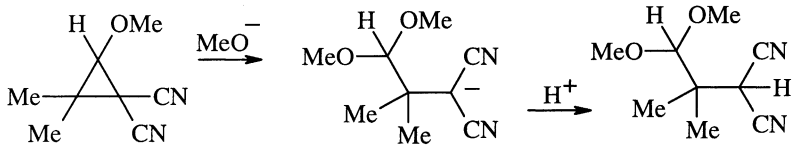


Scheme 1.



Scheme 2.

4.00 (t, $J = 2 \times 6.5$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 23.8$ (CH_3), 37.5 (CH_2), 63.5 (CH_2), 80.6 (C), 84.0 (C), 110.3 (CN), 111.8 (CN), 191.2 (C).

2.3. 3-Isopropylidene-tetrahydrofuran-2,2-dicarbonitrile (*3*) and seqtrans- and seqcis-2-(2-Methoxy-2,3-dimethyl-tetrahydrofuran-3-yl)-malononitrile (*4* and *5*)

The solution of 500 mg (3.09 mmol) **1** in 50 ml methanol was placed under argon in a 50 ml quartz vessel featuring internal cooling by tap water. The vessel was placed inside a Rayonet photoreactor equipped with low-pressure mercury lamps of 120 W overall output and was irradiated for 26 h. Removal of solvent left a residue which consisted of **3**–**5** in a ratio of 23:68:9 and no further products (^{1}H NMR analysis). Distillation at 100–140 °C (bath) and 1.3 mbar yielded 360 mg distillate which on crystallization from ether/pentane at −23 °C furnished 157.4 mg **4**, mp 83–85 °C. Removal of solvent from the mother liquor and chromatography of the residue over 50 g silica gel with dichloromethane furnished consecutively 58.6 mg **3**, 38.5 mg **5**, 1.8 mg unidentified mixture, 51.0 mg **4**, 7.9 mg unidentified mixture. A solution of **4** in methanol-d_4 containing a trace of *p*-toluene sulfonic acid in an NMR tube at room temp. was completely converted within few hours to a solution of **5** the methoxy group of which was completely replaced by trideuteriomethoxy. Compound **3**: ^{1}H NMR ($CDCl_3$): $\delta = 1.82$ (t, $J = 2 \times 1.0$ Hz, 3H), 2.00 (t, $J = 2 \times 2.0$ Hz, 3H), 2.70 (bt, $J = 2 \times 6.9$ Hz, 2H), 4.16 (t, $J = 2 \times 6.9$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 21.4$ (CH_3), 23.2 (CH_3), 30.3 (CH_2), 67.3 (C), 70.0 (CH_2), 112.9 (CN), 127.9 (C), 135.3 (C). Compound **4**: ^{1}H NMR ($CDCl_3$): $\delta = 1.37$ (s, 3H), 1.39 (s, 3H), 2.15 (dddq, $J = 13.4$, 8.6, 4.1, 3×0.5 Hz, 1H), 2.23 (ddd, $J = 13.4$, 10.0, 7.7 Hz, 1H), 3.20 (s, 3H), 3.67 (s, 1H), 3.76 (ddd, $J = 10.0$, 8.8, 4.1 Hz, 1H), 3.89 (ddd, $J = 8.8$, 8.6, 7.7 Hz, 1H). ^{1}H, ^{1}H NOE enhancements: 1.37/3.20, 1.37/3.67, 1.39/2.23, 1.39/3.67, 2.15/3.67, 3.67/3.89. ^{13}C NMR ($CDCl_3$): $\delta = 15.2$ (q, $J = 3 \times 127.4$ Hz), 17.7 (qt, $J = 3 \times 128.8$, 2×4.0 Hz), 31.2 (dsext, $J = 140.9$, 5×6.5 Hz), 35.2 (bt, $J = 2 \times 133.8$ Hz), 48.1 (q, $J = 3 \times 142.6$ Hz), 52.5 (bs), 63.3 (td, $J = 2 \times 149.3$, 3.8 Hz), 106.9 (bs), 112.3 (d, $J = 11.9$ Hz, 2CN). Compound **5**: ^{1}H NMR ($CDCl_3$): $\delta = 1.36$ (s, 3H), 1.40 (s, 3H), 1.93 (ddd, $J = 12.0$, 8.4, 3.8 Hz, 1H), 2.16 (ddd, $J = 12.0$, 9.8, 7.5 Hz, 1H), 3.23 (s, 3H), 3.78 (ddd, $J = 9.8$, 8.6, 3.8 Hz, 1H), 3.89 (ddd, $J = 8.6$, 8.4, 7.5 Hz, 1H), 4.27 (s, 1H). ^{1}H, ^{1}H NOE enhancements: 1.36/1.93, 1.36/3.89, 1.36/4.27, 1.40/3.23, 1.40/4.27, 2.16/4.27, 3.23/3.78, 3.23/4.27. ^{13}C NMR ($CDCl_3$): $\delta = 15.8$ (q, $J = 3 \times 127.6$ Hz), 19.7 (qq, $J = 3 \times 128.1$, 3×5.6 Hz), 29.2 (dquint, $J = 144.7$, 4×5.5 Hz), 37.0 (bt, $J = 2 \times 133.1$ Hz), 48.6 (q, $J = 3 \times 142.9$ Hz), 50.1 (bs), 63.3 (td, $J = 2 \times 149.3$, 4.4 Hz), 106.9 (bs), 111.9 (d, $J = 11.9$ Hz), 112.6 (d, $J = 11.6$ Hz).

