First example of carbonyl condensation of cyclopentadienone hydrazone giving mixed azine and its subsequent *endo*-dimerization into the tricyclo[5.2.1.0^{2,6}]decadiene system

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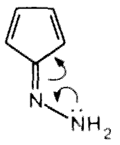
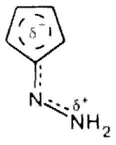
The monomeric hydrazone of cyclopenta-2,4-dienone (cyclone) undergoes condensation with 2-hydroxy-3-methoxybenzaldehyde to yield the corresponding mixed azine, which spontaneously dimerizes to 4,10-bis(2-hydroxy-3-methoxybenzalazino)tricyclo[5.2.1.0^{2,6}]deca-3,8-diene.

Key words: cyclopentadienone, hydrazones, azines, Diels—Alder condensation.

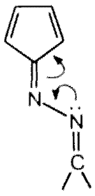
In the course of our studies on the synthesis of polyheteroatomic "cascade" metal complexes,[1] we have called attention to the hydrazone of cyclopenta-2,4-dienone (cyclone) (**1**).[2] If this compound would undergo Schiff condensation type reactions at the free amino group, it would give rise to new classes of polyconjugated azine ligands (**2**) containing a terminal cyclopentadiene group, bound through a two-nitrogen-bridge to other structural fragments capable of coordinating transition metals.



1



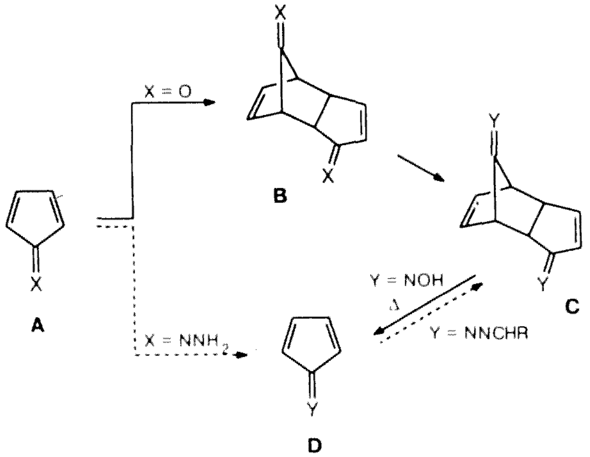
1a



2

However, up to now, hydrazones of cyclopentadienone derivatives have been considered to be fairly chemically inert;[3] this may be due to the fact that the type **1a** bipolar form makes a substantial contribution to their structure, which has been discussed in some published papers.[2,4] Compound **1** is also of interest because under ambient conditions it exists in the monocyclic form, which is not typical for the non-benzenoid aromatic compounds of the cyclopentadiene series, since they tend (Scheme 1) to undergo spontaneous dimerization according to the Diels—Alder reaction pattern to yield tricyclic systems (**A** → **B**).[5] The elucidation of the possible roles of the monomeric and dimeric structures in the series of imino-substituted cyclopentadienylidene synthons constituted the subject of a study[6] in which a convenient synthetic strategy was developed for the transformation of cyclopentadienone dimers into bis-oximes (**A** → **B** → **C**), which were converted into the corresponding monocyclic oximes by thermolysis (**C** → **D**).

Scheme 1



We showed that hydrazone **1** actually does not react with relatively inert ketones: for example, it does not react with 4-methyl-4-trichloromethylcyclohexa-2,5-dien-1-one or 4-methyl-4-trichloromethyl-1-(4,4-dimethyl-2,6-dioxocyclohexylidene)cyclohexa-2,5-diene in a MeOH solution (20 °C, 6 days). Nevertheless, hydrazone **1** reacts with aldehydes at reasonable rates. For example, when compound **1** is kept (72 h) with *o*-vanilline (**3**) in anhydrous MeOH in an argon atmosphere at 20 °C, Schiff condensation occurs without acid catalysts* and is accompanied by spontaneous dimerization of the expected monocyclic form (**4**) of the mixed azine to give a

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* The use of inorganic acids (HCl traces), which are normally employed in such situations, led to instantaneous resinification of compound **1**.

