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Photochemistry of β-(4-sydnonyl)-*o*-divinylbenzene: competitive *cis–trans* isomerization and photolysis

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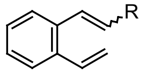
Abstract—New *cis*- and *trans*-3-aryl-4-[2-(2-vinylphenyl)ethenyl]sydnones **2**, aryl = phenyl, *p*-tolyl were prepared and transformed on irradiation in the presence of acrolein to a pyrazoline derivative that aromatized during isolation to *trans*-1-tolyl-3-[2-(2-vinylphenyl)ethenyl]pyrazole **7** and *trans*-5-formyl-1-tolyl-3-[2-(2-vinylphenyl)ethenyl]pyrazole **8**.

Previous work within our group has illustrated the potential of photochemical cycloaddition reactions of furan **1a**[1] and pyrrole **1b**[2] *o*-divinylbenzene derivatives. In developing the photochemical approach to the formation of heteropolycyclic compounds we turned our attention to sydnone derivatives of *o*-divinylbenzenes **2**.

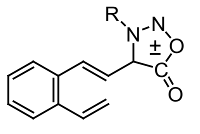
Sydnones belong to five-membered heterocyclic compounds known as 'mesoionic' and can be represented as hybrids of a number of mesomeric ionic structures.[3] They undergo intermolecular 1,3-dipolar cycloaddition in the presence of dipolarophiles followed by carbon dioxide evolution and aromatization to pyrazoles.[4] Sydnones[5a] as well as pyrazoles[5b] are interesting compounds because of their biological activities.

Photolysis of sydnones, a topic of extensive research by several groups,[6] appears to give a nitrile imine intermediate, proved by their intermolecular [3+2] cycloaddition reactions with alkene and alkyne derivatives, leading to pyrazolines and pyrazoles, respectively. The intramolecular trappings of photochemically formed nitrile imines have been studied only on 4-phenyl-3-(2-allylphenyl)sydnone[6h] and a few examples of 4-phenyl-3-(2-alkenyloxyphenyl)sydnones.[6q]

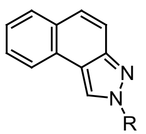
In this work we describe the irradiation of 4-aryl-3-(*o*-vinylstyryl)sydnones **2** that might yield pyrazolonaphthalene derivative **3** through the intramolecular [3+2] cycloaddition of the vinyl group and the primarily formed nitrile imine intermediate, or bicyclo[2.1.1]hexene derivative **4** by intramolecular [2+2] cycloaddition.



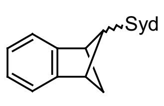
1a R= 2-furyl
1b R= 2-pyrrolyl



2a R= phenyl
2b R= *p*-tolyl



3a R= phenyl
3b R= *p*-tolyl



4a R= phenyl
4b R= *p*-tolyl

Keywords: Sydnones; Pyrazoles; Photochemistry; Nitrile imines; Dipolar cycloaddition.

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The starting compounds **2** were prepared by a Wittig reaction following the described procedure[1c] from a diphosphonium salt and the corresponding sydnone aldehydes.[7]

The new compounds, *cis*- and *trans*-**2** were separated by column chromatography and completely analysed and identified spectroscopically.[†]

The irradiation experiments on *cis*- and *trans*-**2** were performed in 10^{-3} M solutions of benzene, acetonitrile or methanol, respectively, at 350 nm. Besides some tarry materials and a *trans*-starting compound the photomixture contained various products but in quantities too small to be isolated. No formation of a major product was found. When the ethanol solution of *cis*-**2b** (10^{-5} M) was irradiated and the process followed by UV spectral change the first measurements showed a bathochromic shift and increase of the absorption maximum (Fig. 1). As can be seen, after 30 s the absorption maximum decreases. When the irradiation of *trans*-**2b** was followed by UV the absorption maximum gradually decreases (see Fig. 2). From these experiments it can be presumed that the *cis*–*trans* isomerization is competing with photolysis.

