Photoisomerization of 2,4,4,6-tetraaryl-4*H*-selenopyrans: a new heterocyclic ring contraction

Jiří Kroulík,*[a] Jan Čejka,[b] Pavel Šebek,[a] Petr Sedmera,[c] Petr Halada,[c] Vladimír Havlíček,[c] Stanislav Nešpůrek,[d] Bohumil Kratochvíl[b] and Josef Kuthan[a]

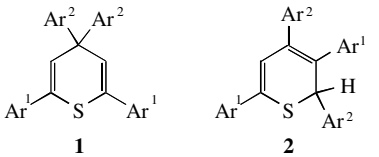
[a] *Department of Organic Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic. Fax: +42 022 431 1082; e-mail: Jiri.Kroulik@vscht.cz*
[b] *Department of Solid State Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic*
[c] *Institute of Microbiology, Academy of Sciences of the Czech Republic, 141 20 Prague 4, Czech Republic. Fax: +42 022 475 2749*
[d] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic. Fax: +42 022 251 6969*

10.1070/MC2001v011n03ABEH001430

The UV illumination of title compounds **3a**,**b** in acetonitrile solutions leads to corresponding five-membered ring isomers **4a**,**b**, probably, *via* open-ring intermediates, whereas the photocolouration was observed in the solid state.

The photochromism has recently highlighted a considerable application potential for data storage technologies.[1] The increasing activity focused on the development and features of new compounds with photochromic properties[1] prompted us to investigate possible consequences of the integration of selenium with a favourable photochromic system. 2,4,4,6-Tetraaryl-4*H*-thiopyrans **1** are known to exhibit UV photocolouration[2] followed by multi-step transformations to final 2,3,4,6-tetraaryl-2*H*-thiopyrans **2**.[2(c),(d)] Contrary, the properties and photochemistry of analogous 2,4,4,6-tetraaryl-4*H*-selenopyrans **3** remain almost unknown.[3] Hitherto reports are mostly intent on similar 2,4,6-triphenyl-4*H*-selenopyrans.[3] Of the considered 2,4,4,6-tetraphenyl derivatives, only parent 2,4,4,6-tetraphenyl-4*H*-selenopyran **3a**, prepared by the reaction of a 2,4,6-triphenylselenopyrylium salt with phenylmagnesium bromide, and its reaction with bromine have been reported.[4] Hence, here we report that the replacement of the sulfur 1-heteroatom by selenium dramatically changes the photoisomerization. Thus, acetonitrile solutions of 2,4,4,6-tetraphenyl-4*H*-selenopyran **3a** or 2,6-bis(4-fluorophenyl)-4,4-diphenyl-4*H*-selenopyran **3b**, prepared by the cyclocondensations of corresponding 1,5-diones $(ArCOCH_2)_2CPh_2$ with the H_2Se–HCl reagent, have been directly irradiated with a high-pressure 125 W mercury UV lamp in a quartz photoreactor at 12 °C for 1 h under argon† to afford approximately 2:3 equilibrium mixtures of (*E*)-3,3,5-triphenyl-2-(phenylmethylidene)-2,3-dihydroselenophene **4a** or (*E*)-5-(4-fluorophenyl)-2-[(4-fluorophenyl)methylidene]-3,3-diphenyl-2,3-dihydroselenophene **4b** and starting 4*H*-selenopyran **3a** or **3b**. Prolonged UV exposures lead to irreversible degradation of photoisomers **3a**,**b** and **4a**,**b** to complex mixtures of unidentified compounds. In the solid state, a photocolouration was observed. A sample of the polycrystalline powder of **3a** in MgO showed a green photocolouration after irradiation (300 s) with a high-pressure 200 W mercury discharge lamp.

