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Reductive Degradation of Photochromic Spiro-Oxazines. Reaction of the Merocyanine Forms with Free Radicals†

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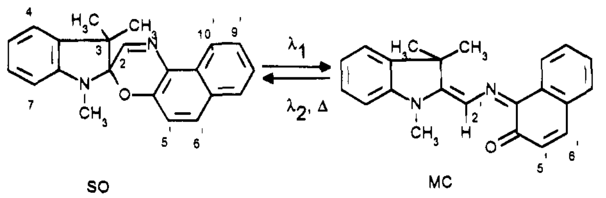
Photochromic spiro(indolino-naphthoxazine)s (SO) **1** and **2** react easily in their open merocyanine (MC) forms with free radicals to give deeply colored reduced free-radical adducts (FRA), **3**–**7**, devoid of photochromic activity. The adducts absorb in the 510–560 nm region and are characterized by high molar absorptivities.

Introduction

The photochromic property of spiro(indolino-naphtho)-oxazines is based on the reversible reaction that the colorless spiro-form SO undergoes to give colored merocyanine(s) MC when liquid solutions or polymer matrices containing SO are exposed to UV-light[2] (Scheme 1).

The metastable MC reverts back to SO either thermally[3] or photochemically.[4] Potential applications for photochromes have been envisaged in fields such as data storage and retrieval, optical filters, displays, special gadgets, etc. Unfortunately the photochromic phenomenon is not indefinitely reversible, as oxidative degradation processes (route a of Scheme 2) slowly convert, as we have recently shown,[5,6] the spiro-oxazines to products such as e.g. **1′** and **2′** devoid of photochromic activity. As part of our effort to define the parameters that affect the durability of spiro-oxazines with respect to photoexcitation, we have investigated their photochemistry under hypoxic conditions and found out that even in the absence of oxygen, SO's undergo degradation in solution and most importantly in polymer matrices as they react easily, in their open merocyanine form(s), with free radicals derived from adventitious radical sources and/or residual polymerization initiators. The radicals attack the C5′=C6′ double bond of MC and yield stable deeply colored mono- and/or disubstituted free-radical adducts (FRA) (Scheme 2, route b) that are no longer able to close back to the corresponding spiro-form. This constitutes a major problem for certain photochromic polymer matrices as they turn reddish on aging with a concomitant reduction of their useful lifetime.

Scheme 1



Results and Discussion

The 2-cyano-2-propyl radicals $C(CH_3)_2CN$ formed by UV-A (315–380 nm) photolysis of 2,2′-azobis(isobutyronitrile) (AIBN), a typical thermal and photochemical free-radical polymerization initiator, react in Ar-purged acetonitrile solutions of 1,3,3,4,5-pentamethylspiro[indoline-2,3′-[3*H*]naphth[2,1-*b*][1,4]oxazine], **1**, and 8′-propionyl-1,3,3,5,6-pentamethylspiro[indoline-2,3′-[3*H*]naphth-[2,1-*b*][1,4]oxazine], **2**, to give mono- and disubstituted reduced merocyanines (FRA) **3**, **5**, **4**, and **6** (ca. 5–20% yield) in a ratio that depended on the photolysis time, the reactivity of the attacking radical, and the nature of the substituent on the naphthoxazine moiety (Scheme 2).

The mass spectra (MS) of **3** and **4** have peaks at *m/e* 425, 492, respectively. The IR nitrile CN stretching frequencies are 2200 and 2230 cm^{-1} in the case of mono- and disubstituted compounds, respectively, whereas the carbonyl and imino group frequencies are $\nu_{C=O}$ = 1710 and $\nu_{C=N}$ = 1654 cm^{-1}. **3** and **4** are deeply colored and absorb at 518 nm (ϵ_{max} = 47 700) and 542 nm (ϵ_{max} = 14 200), respectively. The likely reaction mechanism requires the attack of a $C(CH_3)_2CN$ free radical on the C6′ position of MC followed by H-atom abstraction by the C5′ centered carbon radical from an otherwise unidentified H-donor (most likely AIBN) to give **3** or alternatively its reaction with a second $\dot{C}(CH_3)_2CN$ radical to yield **4** (Scheme 3).