To investigate the irradiation process, and to prove the formation of the nitrile imine as the intermediate, the irradiation of **2b** in the presence of the dipolarophile, acrolein was performed. The alkene was chosen as dipolarophile to trap the nitrile imine intermediate and give

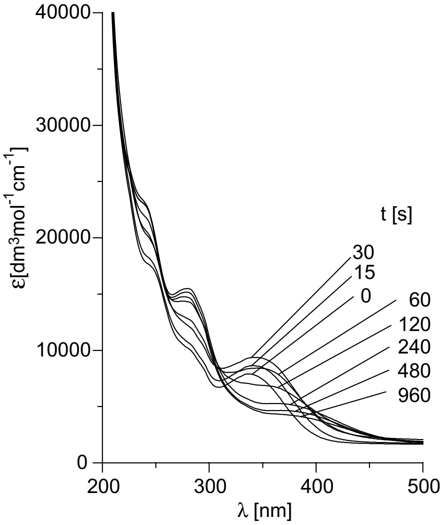


Figure 1. UV spectra after irradiation of *cis*-**2b** (ethanol, 366 nm).

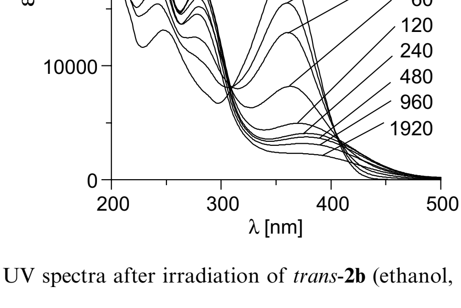


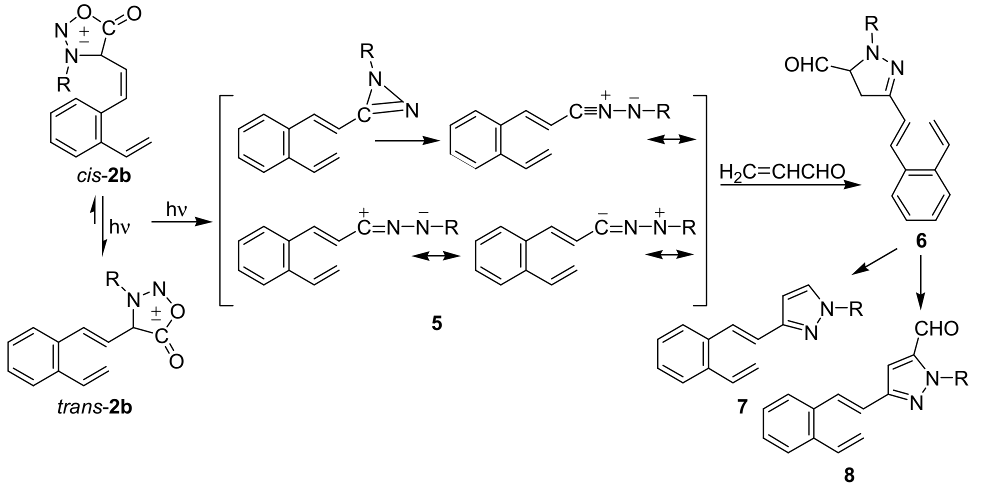
Figure 2. UV spectra after irradiation of *trans*-**2b** (ethanol, 366 nm).

[†] *cis*-3-Phenyl-4-[2-(2-vinylphenyl)ethenyl]sydnone (*cis*-**2a**): yellow crystals; mp 114–116 °C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 221 (15503), 246 (14,375), 287 (7047), 343 (6765); IR (KBr) ν_{max}/cm^{-1}: 1733 (CO); ^{1}H NMR (CDCl$_3$) δ/ppm (300 MHz): 7.52–7.36 (m, 3H), 7.31 (d, 1H, $J = 8.1$ Hz), 7.23–7.30 (m, 2H), 7.19 (d, 1H, $J = 7.8$ Hz), 7.10 (d, 1H $J = 7.8$ Hz), 6.96 (d, 1H, $J = 7.8$ Hz), 6.82 (d, 1H, $J = 12.0$ Hz), 6.56 (dd, 1H, $J = 10.8$ and $J = 17.4$ Hz), 6.23 (d, 1H, $J = 12.0$ Hz), 5.48 (dd, 1H, $J = 17.4$ and 1.2 Hz), 5.19 (dd, 1H, $J = 10.8$ and 1.2 Hz); ^{13}C NMR (CDCl$_3$) δ/ppm (75 MHz): 166.64 (s), 136.43 (s), 134.99 (d), 134.88 (d), 134.88 (s), 134.47 (s), 131.81 (d), 129.90 (d), 128.65 (d), 128.55 (d), 127.78 (d), 126.28 (d), 123.82 (d), 116.26 (t), 112.76 (d), 106.50 (s); MS *m*/*z* (%, fragment): 292 (10, M$^+$ + 2H), 290 (15, M$^+$), 231 (100), 230 (88), 217 (57), 129 (58), 128 (98).

