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Synthesis of photochromic dihetarylethenes with a cyclopentenedione bridge fragment

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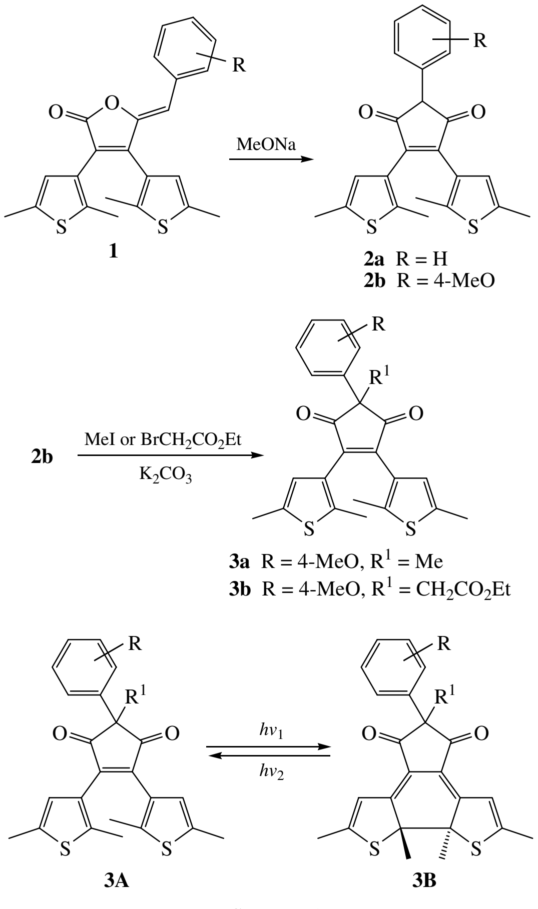
Dihetarylsubstituted furanones 1 treated with sodium methylate undergo rearrangement to cyclopentenediones 2, the alkylation of which leads to corresponding photochromic derivatives 3.

The chemistry of photochromic dihetarylethenes, which are very promising for the creation of a new type of devices for data recording, storage and reading, is being developed intensively. During the last decade, a wide range of dithienylethenes with different substituted and fused thiophene rings have been prepared. Among them are compounds with several bridge fragments, such as dihetarylethenes based on perfluorocyclopentene,[1] maleic anhydride[2] and maleimide.[3] Thus, the development of synthetic methods for compounds with new photochromic bridges, providing high fatigue resistance, is of considerable current interest.



Scheme 1

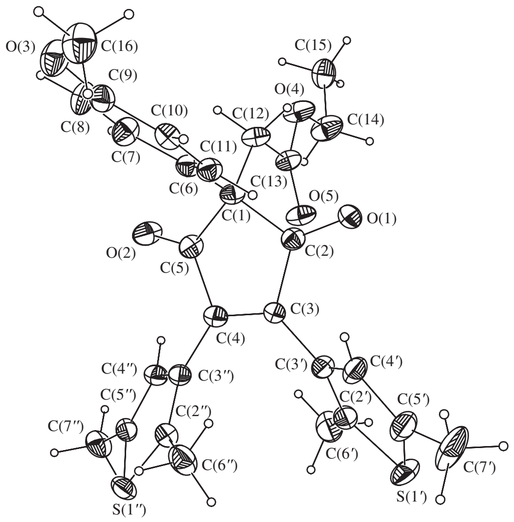


Figure 1 Structure and conformation of **3b**.

Earlier, we have developed a convenient general method of the synthesis of furanones **1**,[4] which allowed us to obtain these products with different combinations of heteroaromatic substituents. The use of products **1** as a starting material grants access to photochromic dihetarylethenes with non-traditional bridge fragments. Here we describe the synthesis of a new type of photochromic compounds, in which thienyl substituents are bound to the cyclopentenedione bridge.

We found that, by treating furanones **1a**,**b** with sodium methoxide, a rearrangement occurs that leads to dihetarylsubstituted cyclopentenediones **2** (Scheme 1). This reaction is general and allows obtaining products with different aromatic and heterocyclic substituents. The availability of starting compounds **1** and the high yields of products **2** (86–95%) allow us to consider this isomerization as a convenient method for the synthesis of photochromes with the new bridge fragment.

To avoid keto-enol tautomerization, which can lead to side-channels of phototransformation and irreversible photodegradation, and also to improve the photochromic properties of the obtained compounds, we synthesised diketone **3**. Cyclopentenediones **2** easily react with alkyl halides in DMF with the use of K_2CO_3 as a base. The reaction of **2b** leads to alkyl-substituted cyclopentenediones **3a**,**b** in high yields (91–94%).[†]

The molecular and crystal structures of **3b** were proved by X-ray data (Figure 1).[‡] The molecule has an *anti*-parallel conformation. Dihedral angles between thienyl rings and the plane cyclopentene fragment [C(2)C(3)C(4)C(5)] are 49.92° and 42.98°. This is close to classical angles for photochromic dihetarylethenes (47° for a disubstituted maleic anhydride[2]). The C(3)–C(4) bond length (1.350 Å) a little exceeds the standard double bond length C=C (1.33 Å).[5] The intramolecular distance C(2′)···C(2″) (3.520 Å) corresponds to a normal van der Waals contact. This points to the fact that in a crystal state the structure of **3b** possesses all features of photochromic compounds.

Thus, we have developed a convenient general approach to the synthesis of new dihetarylethenes with the cyclopentenedione bridge fragment. Synthesised compounds **2** and **3** possess photochromic properties (λ_A = 370–400 nm, λ_B = 500–540 nm).