When operating in CD_3CN no deuterium insertion at C5′ was observed. It is noteworthy that by photolysis with a high-power excimer laser (XeCl, 308 nm, 140 mJ/p, 30 ns duration) the disubstituted compound **4** was formed almost exclusively. We believe that the high local free radical concentration generated by the laser light high-photon density (10 MW peak-power) favors radical–radical reactions that yield **4**, over the radical/H-atom abstraction from a suitable donor that would give **3** instead. Similarly when **2** was photolyzed in ACN in the presence of AIBN the mono- and diadduct **5** (ϵ_{max} = 55 800, λ_{max} = 540 nm) and **6** (ϵ_{max} = 19 800, λ_{max} = 556 nm) were isolated. The conformation of **3** and **4** is that reported in Scheme 2, i.e. trans-trans-cis (TTC) with respect to the α, β, and γ bonds as required by the NOESY NMR data. Indeed H2′ (δ = 9.03 ppm for **3**; 9.19 ppm for **4**) correlates with NCH_3 (δ = 3.35 ppm for **3**;

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† Dedicated to Professor Glen A. Russell on the occasion of his 70th birthday.

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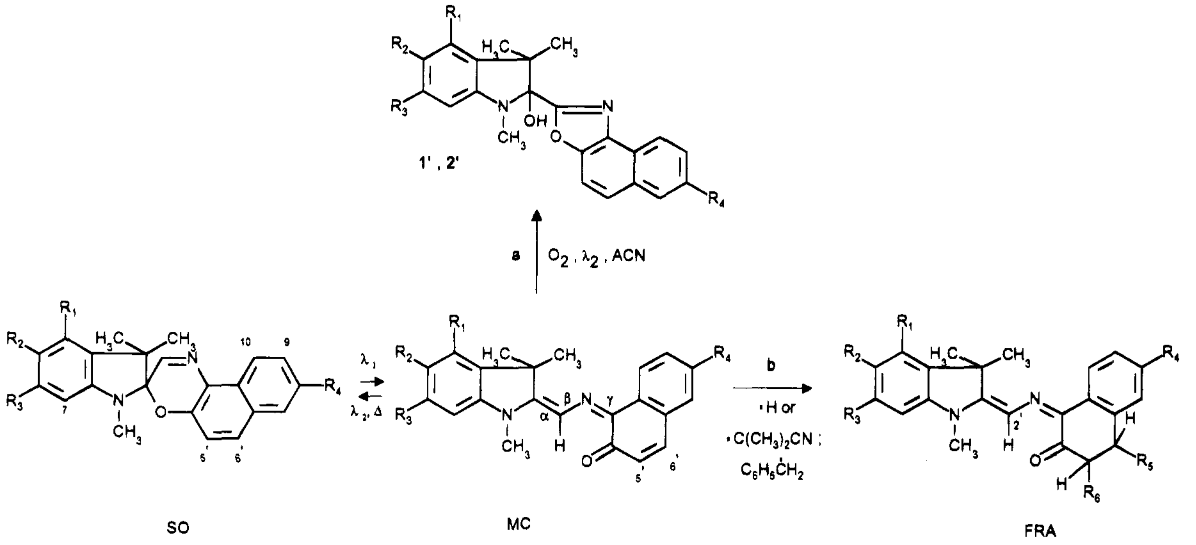
Scheme 2

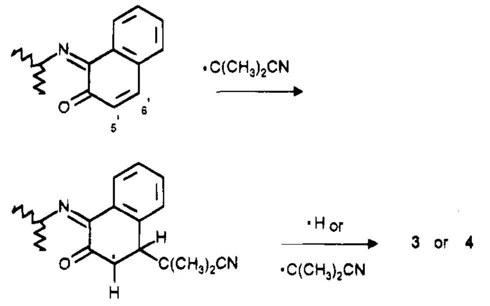


1 $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
2 $R_1 = H$; $R_2 = R_3 = CH_3$; $R_4 = COEt$