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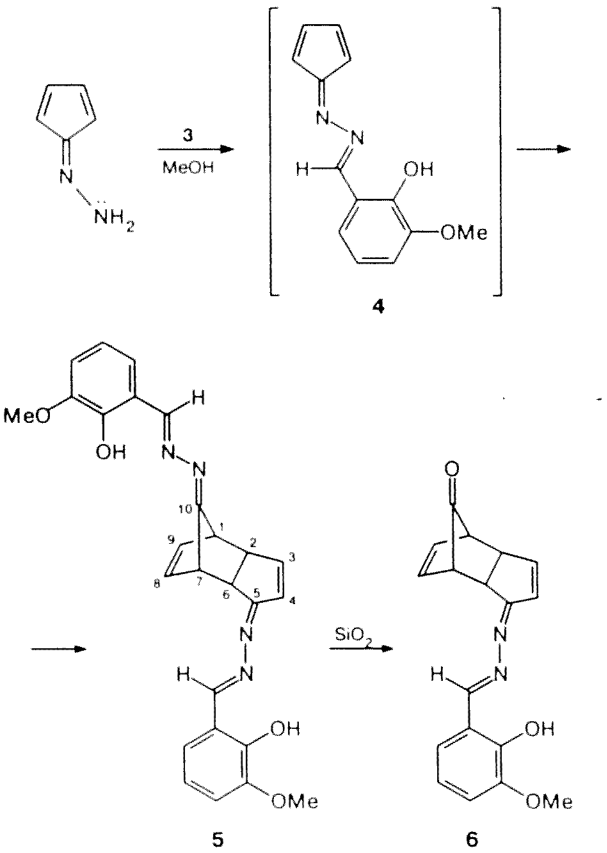
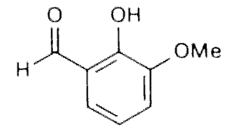
product with the tricyclo[5.2.1.$0^{2,6}$]decadiene structure (**5**) (Scheme 2). The latter compound was isolated by column chromatography on SiO_2. In addition, small amounts of azinoketone (**6**) arising due to partial hydrolysis of one of the azino groups of the major product **5** on silica gel* and of the azine of *o*-vanilline (**7**) apparently resulting from the competing process of symmetrization of bis-azine **5** according to the known trans-hydrazonation[8] pattern, were isolated from the reaction mixture.

Scheme 2





(**3**)

The structures of all the compounds obtained were determined from the data of elemental analysis, ^1H NMR spectroscopy, and mass spectrometry. The mass spectra make it possible to simultaneously observe both the molecular ion of the skeletal dimer **5** with *m/z* 456 and the ion of the corresponding monocyclic azine **4**, formed by its cyclodestruction, with half mass number, *m/z* 228. The study of compound **5** by two-dimensional $^1H-^1H$ correlated spectroscopy (COSY), which enabled the chemical shifts of the signals for all the protons in its carbon skeleton to be unambiguously assigned and its spin-spin coupling constants to be measured, showed that **5** has the expected *endo*-configuration, which is also normal for other Diels—Alder adducts of cyclopentadienone.[9] This is confirmed, first, by the presence of fairly strong spin-spin coupling of the H-2 and H-6 protons with the bridgehead H-1 and H-7 protons nearest to them (the constants are 4.3 and 4.8 Hz, respectively, whereas the spin-spin coupling of the analogous *endo*-protons in *exo*-norbornene derivatives normally does not exceed 2 Hz)[10] and, second, by the adequate spin-spin coupling constant between the H-2 and H-6 protons (6.6 Hz), fairly close to that observed for cyclopentadienone adducts known to have the *endo*-configuration (6.3 Hz).[11]

Thus, we performed for the first time a new **A** → **D** → **C** strategy for the synthesis of functionally hetero-substituted derivatives of the tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene skeleton from a monomeric cyclopentadienylidene precursor.

Experimental

The course of the reaction was monitored by TLC. The R_f values are given for a fixed layer of Silufol UV-254 SiO_2 and for $CHCl_3-Et_2O$, 10:1, as the eluent. Visualization was carried out by ultraviolet light or by iodine vapor. Column chromatography was performed with Chemapol 40/100 SiO_2.

IR spectra were recorded on a UR-20 spectrophotometer (Karl Zeiss); ^1H NMR spectra were obtained on a Bruker AMX-400 instrument operating at 400.1 MHz with tetramethylsilane as the internal standard. EI mass spectra were obtained on an MS-890 spectrometer (70 eV).

Hydrazone **1** was obtained by a previously described procedure,[2] and commercial *o*-vanilline **3** was additionally recrystallized from heptane.