The correct structures of **3a**,**b** of the starting 4*H*-selenopyrans follow from their ^{1}H and ^{13}C NMR and EI mass spectra.† On the other hand, the molecular structures of their photoisomers could not be positively derived in the same way. Therefore, the photoproduct from difluoro derivative **3b** was analysed by X-ray diffraction,‡ which confirmed the structure of **4b** (Figure 1). Then, the analogous structure of **4a** can be assigned to the photoisomer of **3a** by comparison of the corresponding spectral data.§



a Ar = Ph
b Ar = 4-FC_6H_4

The results indicate that the photochemically induced isomerization **3** → **4** in the 4*H*-selenopyran series surprisingly differs from the isomerization **1** → **2** in the 4*H*-thiopyran series and probably proceeds *via* a labile acetylenic intermediate like PhC≡C–CPh_2–CH=C(SeH)Ph, which may undergo two parallel intramolecular ring-closures to either 2,3-dihydroselenophenes **4** or to 4*H*-selenopyrans **3**.

For the sake of completeness, the UV–VIS absorption spectrum of an acetonitrile solution consists of a main maximum at 238 (log ε = 3.73 dm^3 mol^{-1} cm^{-1}) or 273 nm (log ε =

† The photochemical reactions were monitored by HPLC with an UV detector (254 nm) on Separon SGX C18 (Tessek, Czech Republic), particle size of 5 μm, eluent MeOH. The photoisomer mixtures were separated by preparative TLC. NMR spectra were measured on a Varian VXR-400 or INOVA-400 (399.90 and 100.57 MHz for ^{1}H and ^{13}C, respectively) instrument in $CDCl_3$ solutions at 25 to 30 °C. The assignments were based on COSY, HOM2DJ, HMQC, HMBC, 1D-TOCSY, and 1D-NOE experiments; the methine (exocyclic) carbon of compounds **4** is indicated with the number 6; *i- ipso*, *o- ortho*, *m- meta*, *p- para*. In fluorine-containing compounds, capital letters denote multiplicity due to protons, lowercase letters are used for fluorine-related multiplicity. Positive-ion mass spectra were recorded on a Finnigan MAT 95 double-focusing instrument of BE geometry equipped with an EI ion source [ionization energy of 70 eV, source temperature of 250 °C, emission current of 0.5 mA, accelerating voltage of 5 kV, direct inlet (150–160 °C)]. For high resolution experiments, the instrument was tuned to a resolution of about 8000 (10% valley definition), and the measurements were carried out by the peak-matching method against the Ultramark 1600F (PCR Inc. Gainesville, USA) as an internal standard.

For **3a**: mp 138–140 °C (lit.,[4] mp 138–139 °C). ^{1}H NMR ($CDCl_3$) δ: 6.453 (s, 2H, 3,5-H), 7.240 (m, 4H, *m*-2,6-Ph), 7.293–7.380 (m, 12H, aromatic), 7.560 (m, 4H, *o*-2,6-Ph). ^{13}C NMR ($CDCl_3$) δ: 56.11 (s, 1C, 4-C), 126.37 (d, 2CH, *p*-4,4-Ph), 126.87 (d, 4CH, *o*-2,6-Ph), 127.49 (d, 2CH, 3,5-CH), 128.24 (d, 4CH, *m*-4,4-Ph), 128.36 (d, 4CH, *o*-4,4-Ph), 128.41 (d, 2CH, *p*-2,6-Ph), 128.61 (d, 4CH, *m*-2,6-Ph), 130.71 (s, 2C, *i*-2,6-Ph), 139.74 (s, 2C, *i*-4,4-Ph), 147.56 (s, 2C, 2,6-C). MS, *m*/*z* (%): 450.0884 (100, M$^+$, $C_{29}H_{22}Se$), 373.0495 (85), 291.1174 (56), 267.1174 (19), 215.0861 (25), 191.0861 (16), 165.0704 (22).