ACN / AIBN
light, Ar
3 $R_1 = R_2 = CH_3$; $R_3 = R_4 = R_6 = H$; $R_5 = C(CH_3)_2CN$
4 $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$; $R_5 = R_6 = C(CH_3)_2CN$
5 $R_1 = R_6 = H$; $R_2 = R_3 = CH_3$; $R_4 = COEt$; $R_5 = C(CH_3)_2CN$
6 $R_1 = H$; $R_2 = R_3 = CH_3$; $R_4 = COEt$; $R_5 = R_6 = C(CH_3)_2CN$

$C_6H_5CH_3$ / BOOB
7 $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$; $R_5 = R_6 = C_6H_5CH_2$

Scheme 3



3.41 ppm for 4) and H10′ with *gem*-CH_3 at C3 (δ = 1.89, 1.95 ppm for **3**, and 1.89, 1.97 ppm for **4**). It is therefore very likely that the reactive merocyanine form has the same TTC conformation. Theoretical studies,[7] NMR,[8] and time-resolved spectroscopic investigations[9] indicate that out of the eight possible isomers of MC the TTC conformer is the most stable and possibly the only one present in solution under our experimental conditions, as the reaction products that we have isolated have the same conformation. **3** and **4** may be considered as stable frozen forms of the metastable MC. For the latter the H2′ and NCH_3 proton resonances are downfield shifted to 10.22 and 3.79 ppm (cf. 9.19 and 3.14 ppm for **4**) probably because of the more extended conjugation and better planarity in MC (Scheme 1).[7,8] The carbonyl and imino group carbon atom resonances of **3** and **4** are at δ 193.77, 170.24, 190.48, and 172.05, respectively. The same reasoning applies in the case of **5** and **6**.

When an Ar-purged toluene solution of **1** containing di-*tert*-butyl peroxide (BOOB) was photolyzed with UV-A light the 5′,6′-dibenzyl substituted merocyanine **7** was isolated as almost sole product (ϵ_{max} = 14 900 at 518 nm). The hypochromicity and blue-shift of the visible absorption band of **7** with respect to that of **4** strongly indicate that **7** is less planar than **4** probably because of the steric hindrance introduced by the bulky two benzyl groups. The more distorted and less conjugated structure of **7** with respect to **4** is inferred also from the value of the ^{13}C chemical shift of the C=O of **7** that is downfield shifted to 197.7 ppm while, for the same reason, the H2′ signal is upfield shifted to 8.92 ppm (cf. 190.48 and 9.19 ppm for **4**). Interestingly **7** is also formed by γ-irradiation of deaerated toluene solutions of **1**.[10] However when benzene was used as a solvent and BOOB as radical source trace amounts of the methyl-substituted merocyanines were identified by MS analysis. In this case the electrophilic *tert*-butoxy radical is predicted not to add to the electron-poor double bond of the C=C—C=O system.[11] The trace amounts of CH_3 adducts must originate from attack of the methyl radicals derived from the *tert*-butoxy radical β-cleavage. All the radical adducts are photochemically stable in the absence of O_2 but undergo bleaching when their air-equilibrated solutions are irradiated with visible light. Similar results have been obtained with free radicals derived from other polymerization initiators, e.g. alkyl and cycloalkyl per-

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[11] The $C(CH_3)_2CN$ and $C_6H_5CH_2$ radicals add to the electron-poor double bond of methacrylates with rate constants 1590[12] and ca. 1300[13] M^{-1} s^{-1}, respectively. Whereas the benzyl radical is clearly nucleophilic, the ambiphilic 2-cyano-2-propyl radical reacts as a nucleophile with acrylates because of the high electron affinity of the latter.[12] Most likely however the reactivity of the two radicals is determined more by enthalpic than by polar factors.[12,13]

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oxides, whereas peresters such as dibenzoyl peroxide yield oxidation products of the type reported in ref 5 formed presumably through electron-transfer processes. The details will be reported elsewhere.