Reaction of hydrazone 1 with *o*-vanilline (3). A solution of compound **3** (0.184 g, 1.21 mmol) in 2 mL of anhydrous MeOH was added to a solution of compound **1** (0.11 g, 1.21 mmol) in 4 mL of anhydrous MeOH. The resulting mixture was stirred under argon for 3 days at 20 °C and then concentrated *in vacuo*. The residue was dissolved in $CHCl_3$ (2 mL) and chromatographed on a column with SiO_2 (l = 20, d = 2 cm, $CHCl_3-Et_2O$, 10:1, as the eluent).

Fractions with R_f = 0.55 were combined and concentrated *in vacuo*, and the residue was crystallized from a $CHCl_3$—*n*-hexane mixture (5:1) to give 0.01 g (2.7 %) of *o*-vanilline azine **7**, m.p. 195—196 °C (lit. data: 198—199 °C).[12] MS, *m/z* (I_{rel}(%)): 300 $[M]^+$ (92), 150 (100).

Fractions with R_f = 0.22 were combined, concentrated *in vacuo*, and crystallized from Et_2O to give 0.05 g (18 %) of

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* The relatively high-frequency position of the maximum of the absorption band corresponding to the arising carbonyl group in the IR spectrum of compound **6** (1780 cm^{-1}) indicates that of the two structurally nonequivalent azine groups present in molecule **5**, the group located at the *endo*-bridging carbon atom is the first to be hydrolyzed (*cf.* results obtained in Ref. 7).

4,10-bis[(2-hydroxy-3-methoxy)benzalazino]tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**5**), m.p. 135—137 °C. Found (%): C, 68.13; H, 4.94; N, 12.15. $C_{26}H_{24}N_4O_4$. Calculated (%): C, 68.41; H, 5.29; N, 12.27. ^{1}H NMR (C_6D_6), δ: 2.73 (m, 1 H, H-2), 3.25 (dd, 1 H, H-6, $^3J_{6-2}$ = 6.65 Hz, $^3J_{6-7}$ = 4.8 Hz), 3.46 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.60 (dd, 1 H, H-1, $^3J_{1-2}$ = 4.3 Hz, $^3J_{1-9}$ = 3.2 Hz), 4.07 (dd, 1 H, H-7, $^3J_{7-6}$ = 4.8 Hz, $^3J_{7-8}$ = 3.2 Hz), 5.38 (dd, 1 H, H-9, $^3J_{9-8}$ = 6.25 Hz, $^3J_{9-1}$ = 3.2 Hz), 5.73 (dd, 1 H, H-8, $^3J_{8-9}$ = 6.25 Hz, $^3J_{8-7}$ = 3.2 Hz), 5.75 (dd, 1 H, H-3, $^3J_{3-4}$ = 5.6 Hz, $^3J_{3-2}$ = 2.6 Hz), 6.25 (dd, 1 H, H-4, $^3J_{4-3}$ = 5.6 Hz, $^4J_{4-2}$ = 1.5 Hz), 6.63 (m, 6 H, Ar), 8.54 (s, 1 H, CH=N), 8.62 (s, 1 H, CH=N), 12.29 (s, 1 H, OH), 12.57 (s, 1 H, OH). MS, *m/z* (I_{rel}(%)): 456 [M]$^+$ (0.1), 228 (100). Column chromatography of the mother liquor on SiO_2 afforded 0.02 g (5.0 %) of 5-(2-hydroxy-3-methoxy)benzalazinotricyclo[5.2.1.$0^{2,6}$]deca-3,8-dien-10-one **6** (R_f = 0.31). IR (KBr), ν/cm^{-1}: 1630 (C=C), 1780 (C=O). ^{1}H NMR (C_6D_6), δ: 2.2 (dd, 1 H, H-1), 2.68 (m, 1 H, H-2), 3.02 (dd, 1 H, H-6, $^3J_{6-2}$ = 6.3 Hz, $^3J_{6-7}$ = 4.8 Hz), 3.46 (s, 3 H, OMe), 6.67 (dd, 1 H, H-7), 5.55 (dd, 1 H, H-9, $^3J_{9-8}$ = 6.7 Hz), 5.67 (dd, 1 H, H-8), 5.68 (dd, 1 H, H-3), 6.27 (dd, 1 H, H-4, $^3J_{4-3}$ = 5.6 Hz, $^4J_{4-2}$ = 1.5 Hz), 6.61 (m, 3 H, Ar), 8.6 (s, 1 H, CH=N), 12.41 (s, 1 H, OH). MS, *m/z* (I_{rel}(%)): 308 [M]$^+$ (1.6), 280 [M−CO]$^+$ (100).

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