trans-3-Phenyl-4-[2-(2-vinylphenyl)ethenyl]sydnone (*trans*-**2a**): yellow crystals; mp 121–123 °C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 246 (14,642), 289 (8331), 359 (20,196); IR (KBr) ν_{max}/cm^{-1}: 1747 (CO); ^{1}H NMR (CDCl$_3$) δ/ppm (600 MHz): 8.07 (d, 1H, $J = 15.9$ Hz), 7.73 (t, 1H, $J = 8.4$ Hz), 7.69 (t, 2H, $J = 8.4$ Hz), 7.61 (d, 2H, $J = 8.4$ Hz), 7.47 (d, 1H, $J = 7.6$ Hz), 7.30 (d, 1H, $J = 7.6$ Hz), 7.25 (t, 1H, $J = 7.6$ Hz), 7.20 (t, 1H, $J = 7.6$ Hz), 7.08 (dd, 1H, $J = 10.8$ and 17.4 Hz), 6.49 (d, 1H, $J = 15.9$ Hz), 5.64 (dd, 1H, $J = 17.4$ and 1.2 Hz), 5.37 (dd, 1H, $J = 10.8$ and 1.2 Hz); ^{13}C NMR (CDCl$_3$) δ/ppm (75 MHz): 166.08 (s), 136.86 (s), 134.34 (d), 134.34 (s), 133.40 (s), 132.26 (d), 130.22 (d), 128.85 (d), 128.43 (d), 127.71 (d), 126.65 (d), 125.57 (d), 124.93 (d), 117.07 (t), 111.92 (d),108.72 (s); Elemental analysis of the isomer mixture calcd for $C_{18}H_{14}N_2O_2$ (Mr = 290.324): C, 74.47; H, 4.86; N, 9.65%. Found: C, 74.24; H, 5.00%.

cis-3-(*p*-tolyl)-4-[2-(2-vinylphenyl)ethenyl]sydnone (*cis*-**2b**): yellow crystals; mp 68–70 °C; UV (EtOH), λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 337.6 (8350); ^{1}H NMR (CDCl$_3$) δ/ppm (300 MHz): 7.32 (d, 1H, $J = 7.5$ Hz), 7.21–7.06 (m, 6H), 6.97 (d, 1H, $J = 7.5$ Hz), 6.80 (d, 1H, $J = 11.7$ Hz), 6.57 (dd, 1H, $J = 10.5$ and 17.4 Hz), 6.20 (d, 1H, $J = 11.7$ Hz), 5.50 (dd, 1H, $J = 17.4$ and 1.0 Hz), 5.18 (dd, 1H, $J = 10.5$ and 1.0 Hz), 2.38 (s, 3H); ^{13}C NMR (CDCl$_3$) δ/ppm (75 MHz): 166.00 (s), 142.88 (s), 136.75 (s), 134.38 (s), 134.23 (d), 130.80 (s), 130.63 (d), 128.52 (d), 128.29 (d), 127.60 (d), 126.54 (d), 125.43 (d), 124.57 (d), 117.00 (t), 112.01 (d), 108.60 (s), 21.37 (q); MS *m*/*z* (%, fragment): 304 (100, M$^+$).

trans-3-(*p*-tolyl)-4-[2-(2-vinylphenyl)ethenyl]sydnone (*trans*-**2b**): yellow crystals; mp 163–165 °C; UV (EtOH), λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 359.0 (18,770); IR (KBr), ν_{max}/cm^{-1}: 1728 (CO); ^{1}H NMR (CDCl$_3$) δ/ppm (300 MHz): 7.97 (d, 1H, $J = 16.0$ Hz), 7.46–7.34 (m, 4H), 7.27–7.08 (m, 4H), 7.01 (dd, 1H, $J = 10.8$ and 17.1 Hz), 6.42 (d, 1H, $J = 16.0$ Hz), 5.57 (dd, 1H, $J = 17.1$ and 1.2 Hz), 5.29 (dd, 1H, $J = 10.8$ and 1.2 Hz), 2.44 (s, 3H); ^{13}C NMR (CDCl$_3$) δ/ppm (75 MHz): 166.17 (s), 142.00 (s), 135.93 (s), 134.63 (s), 134.49 (d), 134.25 (d), 131.53 (s), 130.05 (d), 128.30 (d), 128.13 (d), 127.34 (d), 125.64 (d), 123.22 (d), 115.54 (t), 112.52 (d), 105.00 (s), 21.18 (q); MS *m*/*z* (%; fragment): 304 (100, M$^+$); Elemental analysis of the isomer mixture calcd for $C_{19}H_{16}N_2O_2$ (Mr = 304.33): C, 74.98; H, 5.30; N, 9.20%. Found: C, 75.29, H, 5.47, N 9.12%.