For **3b**: mp 113–115 °C. ^{1}H NMR ($CDCl_3$) δ: 6.368 (s, 2H, 3,5-H), 7.041 (m, 4H, *o*-2,6-C_6H_4F, 2×0.5 of AA′BB′X spectrum, J_{HF} 8.5 Hz, $\sum J$ 8.9 Hz), 7.242 (m, 2H, *p*-4,4-Ph), 7.285 (m, 4H, *o*-4,4-Ph), 7.338 (m, 4H, *m*-4,4-Ph), 7.506 (m, 4H, *m*-2,6-C_6H_4F, 2×0.5 of AA′BB′X spectrum, J_{HF} 5.3 Hz, $\sum J$ 8.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 56.17 (S, 1C, 4-C), 115.56 (Dd, 4CH, *m*-2,6-C_6H_4F, J_{CF} 21.7 Hz), 126.51 (D, 2CH, *p*-4,4-Ph), 127.68 (D, 2CH, 3,5-CH), 128.18 (D, 4CH, *m*-4,4-Ph), 128.44 (D, 4CH, *o*-4,4-Ph), 128.63 (Dd, 4CH, *o*-2,6-C_6H_4F, J_{CF} 8.2 Hz), 129.69 (S, 2C, *i*-4,4-Ph), 135.78 (Sd, 2C, *i*-2,6-C_6H_4F, J_{CF} 3.2 Hz), 147.48 (S, 2C, 2,6-C), 162.85 (Sd, 2CF, *p*-2,6-C_6H_4F, J_{CF} 248.2 Hz). MS, *m*/*z* (%): 486.0692 (100, M$^+$, $C_{29}H_{20}F_2Se$), 409 (78), 391 (5), 327 (27), 309 (25), 285 (22), 251 (7), 233 (15), 209 (13), 165 (17).

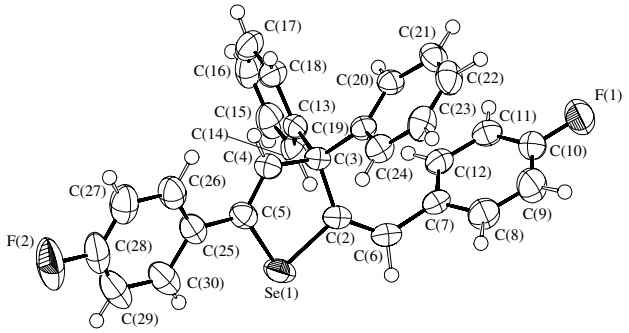


Figure 1 Molecular structure of compound **4b**. Selected bond lengths (Å): Se(1)–C(2) 1.920(3), Se(1)–C(5) 1.907(3), C(2)–C(6) 1.331(4), C(2)–C(3) 1.531(3), C(3)–C(4) 1.519(3), C(4)–C(5) 1.329(4); selected bond angles (°): C(2)–Se(1)–C(5) 87.43(9), Se(1)–C(2)–C(3) 110.8(2), C(2)–C(3)–C(4) 105.7(2), C(3)–C(4)–C(5) 120.2(2), Se(1)–C(5)–C(4) 112.1(2), Se(1)–C(2)–C(6) 119.2(2); selected torsion angles (°): C(2)–Se(1)–C(5)–C(4) 7.8(2), C(5)–Se(1)–C(2)–C(3) –16.4(2), Se(1)–C(2)–C(3)–C(4) 20.1(2), Se(1)–C(2)–C(6)–C(7) –179.9(2).

= 3.79 dm^3 mol^{-1} cm^{-1}) and a shoulder at about 287 or 283 nm for compound **3a** or **3b**, respectively. A similarity between the UV–VIS spectra of selenopyrans and appropriate derivatives of thiopyrans[2(c)] is evident, and it can be attributed to identical quantal transitions.

To our knowledge, the described conversion **3** → **4** is a unique example of photochemical ring conversion among six-membered selenium heterocycles[5] and, contrary to other 2,4,4,6-tetraaryl-4*H*-(hetero)pyrans,[2] no photochemical di-π-methane rearrangement of one of the 4,4-phenyl groups has been observed. The photochemistry of such di-π-selenide systems belongs to an unexplored area.[6] Laser-induced photolysis of selenophene seems to be a formally similar process.[7] Note that a topologically analogous isomerization has been only observed[8] after lithiation of 2,6-di-*tert*-butylseleno-4-pyron, where the acetylenic intermediate Bu^{t}C≡C–CO–CH=C(SeMe)Bu^t was evidently trapped with methyl triflate. The selenopyran derivatives and their reactivity, including the solid-state UV photocolouration of **3**-like 4*H*-selenopyrans, will be considered in detail elsewhere.