2.4. 2-(2-Methoxy-2-methyl-propylidene)-malononitrile (*6*)

From 2-methoxy-isobutyraldehyde [7] and malononitrile according to the standard procedure [6]. Purification of the crude product by crystallization from chloroform/petrol ether at −70 °C, followed by crystallization at −70 °C from a large volume of petrol ether after filtration from a brown insoluble oil. Mp 49–52 °C, colourless. UV (*n*-hexane): λ_{max} ($\log \varepsilon$) = 222.7 nm (3.96); $\varepsilon_{253.7\,nm} = 849$. ^{1}H NMR ($CDCl_3$): $\delta = 1.43$ (s, 6H), 3.29 (s, 3H), 7.21 (s, 1H).

2.5. 2-(1,2,2-Trimethyl-pyrrolidin-3-ylidene)-malononitrile (*8*)

From 1,2,2-trimethyl-pyrrolidin-3-one [8] and malononitrile according to the standard procedure [6]. The crude product was purified by distillation, bp 80 °C/0.05 mbar. Mp 67–69 °C (from ether at −70 °C, yellow). The compound must be stored below −20 °C. UV (*n*-hexane): λ_{max} ($\log \varepsilon$) = 233 (4.05), 300 (2.27), 405 nm (1.12); $\varepsilon_{253.7\,nm} = 4912$. ^{1}H NMR ($CDCl_3$): $\delta = 1.36$ (s, 6H), 2.33 (s, 3H), 2.87 (t, 2×6.0 Hz, 2H), 2.98 (t, 2×6.0 Hz, 2H). ^{13}C NMR

($CDCl_3$): $\delta = 19.5, 33.5, 35.0, 50.0, 66.0, 81.0, 110.5, 112.5, 194.5$.

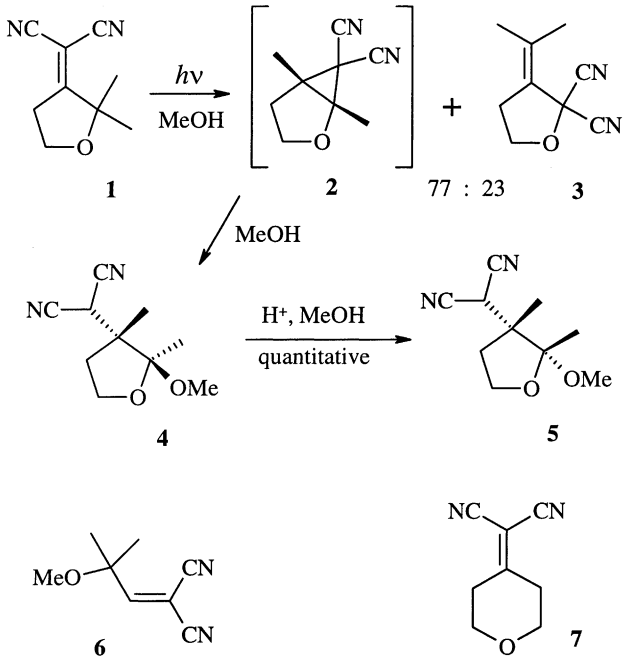
3. Results

When the 3-alkoxy-DCNA **1** and **6** were irradiated in cyclohexane to low conversions and the reaction mixtures immediately thereafter were investigated by GLC, the analyses revealed the formation of essentially one prevailing primary product in each case. However, these primary photoproducts according to GLC and NMR rapidly decayed to very complicated mixtures which we did not elucidate. The unstable primary products appeared to be the anticipated (vide supra) unstable [2] 2-alkoxy-1,1-dicyano-cyclopropanes. If so, they might be susceptible to the trapping reaction with methanol before decay [2,3]. When **1** was irradiated in methanol a result entirely different from that in cyclohexane was obtained; no decomposition products but a clean chemical reaction was observed (Scheme 3). Constitution and configuration of the main product **4** indicate its origin from the anticipated primary 2-alkoxy-1,1-dicyano-cyclopropane **2** by reaction with methanol; [3] methanol reacted by an SN_2 type attack on **2** leading to ring opening under Walden inversion. On acid catalysis, **4** was quantitatively converted to the more stable epimer **5**. We believe that the 9% of **5** found besides **4** and **3** in the irradiation mixture were due to such secondary rearrangement of **4**.

