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Synthesis of unsymmetrical dienones with heteroaromatic substituents*

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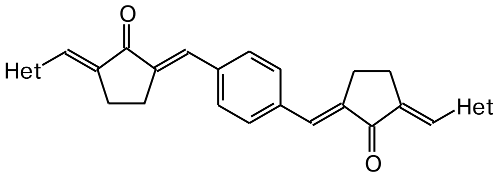
Condensation of heteroaromatic aldehydes with 2-benzylidenecyclopentanone in a basic medium afforded a number of unsymmetrical 2,5-diarylidenecyclopentanones. According to ^{1}H NMR data, the dienones obtained were the *E*,*E*-isomers.

Key words: unsymmetrical dienones, 2-benzylidenecyclopentanone, pyridinecarbaldehyde, thiophenecarbaldehyde, condensation.

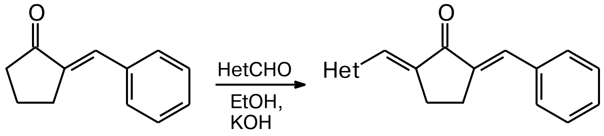
The chemistry of coordination polymers is a fast-developing line of modern supramolecular chemistry.[1] Coordination polymers, which are infinite ensembles of metals with *exo*-dentate ligands, are promising as catalytic, luminescent, magnetic, and porous materials. The properties of coordination polymers are largely determined by the nature of the ligand. Recently, we have proposed to use symmetrical conjugated dienones ("diarylidenes"), which are condensation products from cyclic ketones and heteroaromatic aldehydes, as *exo*-dentate ligands.[2] A subsequent development of this project was aimed at obtaining bis(dienones) containing a longer conjugation chain and at studying their properties.



At the first stage, we investigated the possibility of using cyclopentanone for the synthesis of scantily documented[3,4] unsymmetrical diarylidenes. Earlier, they have been synthesized by condensation of 2-arylidenecyclopentanone with an aromatic aldehyde in a basic[3] or acidic medium.[4]

We obtained hetaryl dienones **1** by condensation of 2-benzylidenecyclopentanone[5] (**2**) with heteroaromatic aldehydes under basic conditions (Scheme 1).

Scheme 1



2 **1a—d**

Het = 4-pyridyl (**a**), 3-pyridyl (**b**), 2-pyridyl (**c**), 2-thienyl (**d**)

The structures of dienones **1** were confirmed by spectroscopic and elemental analysis data. Compound **1d** has been synthesized earlier.[3] However, its structure was proved only by elemental analysis for the sulfur content and IR and UV spectroscopy.

The IR spectra of products **1** contain two bands at 1680—1675 and 1630—1600 cm^{-1} characteristic of a conjugated system of a carbonyl group and double bonds. The ^{1}H NMR spectra of compounds **1** show signals for the aliphatic protons at δ 3.2 characteristic of the AA´BB´ system. The signals for the methine protons at δ 7.38—7.84 are characteristic of the *E*-isomers of mono-[6—10] and dienones,[11] while signals for the protons of the *Z*-isomers appear at δ 6.5—6.9.

Results of our further studies concerning the synthesis and properties of bis(dienones) will be published elsewhere.

Experimental

The course of the reactions was monitored and the purity of the compounds obtained was checked by TLC on Silufol plates. IR spectra (Nujol) were recorded on UR-20 and Specord 75 IR instruments. ^{1}H NMR spectra were recorded on a Bruker-Avance-400 spectrometer (400.13 MHz) at 28 °C. Chemical shifts are referenced to HMDS as the internal standard. Melting points were determined in open capillaries. Melting and boiling points are given uncorrected. Elemental analysis was carried out on a Carlo Erba CHN-analyzer.

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2-Benzylidenecyclopentanone (2). A mixture of cyclopentanone (8.4 g, 0.1 mol) and benzaldehyde (5.3 g, 0.05 mol) was added to a solution of NaOH (2.5 g) in water (100 mL) and stirred at room temperature for 1 h. The solution was neutralized with HCl, the resulting oily layer was separated, and the product from the aqueous layer was extracted with ether. The ethereal extracts were combined with the oil and dried over K_2CO_3. The combined extract was concentrated and the residue was distilled *in vacuo* and recrystallized. The yield of compound **2** was 2.89 g (34%), m.p. 68—69 °C (from heptane) (*cf.* Ref. 5: m.p. 69—70 °C). ^{1}H NMR ($CDCl_3$), δ: 2.02 (quint, 2 H, C(4)—CH_2—, J = 7.2 Hz); 2.40 (t, 2 H, C(5)—CH_2—, J = 7.8 Hz); 2.97 (td, 2 H, C(3)—CH_2—, J = 7.0 Hz, J = 2.7 Hz); 7.34—7.44 (m, 4 H, *m*-H_{Ph}, *p*-H_{Ph}, =CH—Ph); 7.53 (d, 2 H, *o*-H_{Ph}, J = 7.3 Hz).