Scheme 1.

an adduct which would not absorb at the same wavelength as the starting compound.

The irradiation of an acetonitrile solution of either *cis*- or *trans*-**2b** in the presence of acrolein gave, regioselectively, the *trans*-styrylpyrazoline derivative **6** in more than 90% yield based on the ^{1}H NMR spectrum of the crude mixture (Scheme 1). The formation of cycloadduct **6** was obvious from the presence of vinyl protons and ethylenic protons with a *trans* coupling constant in the aromatic region. In the aliphatic region of the ^{1}H NMR spectrum, an ABX system of three protons was found: two doublets of doublets at 3.48 and 3.24 ppm that were assigned to geminal protons, and a multiplet, due to the coupling with geminal and aldehyde protons, at 4.65 ppm. The doublet at 9.63 ppm indicated the presence of an aldehyde group on a saturated carbon atom.The corresponding signals of the aliphatic carbons in the ^{13}C NMR spectrum are at 67.86 (d) and 34.10 (t).[‡] During the purification by column chromatography on silica gel, two products were isolated, neither of which showed the characteristic ABX signals. From the analysis of the NMR spectra and mass spectra it was concluded that the pyrazoline **6** aromatizes to *trans*-1-tolyl-3-[2-(2-vinylphenyl)ethenyl]pyrazole (**7**, 30%) and *trans*-5-formyl-1-tolyl-3-[2-(2-vinylphenyl)ethenyl]pyrazole (**8**, 10%) by loss of formaldehyde or hydrogen, respectively.[§] In the ^{1}H NMR, compound **7** had doublets due to pyrazole protons at 7.86 and 6.68 ppm with a characteristic coupling constant of 2.4 Hz and M^+ 286 in its MS spectrum. Compound **8** has a singlet due to an aldehyde proton at 9.86 ppm in its ^{1}H NMR spectrum and M^+ 314 in the MS spectrum.

The structure of pyrazole derivative **8** was also proved by X-ray structure analysis (Fig. 3).

Based on these experiments it can be concluded that the 3-aryl-4-[2-(2-vinylphenyl)ethenyl]sydnones (**2**, aryl = phenyl, *p*-tolyl) undergo fast isomerization to the *trans*-isomer and competitive photolysis of the sydnone moiety giving the nitrile imine **5** which cannot react intramolecularly. The existence of the nitrile imine **5** was confirmed on irradiation in the presence of acrolein and by regioselective formation of the *trans*-styrylpyrazoline derivative **6** that during isolation aromatizes to the pyrazole derivatives **7** and **8**.

[‡] *trans*-5-Formyl-1-tolyl-3,4-dihydro-3-[2-(2-vinylphenyl)ethenyl]pyrazole **6**: ^{1}H NMR (CDCl$_3$) δ/ppm (600 MHz): 9.63 (d, 1H, $J = 3.6$ Hz), 7.55 (d, 1H, $J = 9.0$ Hz), 7.46 (d, 1H, $J = 9.0$ Hz), 7.30–7.27 (m, 2H), 7.11 (d, 2H, $J = 8.4$ Hz), 7.07 (d, 1H, $J = 16.5$ Hz), 7.02 (dd, 1H, $J = 10.8$ and 17.4 Hz), 6.98 (d, 2H, $J = 8.4$ Hz), 6.93 (d, 1H, $J = 16.5$ Hz), 5.64 (dd, 1H, $J = 17.4$ and 0.8 Hz), 5.39 (dd, 1H, $J = 10.8$ and 0.8 Hz), 4.65 (m, 1H), 3.48 (dd, 1H, $J = 16.8$ and 13.2 Hz), 3.24 (dd, 1H, $J = 16.8$ and 7.8 Hz), 2.29 (s, 3H); ^{13}C NMR (CDCl$_3$) δ/ppm (75 MHz): 199.39 (d), 149.02 (s), 142.27 (s), 136.68 (s), 136.67 (s), 134.57 (d), 134.22 (s), 131.11 (d), 130.02 (d), 128.43 (d), 128.05 (d), 126.97 (d), 126.07 (d), 122.64 (d), 117.41 (t), 113.27 (d), 67.86 (d), 34.10 (t), 20.54 (q).