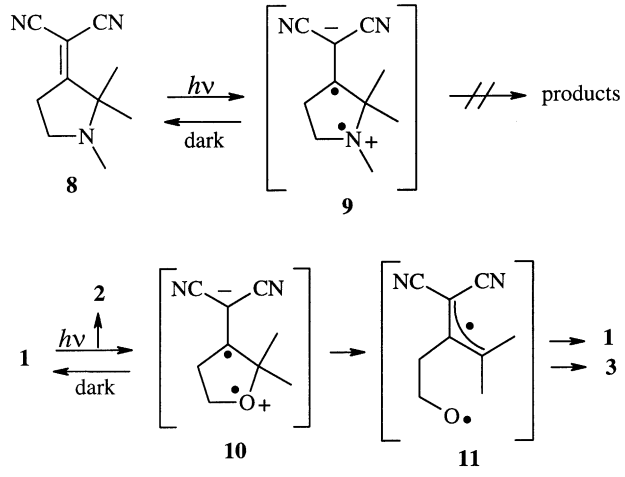
As anticipated (vide supra), the quantum yields of the photorearrangements of **1** (0.13) and of **6** (0.62), being primarily due to OCPR via the ionic mechanism (Scheme 1), are much higher than those for comparable DCNA bearing methyl in place of alkoxy (0.0058 and 0.043, respectively) [1].

For the sake of comparison, we also irradiated **7** which is not a 3-alkoxy, but a 4-alkoxy-DCNA. Compound **7** differs spectroscopically from **1** and **6**. While the UV–VIS absorption spectra of **1** and **6** are indistinguishable from those of plain DCNA lacking heteroatoms, above 200 nm showing one single band peaking at 235 nm and 223 nm, respectively ($\log \varepsilon = 4$), this band is split into two well-separated bands in the case of **7** [9]. The reason is a through-bond conjugation between the DCNA chromophore and the oxygen in **7**, made possible by the favorable chair geometry of the pyran ring [9]. The spectroscopic difference entails a difference in photochemical behavior: on irradiation with 253.7 nm in *t*-butanol, **7** decomposed very slowly (quantum yield 0.00033) to yield a complicated mixture of products which we did not elucidate; according to 400 MHz ^1H NMR analysis, a large part of the mixture was due to photoreaction with the solvent and only a minor part could have been due to OCPR. By contrast, cyclohexylidene malononitrile, which differs from **7** by having the oxygen replaced by methylene, in *t*-butanol undergoes OCPR (quantum yield 0.00033) as the principal reaction besides reaction with the solvent.

Compound **8** (Scheme 4) is the analogue of **1** bearing methylamino in place of oxygen. The UV–VIS spectrum of **8** differed markedly from that of **1** in that it exhibited two additional bands at longer wavelengths, at least one of them presumably being due to intramolecular charge-transfer. On one hand, **8** might have been anticipated to undergo OCPR via the ionic mechanism even more efficiently than **1** since dialkylamino is an even better stabilizer of a positive charge than alkoxy. On the other hand, the tertiary amine moiety could be anticipated to intramolecularly quench the photoexcited DCNA chromophore via single electron transfer in close analogy to the efficient intermolecular quenching observed between separated DCNA and tertiary amine molecules [4]. When irradiated with 253.7 nm in cyclohexane, **8** remained unchanged, in striking contrast to **1**.



Scheme 3.



Scheme 4.

Compound **8** did not even react with the solvent, in striking contrast to all DCNA (except 2-cyclopropyl-DCNA) that we investigated [1,4]. We conclude that intramolecular quenching of photoexcited **8** by single electron transfer to primarily afford **9** prevents all other photoreactions of **8** (Scheme 4). The behavior of **8** hints at the possible origin of the minor photoproduct from **1**, viz. **3**. As the results show, most of the photoexcited **1**, in contrast to **8**, does not undergo intramolecular single electron transfer since removal of an electron from oxygen requires more energy than from amino nitrogen. Only a minor amount of the photoexcited **1** might, therefore, form the analogue of **9**, viz. **10**. Compound **10** due to its higher energy as compared to **9**, might cleave to **11** (Scheme 4) which in turn would collapse to **1** and/or **3**.

4. Conclusion

3-Alkoxy-DNCA such as **1** and **6** undergo olefin-to-cyclopropane rearrangement much more efficiently than DCNA bearing methyl in place of alkoxy. The resulting cyclopropanes are thermally unstable, but can be trapped with methanol to furnish stable products such as the methanol adduct **4** formed from **1** in good chemical yield. The analogue of **1** bearing methylamino in place of oxygen, **8**, in contrast to **1** is photostable due to intramolecular quenching of the excited dicyanoalkene chromophore by singlet electron transfer from the amine nitrogen atom.

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