Experimental Section

Materials. Acetonitrile (ACN), toluene, and benzene were HPLC grade Aldrich products and were used as received. Hexane and ethyl acetate were Carlo Erba RPE grade. AIBN, BOOB, and other peroxides were Merck products. **1** and **2** were synthesized according to methods previously reported in the literature.[2]

Reaction of 1 and 2 with Free Radicals. General Procedure. The preparation of **3**–**6** was carried out at room temperature, by irradiating Ar-purged ACN solutions (3×10^{-3} M) of **1** and **2** containing an initial 4-fold excess of AIBN, in a Applied Photophysics photoreactor, mounting white fluorescent lamps peaking at 310 nm. Alternatively a Lambda Physik EMG 102 Excimer laser operating at 308 nm (XeCl) was used. **7** was prepared by irradiation of a deaerated toluene solution of **1** containing di-*tert*-butyl peroxide (1:4 initial ratio). After several hours (minutes in the case of laser photolysis) the solutions turned reddish and the coloration became deeper with time. From time to time more initiator was added to replenish the system, more Ar bubbled through, and the photolysis continued. No efforts were made to maximize the yields. The reaction mixture was first chromatographed on a silica column to eliminate the residual starting material (elution, hexane:ethyl acetate, 100% to 80:20% v/v).

The reaction products were then separated by HPLC (Waters 600 MS, diode array detector Waters PAD 991) on an analytical silica column (Sigma-Aldrich, Spherisorb, 5 μm, 250 mm, 4.6 mm o.d.) eluted with a hexane–ethyl acetate mixture whose composition was varied between 100% and 70/30 over 40 min. Satisfactory elemental analyses were obtained for all new products.

IR spectra (liquid film) were recorded on a Digilab FTS-15E FT-IR spectrometer. UV-vis spectra were recorded on a Hewlett-Packard HP-8452 diode array instrument. **3**–**6** were waxy products and it was not possible to determine the melting point. **7** melted between 50–60 °C.

The proton and carbon nuclear magnetic (^{1}H-NMR; ^{13}C-NMR) spectra of deuterated methylene chloride solutions were determined with a Bruker AMX-300 instrument at the frequencies indicated below. TMS was used as internal reference. The structures were fully assigned by 2D homonuclear shift COrrelated SpectroscopY (COSY) and NOE and Exchange SpectroscopY (NOESY). In the case of **3** and **4** complete ^{13}C chemical shift assignments were carried out by using DEPT and two-dimensional heteronuclear shift COrrelated SpectroscopY (HC-COSY).

3: yield 10%; ^{1}H-NMR (300.13 MHz, CD_2Cl_2) δ = 9.03 (s, 1H), 8.09 (m, 1H), 7.43 (m, 1H), 7.27 (m, 1H), 7.24 (m, 1H), 7.08 (d, 1H), 6.68 (d, 1H), 3.35 (s, 3H), 3.16 (t, 1H), 3.00 (d, 2H), 2.39 (s, 3H), 2.26 (s, 3H), 1.95 (s, 3H), 1.89 (s, 3H), 1.31 (d, 3H), 1.28 (d, 3H); ^{13}C-NMR (75.47 MHz, CD_2Cl_2) δ = 193.77 (C=O), 170.24 (C=N), 142.99, 140.32, 137.96, 134.36, 133.04, 132.73, 132.09, 130.92, 129.05, 128.49, 126.23, 126.23, 125.49 (CN), 115.29, 105.8, 49.82, 47.43, 43.48, 37.91, 30.28, 26.31, 26.25, 25.43, 24.73, 19.78, 15.40. IR (liquid film) CN 2200 cm^{-1}, C=O 1710 cm^{-1}, C=N 1654 cm^{-1}. UV-vis (ACN) λ_{max} (log ϵ) 520 (4.68). MS *m/e* 425 (M$^+$, 50), 410 (M$^+$ − 15, 28), 357 (M$^+$ − C(CH$_3$)$_2$CN, 30), 187 (100). Anal. Calcd for $C_{28}H_{31}N_3O$: C, 79.06; H, 7.29. Found: C, 79.32; H, 7.26.