[§] *trans*-1-Tolyl-3-[2-(2-vinylphenyl)ethenyl]pyrazole **7**: yellow crystals; mp 79–81 °C; ^{1}H NMR (CDCl$_3$) δ/ppm (300 MHz): 7.86 (d, 1H, $J = 2.4$ Hz), 7.63–7.56 (m, 3H), 7.51–7.44 (m, 2H), 7.33–7.23 (m, 4H), 7.14 (dd, 1H, $J = 10.8$ and 17.1 Hz), 7.12 (d, 1H, $J = 16.5$ Hz), 6.68 (d, 1H, $J = 2.4$ Hz), 5.67 (dd, 1H, $J = 17.1$ and 1.0 Hz), 5.39 (dd, 1H, $J = 10.8$ and 1.0 Hz), 2.39 (s, 3H); ^{13}C NMR (CDCl$_3$) δ/ppm (75 MHz): 151.92 (s), 137.61 (s), 136.30 (s), 136.14 (s), 135.06 (s), 134.83 (d), 129.84 (d), 128.19 (d), 127.80 (d), 127.75 (d), 127.66 (d), 126.48 (d), 126.10 (d), 122.54 (d), 118.86 (d), 116.55 (t), 104.64 (d), 20.83 (q); MS *m/z* (%, fragment): 286 (100, M^+).

trans-5-Formyl-1-tolyl-3-[2-(2-vinylphenyl)ethenyl]pyrazole **8**: yellow crystals; mp 56–59 °C; ^{1}H NMR (CDCl$_3$) δ/ppm (300 MHz): 9.86 (s, 1H), 7.61–7.56 (m, 2H), 7.51–7.45 (m, 2H), 7.41–7.34 (m, 4H), 7.31–7.24 (m, 2H), 7.11 (dd, 1H, $J = 10.9$ and 17.3 Hz), 7.06 (d, 1H, $J = 16.3$ Hz), 5.65 (dd, 1H, $J = 17.3$ and 1.2 Hz), 5.39 (dd, 1H, $J = 10.9$ and 1.2 Hz), 2.45 (s, 3H); ^{13}C NMR (CDCl$_3$) δ/ppm (75 MHz): 180.05 (d), 151.21 (s), 140.80 (s), 139.19 (s), 136.52 (s), 135.96 (s), 134.62 (d), 134.51 (s), 129.82 (d), 129.53 (d), 128.01 (d), 127.79 (d), 126.60 (d), 126.08 (d), 125.19 (d), 121.10 (d), 116.90 (t), 108.36 (d), 21.07 (q); MS *m/z* (%, fragment): 314 (100, M^+).

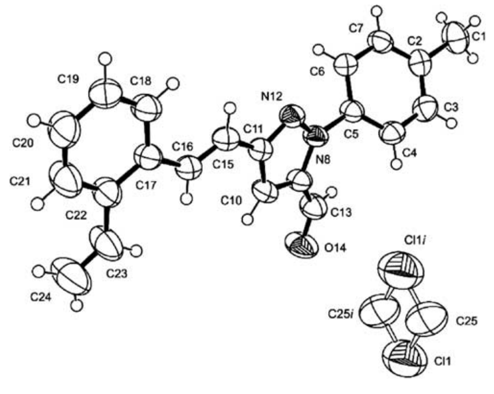


Figure 3. ORTEP drawing of **8** with the ellipsoid scaled at the 50% probability level.[¶] The solvent molecule is disordered (*i*; -x, 1-y,-z, C25 having *p.p.* = 0.5). The hydrogens at the disorderd carbon atoms were not located.

Acknowledgements

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[¶] *Crystal data* for **8** - $C_{21}H_{18}N_2O \times 1/2\ (CH_2Cl_2)$, $M_r = 355.83$, triclinic, $a = 8.516\ (2)$, $b = 9.445(3)$, $c = 12.309(5)$ Å, $\alpha = 103.06(1)$, $\beta = 90.93(1)$, $\gamma = 103.95(2)°$, $V = 933.4(5)$ Å^3, $T = 293(2)$ K, space group: P-1, $Z = 2$, μ(Mo-K_α) = 0.22 mm^{-1}, $R_1[F_o > 4\sigma(F_o)] = 0.0621$, final $wR(F^2) = 0.1522$; CCDC 249339.