Synthesis of compounds 1a—d by condensation of 2-benzylidenecyclopentanone with heteroaromatic aldehydes (general procedure). A solution of 2-benzylidenecyclopentanone (**2**) (1 mmol) and the corresponding aldehyde (1 mmol) in 95% EtOH (10 mL) was stirred in the presence of aqueous 10% KOH (0.5 mL) for 30—40 min. The completion of the reaction was determined by TLC. The precipitate that formed was filtered off and recrystallized from EtOH.

(*E*,*E*)-5-Benzylidene-2-(4-pyridylmethylene)cyclopentanone (1a). The yield was 0.04 g (13%), m.p. 192 °C (from EtOH). Found (%): C, 82.99; H, 5.73; N, 5.22. $C_{18}H_{15}NO$. Calculated (%): C, 82.76; H, 5.75; N, 5.36. IR, ν/cm^{-1}: 1675 (C=O). ^{1}H NMR ($CDCl_3$), δ: 3.17 (br.s, 4 H, CH_2); 7.38—7.51 (m, 6 H, =CH—py, *m*-H_{Ph}, *p*-H_{Ph}, β-H_{py}); 7.58—7.68 (m, 3 H, *o*-H_{Ph}, =CH—Ph); 8.69 (d, 2 H, α-H_{py}, J = 4.5 Hz).

(*E*,*E*)-5-Benzylidene-2-(3-pyridylmethylene)cyclopentanone (1b). The yield was 0.16 g (53%), m.p. 198 °C (from EtOH). Found (%): C, 82.97; H, 5.74; N, 5.63. $C_{18}H_{15}NO$. Calculated (%): C, 82.76; H, 5.75; N, 5.36. IR, ν/cm^{-1}: 1675 (C=O). ^{1}H NMR ($CDCl_3$), δ: 3.15 (br.s, 4 H, CH_2); 7.34—7.52 (m, 4 H, *m*-H_{Ph}, *p*-H_{Ph}, =CH—py); 7.53—7.72 (m, 4 H, *o*-H_{Ph}, =CH—Ph, β-H_{py}); 7.88 (d, 1 H, γ-H_{py}, J = 8.0 Hz); 8.60 (m, 1 H, α-H_{py}); 8.85 (br.s, 1 H, α´-H_{py}).

(*E*,*E*)-5-Benzylidene-2-(2-pyridylmethylene)cyclopentanone (1c). The yield was 0.1 g (33%), m.p. 162 °C (from EtOH). Found (%): C, 82.58; H, 5.67; N, 5.35. $C_{18}H_{15}NO$. Calculated (%): C, 82.76; H, 5.75; N, 5.36. IR, ν/cm^{-1}: 1680 (C=O). ^{1}H NMR ($CDCl_3$), δ: 3.15, 3.39 (both m, 2 H each, CH_2); 7.18—7.24 (m, 1 H, β-H_{py}); 7.34—7.56 (m, 5 H, *m*-H_{Ph}, *p*-H_{Ph}, β´-H_{py}, =CH—py); 7.58—7.67 (m, 3 H, *o*-H_{Ph}, =CH—Ph); 7.72 (td, 1 H, γ-H_{py}, J = 7.8 Hz, J = 2.0 Hz); 8.73 (d, 1 H, α-H_{py}, J = 4.0 Hz).

(*E*,*E*)-5-Benzylidene-2-(2-thenylidene)cyclopentanone (1d). The yield was 0.26 g (84%), m.p. 188 °C (from EtOH) (*cf.* Ref. 3: m.p. 188—189 °C). Found (%): C, 76.80; H, 5.24. $C_{17}H_{14}OS$. Calculated (%): C, 76.69; H, 5.26. IR, ν/cm^{-1}: 1675 (C=O). ^{1}H NMR ($CDCl_3$), δ: 3.03, 3.16 (both m, 2 H each, CH_2); 7.18 (dd, 1 H, β-$H_{thienyl}$, J = 3.7 Hz, J = 5.1 Hz); 7.35—7.48 (m, 4 H, *m*-H_{Ph}, *p*-H_{Ph}, β´-$H_{thienyl}$); 7.55—7.63 (m, 4 H, =CH—Ph, *o*-H_{Ph}, α-$H_{thienyl}$); 7.84 (br.s, 1 H, =CH—C_4H_3S).

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