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[†] The ^{1}H NMR spectra were recorded on Bruker AM-300 (300 MHz) and Bruker WM-250 (250 MHz) instruments in [$^2H_6$]DMSO. Melting points were measured on a Boetius hot stage and not corrected. The reaction mixtures were analysed and the purity of the products was checked by TLC on Merck Silica gel 60 F254 plates using AcOEt–hexane (1:3) for elution.

4,5-Bis(2,5-dimethyl-3-thienyl)-2-phenylcyclopent-4-ene-1,3-dione **2a**. Sodium (12 mg, 0.5 mmol) was dissolved in 2 ml of abs. MeOH, and corresponding arylidene **1a** (196 mg, 0.5 mmol) was added to the solution. The reaction mixture was refluxed for 3 h; then, water (5 ml) and acetic acid (40 μl) were added. The precipitate was filtered off, rinsed with water and recrystallised from ethanol. Yield, 170 mg (86%); mp 112–114 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.87 (s, 6H, Me), 2.33 (s, 6H, Me), 4.58 (s, 1H, CH), 6.60 (s, 2H, H_{Het}), 7.10–7.40 (m, 5H, H_{Ar}). Found (%): C, 70.54; H, 5.31; S, 16.23. Calc. for $C_{23}H_{20}O_2S_2$ (392.54) (%): C, 70.38; H, 5.14; S, 16.34.

4,5-Bis(2,5-dimethyl-3-thienyl)-2-(4-methoxyphenyl)cyclopent-4-ene-1,3-dione **2b**. Yield, 201 mg (95%); mp 168–170 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.90 (s, 6H, Me), 2.35 (s, 6H, Me), 3.75 (s, 3H, OMe), 4.50 (s, 1H, CH), 6.65 (s, 2H, H_{Het}), 6.95 (d, 2H, H_{Ar}, J 7 Hz), 7.10 (d, 2H, H_{Ar}, J 7 Hz). Found (%): C, 68.38; H, 5.31; S, 15.62. Calc. for $C_{24}H_{22}O_3S_2$ (422.57) (%): C, 68.22; H, 5.25; S, 15.78.

General procedure for the alkylation of diketones **2**. Diketone **2b** (0.125 mmol, 50 mg) was dissolved in 2 ml of DMF; potassium carbonate (0.720 mmol, 100 mg) and a corresponding alkylating agent (0.150 mmol) were added. The reaction mixture was stirred for 2 h at room temperature (TLC control; eluent, ethyl acetate–hexane, 1:3) and then poured into water. The precipitated solid was filtered off, rinsed with water and recrystallised from ethanol.

4,5-Bis(2,5-dimethyl-3-thienyl)-2-(4-methoxyphenyl)-2-methylcyclopent-4-ene-1,3-dione **3a**. Yield, 58 mg (94%); mp 106–108 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.60 (s, 3H, Me_{R^1}), 1.87 (s, 6H, Me_{Het}), 2.37 (s, 6H, Me_{Het}), 3.75 (s, 3H, OMe), 6.65 (s, 2H, H_{Het}), 6.95 (d, 2H, H_{Ar}, J 7 Hz), 7.20 (d, 2H, H_{Ar}, J 7 Hz). Found (%): C, 68.89; H, 5.71; S, 14.53. Calc. for $C_{25}H_{24}O_3S_2$ (436.60) (%): C, 68.78; H, 5.54; S, 14.69.

[3,4-Bis(2,5-dimethyl-3-thienyl)-1-(4-methoxyphenyl)-2,5-dioxocyclopent-3-enyl]acetic acid ethyl ester **3b**. Yield 58 mg (91%); mp 139–141 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.10 (t, 3H, MeCH$_2$O, J 8 Hz), 1.83 (s, 6H, Me), 2.35 (s, 6H, Me), 3.35 (s, 2H, CH_2CO$_2$Et), 3.70 (s, 3H, OMe), 4.00 (q, 2H, CH_2Me, J 8 Hz), 6.60 (s, 2H, H_{Het}), 6.95 (d, 2H, H_{Ar}, J 7 Hz), 7.23 (d, 2H, H_{Ar}, J 7 Hz). Found (%): C, 66.35; H, 5.61; S, 12.79. Calc. for $C_{28}H_{28}O_5S_2$ (508.66) (%): C, 66.12; H, 5.55; S, 12.61.

[‡] *Crystallographic data for* **3b**: at 290 K crystals of $C_{28}H_{28}O_5S_2$ are monoclinic, space group *Cc*, a = 12.402(4), b = 19.926(5), c = 11.372(4) Å, β = 110.61(2)°, V = 2630.3(14) Å^3, Z = 4, d_{calc} = 1.284 g cm^{-3}, M = 508.62. The unit cell parameters and the intensities of 2665 independent reflections were measured on a Syntex $P2_1$ diffractometer (MoKα, graphite monochromator, $\theta/2\theta$-scan mode in the $2.03 \le \theta \le 26.06°$ range). The structure was solved by the direct method, which revealed all non-hydrogen atoms, and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were revealed by difference electron density synthesis and refined isotropically by the least-squares calculations. The final R-factors for 2070 deflections with $I > 2\sigma(I)$: R_1 = 0.046, wR_2 = 0.111. For all the independent deflections R_1 = 0.081, wR_2 = 0.125. The Siemens P3/PC[6] and SHELXTL PLUS 5[7] programs were used for calculations.

CCDC 658786 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2007.