4: yield 20%; ^{1}H-NMR (300.13 MHz, CD_2Cl_2) δ = 9.19 (s, 1H), 8.03 (m, 1H), 7.41 (m, 1H), 7.27 (m, 1H), 7.25 (m, 1H), 7.11 (d, 1H), 6.74 (d, 1H), 3.41 (s, 3H), 3.32 (s, 1H), 2.91 (s, 1H), 2.36 (s, 3H), 2.28 (s, 3H), 1.97 (s, 3H), 1.89 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H), 1.26 (s, 3H), 1.14 (s, 3H); ^{13}C-NMR (75.47 MHz, CD_2Cl_2) δ = 190.48 (C=O), 172.05 (C=N), 142.67, 140.30, 138.33, 133.28, 133.16, 132.90, 131.69, 131.67, 129.19, 128.95, 126.50, 124.95, 124.52, 123.84, 116.82, 106.35, 57.44, 50.30, 50.13, 38.52, 36.65, 30.58. 27.15, 26.27, 26.07, 25.79, 25.14, 24.27, 19.84, 15.42. IR (liquid film) CN 2230 cm^{-1}, C=O 1715 cm^{-1}, C=N 1652 cm^{-1}. UV-vis (ACN) λ_{max} (log ϵ) 542 (4.15). MS *m/e* 492 (M$^+$, 60), 477 (M$^+$ − 15, 28), 357 (M$^+$ − C(CH$_3$)$_2$CN, 30), 187 (100). Anal. Calcd for $C_{32}H_{36}N_4O$: C, 78.05; H, 7.32. Found: C, 78.28; H, 7.34.

5: yield 5%; ^{1}H-NMR (300.13 MHz, CD_2Cl_2) δ = 9.16 (s, 1H), 8.13 (d, 1H), 7.96 (d, 1H), 7.87 (s, 1H), 7.10 (s, 1H), 6.77 (s, 1H), 3.41 (s, 3H), 3.21 (t, 1H), 3.03 (q, 2H), 3.01 (d, 2H), 2.31 (s, 3H), 2.28 (s, 3H), 1.80 (s, 3H), 1.74 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H), 1.21 (t, 3H). UV-vis (ACN) λ_{max} (log ϵ) 540 (4.75). MS *m/e* 481 (M$^+$, 6), 466 (M$^+$ − 15, 3), 187 (100). Anal. Calcd for $C_{31}H_{35}N_3O_2$: C, 77.34; H, 7.28. Found: C, 77.54; H, 7.26.

6: yield 5%; ^{1}H-NMR (300.13 MHz, CD_2Cl_2) δ = 9.32 (s, 1H), 8.08 (d, 1H), 7.97 (d, 1H), 7.89 (s, 1H), 7.13 (s, 1H), 6.83 (s, 1H), 3.48 (s, 3H), 3.38 (s, 1H), 3.03 (q, 2H), 2.91 (s, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 1.82 (s, 3H), 1.74 (s, 3H), 1.44 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.21 (t, 3H), 1.17 (s, 3H). UV-vis (ACN) λ_{max} (log ϵ) 556 (4.30). MS *m/e* 548 (M$^+$, 5), 533 (M$^+$ − 15, 3), 187 (100). Anal. Calcd for $C_{35}H_{40}N_4O_2$ C, 76.64; H, 7.30. Found: C, 76.35; H, 7.33.

7: yield 15%. The NMR data are essentially those reported for **4** with the benzyl protons resonating at 2.5–2.8 and C2′H at δ 8.92. ^{13}C-NMR (75.47 MHz, CD_2Cl_2) δ = 197.7 (C=O), 169.4 (C=N). UV-vis (ACN) λ_{max} (log ϵ) 518 (4.17). MS *m/e* 538 (M$^+$, 10), 187 (70), 91 (100). Anal. Calcd for $C_{38}H_{38}N_2O$: C, 84.76; H, 7.06. Found: C, 84.48; H, 7.08.

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