‡ *Crystal data for* **4b**: $C_{29}H_{20}F_2Se$, M = 485.43, monoclinic, space group $P2_1/c$, a = 11.495(2) Å, b = 11.909(4) Å, c = 16.353(1) Å, β = 90.50(1)°, V = 2238.7 Å^3, Z = 4, d_{calc} = 1.44 g cm^{-3}, $F(000)$ = 982.88, μ = 2.52 mm^{-1}. 8525 reflections measured with an Enraf Nonius CAD4 diffractometer (293 K, graphite-monochromated CuKα radiation, λ = = 1.54184 Å, $\omega/2\theta$ scan mode, 2θ range of 5–134°). The structure was solved by direct methods and anisotropically refined by full-matrix least squares.[9] Hydrogen atoms were located from a Δ–ρ map, positions and isotropical thermal motion were refined. The final agreement factors are R = 4.11% and R_w = 4.11%. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/85.

§ For **4a**: mp 150–152 °C, preparative yield 11%. ^{1}H NMR ($CDCl_3$) δ: 6.588 (s, 1H, 6-H), 6.701 (s, 1H, 4-H), 7.218–7.368 (m, 14H, aromatic), 7.382 (m, 4H, *o*-3,3-Ph), 7.480 (m, 2H, *o*-5-Ph). ^{13}C NMR ($CDCl_3$) δ: 74.73 (s, 1C, 3-C), 126.83 (d, 2CH, *o*-5-Ph), 126.92 (d, 2CH, *o*-6-Ph), 127.08 (d, CH, *p*-6-Ph), 127.89 (d, 2CH, *p*-3,3-Ph), 128.32 (d, 4CH, *m*-3,3-Ph), 128.45 (d, 2CH, *m*-5-Ph), 128.49 (d, 1CH, *p*-5-Ph), 128.53 (d, 4CH, *o*-3,3-Ph), 128.60 (d, 2CH, *m*-6-Ph), 129.85 (d, 1CH, 6-CH), 129.91 (d, 1CH, 4-CH), 135.11 (s, 1C, *i*-5-Ph), 136.22 (s, 1C, 5-C), 137.59 (s, 1C, *i*-6-Ph), 144.42 (s, 1C, 2-C), 145.26 (s, 2C, *i*-3,3-Ph). MS, *m*/*z* (%): 450.0885 (100, M$^+$, $C_{29}H_{22}Se$), 373 (47), 291 (52), 278 (9), 215 (35), 191 (23), 165 (11).

For **4b**: mp 159–161 °C, preparative yield 34%. ^{1}H NMR ($CDCl_3$) δ: 6.535 (s, 1H, 6-H), 6.619 (s, 1H, 4-H), 7.034 (m, 2H, *m*-5-C_6H_4F, 0.5 of AA′BB′X spectrum, J_{HF} 8.4 Hz, Σ J 8.9 Hz), 7.060 (m, 2H, *m*-6-C_6H_4F, 0.5 of AA′BB′X spectrum, J_{HF} 8.6 Hz, Σ J 8.7 Hz), 7.265 (m, 2H, *o*-6-C_6H_4F, half of AA′BB′X spectrum, J_{HF} 5.3 Hz, Σ J 8.7 Hz), 7.290 (m, 2H, *p*-3,3-Ph), 7.337–7.367 (m, 8H, *o*-3,3-Ph and *m*-3,3-Ph), 7.442 (m, 2H, *o*-5-C_6H_4F, 0.5 of AA′BB′X spectrum, J_{HF} 5.2 Hz, Σ J 8.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 74.66 (S, 1C, 3-C), 115.41 (Dd, 2CH, *m*-5-C_6H_4F, J_{CF} 21.5 Hz), 115.59 (Dd, 2CH, *m*-6-C_6H_4F, J_{CF} 22.0 Hz), 126.94 (D, 2CH, *p*-3,3-Ph), 128.38 (D, 4CH, *m*-3,3-Ph), 128.48 (D, 4CH, *o*-3,3-Ph), 128.59 (Dd, 2CH, *o*-5-C_6H_4F, J_{CF} 8.3 Hz), 128.87 (Dd, 1CH, 6-CH, J_{CF} 1.5 Hz), 129.50 (Dd, 2CH, *o*-6-C_6H_4F, J_{CF} 8.3 Hz), 129.93 (Dd, 1CH, 4-CH, J_{CF} 1.5 Hz), 131.29 (Sd, 1C, *i*-5-C_6H_4F, J_{CF} 2.9 Hz), 133.77 (Sd, 1C, *i*-6-C_6H_4F, J_{CF} 2.9 Hz), 134.89 (S, 1C, 5-C), 143.31 (S, 1C, 2-C), 145.05 (S, 2C, *i*-3,3-Ph), 161.73 (Sd, 1CF, *p*-6-C_6H_4F, J_{CF} 247.6 Hz), 162.77 (Sd, 1CF, *p*-5-C_6H_4F, J_{CF} 249.0 Hz). MS, *m*/*z* (%): 486.0698 (100, M$^+$, $C_{29}H_{20}F_2Se$), 409 (37), 405 (58), 391 (11), 327 (29), 309 (29), 285 (9), 233 (32), 209 (24), 183 (13), 165 (6).

References

1 *Chem. Rev.*, *Photochromism: Memories and Switches*, ed. M. Irie, 2000, **100** (5).

2 (*a*) Y. Mori and K. Maeda, *J. Chem. Soc., Perkin Trans. 2*, 1991, 2061; (*b*) H. Pirelahi, I. Parchamazad, M. S. Abaii and S. Sheikhebrahimi, *Phosphorus Sulfur Silicon*, 1991, **59**, 251; (*c*) P. Šebek, S. Nešpůrek, R. Hrabal, M. Adamec and J. Kuthan, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1301; (*d*) S. Böhm, P. Šebek, S. Nešpůrek and J. Kuthan, *Collect. Czech. Chem. Commun*., 1994, **59**, 1115; (*e*) J. Kroulík, M. Chadim, M. Polášek, S. Nešpůrek and J. Kuthan, *Collect. Czech. Chem. Commun*., 1998, **63**, 662.

3 J. Kuthan, P. Šebek and S. Böhm, *Adv. Heterocycl. Chem*., 1994, **59**, 179.

4 B. I. Drevko, M. I. Smushkin and V. G. Kharchenko, *Khim. Geterotsikl. Soedin*., 1997, 604 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1997, **33**, 520].

5 L. E. E. Christiaens, in *Comprehensive Heterocyclic Chemistry*, ed. A. McKillop, Pergamon, Oxford, 1996, vol. 5, ch. 5.11, p. 619.

6 A. A. Leone and P. S. Mariano, *Rev. Chem. Intermed*., 1981, **4**, 81.

7 J. Pola and A. Ouchi, *J. Org. Chem*., 2000, **65**, 2759.

8 M. R. Detty and L. W. McGarry, *J. Org. Chem*., 1988, **53**, 1203.

9 (*a*) G. M. Sheldrick, SHELXS-86, *Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1986; (*b*) D. J. Watkin, R. J. Carruthers and P. Betteridge, *CRYSTALS*, Chemical Crystallography Laboratory, Oxford, UK, 1998, issue 10; (*c*) J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698; (*d*) L. Zsolnai and G. Huttner, *XPMA, ZORTEP*, University of Heidelberg, 1994.

Received: 25th January 2001; Com. 01/1756