Letters to the Editor

3-Iodolevoglucosenone and chiral cyclopropane

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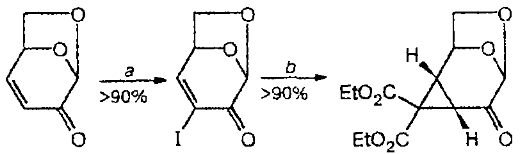
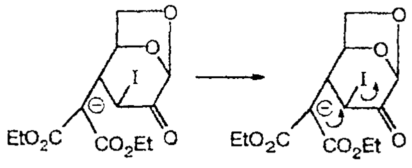
Using the reaction of the malonate anion with iodovinyl ketone (**2**) obtained from levoglucosenone (**1**)[1,2] as an example, we suggest a new approach for the construction of the enantiomerically pure functionalized type **3** cyclopropanes that find wide applications in organic synthesis.[3–5]



1 **2** **3**

Reagents and conditions: *a*. 1.3 equiv. I_2, 1 equiv. Py, $CHCl_3$, 5 min; *b*. 1 equiv. $CH_2(CO_2Et)_2$ + 1.5 equiv. NaH, THF, 5 min.

Smooth cyclopropanation is also observed in the case of other CH-acids (ethyl acetoacetate, acetylacetone and others). Note that if iodide **2** is replaced with 3-bromolevoglucosenone,[6] the cyclopropane derivative **3** is not formed. The mechanism of this tandem process seems to involve intramolecular 1,3-migration of a carbanion in the initial Michael's adduct **4** to produce carbanion **5** required to close the cycle.



4 **5**

(1*S*,5*R*)-3-Iodo-6,8-dioxabicyclo[3.2.1]oct-2-ene-4-one (2). M.p. 58–61 °C, $[\alpha]_D^{20}$ −388.0° (*c* 1.0, CH_2Cl_2). IR, ν/cm^{-1}: 980, 1100, 1320, 1460, 1580, 1700, 2950. ^{1}H NMR, δ: 3.80 (d, 1 H, C(7)$_{endo}$H, *J* = 8.1 Hz); 3.86 (ddd, 1 H, C(7)$_{exo}$H, *J* = 8.0 Hz, 4.5 Hz, 1.0 Hz); 4.95 (dd, 1 H, C(1)H, *J* = 4.5 Hz, 5.0 Hz); 5.50 (d, 1 H, C(5)H, *J* = 1.0 Hz); 8.00 (d, 1 H, C(2)H, *J* = 5.1 Hz). ^{13}C NMR, δ: 66.55 (C(6)); 74.27 (C(5)); 99.75 (C(4)); 100.79 (C(3)); 155.90 (C(4)); 183.26 (C(2)).

Diethyl (1*S*,2*S*,4*S*,6*R*)-5-oxo-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonane-3,3-dicarboxylate (3). Syrup, $[\alpha]_D^{18}$ −89.1° (*c* 1.0, $CHCl_3$). IR, ν/cm^{-1}: 1160, 1180, 1240, 1260, 1370, 1440, 1730, 2980. ^{1}H NMR, δ: 1.27 (t, 3 H, CH_3, *J* = 7.1 Hz); 1.28 (t, 3 H, CH_3, *J* = 7.1 Hz); 2.27 (dd 1 H, C(2)H, *J* = 8.1 Hz, 1.3 Hz); 2.45 (d 1 H, C(4)H, *J* = 8.1 Hz); 3.90 (dd, 1 H, C(8)$_{exo}$H, *J* = 7.1 Hz, 4.6 Hz); 4.11 (d, 1 H, C(8)$_{endo}$H, *J* = 7.1 Hz); 4.22 (m, 4 H, $2CH_2O$); 4.90 (s, 1 H, C(6)H); 5.03 (dd, 1 H, C(1)H, *J* = 4.6 Hz, 1.0 Hz). ^{13}C NMR, δ: 13.62 and 13.82 (2 CH_3); 26.67 (C(2)); 30.74 (C(4)); 38.16 (C(3)); 62.0 and 62.72 (2 CH_2O); 68.43 (C(8)); 70.50 (C(1)); 99.19 (C(6)); 164.65 and 167.65 (2 COO); 191.51 (C(5)).

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Complexes of *meso*-tetrametallocenylporphyrins with Zn^{II} ion and their stability constants with imidazole

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Recently we have obtained the first representatives of a novel class of porphyrins containing metallocenyl groups (ferrocenyl, ruthenocenyl, and cymantrenyl) in *meso*-positions.[1—3] A direct bond of the macroheterocycle skeleton to the metallocenyl fragments with their specific geometry and reactivity opens up new possibilities for obtaining porphyrins and their metallocomplexes with useful practical properties.

The constants of equilibrium of the formation of the extraligand complexes are important characteristics of porphyrin metallocomplexes, determining their behavior in various processes. In this work, complexes of the Zn^{II} ion with tetracymantrenylporphyrin (**1**), qtetraferrocenylporphyrin (**2**), and tetraruthenocenylporphyrin (**3**) are first described, and the stability constants (K_{st}) of extraligand metallocomplexes **1a—3a** with imidazole (Im) have been determined.

Complexes **1a—3a** were obtained by interaction of porphyrins **1—3** with zinc acetate or zinc chloride in DMF in 85—90% yield and characterized by ^1H NMR, electronic and mass spectra (FAB). UV spectra ($CHCl_3$), λ_{max}/nm: **1a** — 464, 559, 595, and 643; **2a** — 436, 618, and 673; **3a** — 438, 599, and 647. ^1H NMR (200 MHz, $CDCl_3$), δ: **1a** — 9.67 (s, 8 H, β-H); 5.79 (m, 8 H, Cp); 5.30 (m, 8 H, Cp); **2a** — 9.84 (s, 8 H, β-H); 5.37 (m, 8 H, Cp); 4.80 (m, 8 H, Cp); 4.07 (s, 20 H, Cp); **3a** — 9.79 (s, 8 H, β-H); 5.71 (m, 8 H, Cp); 5.05 (m, 8 H, Cp); 4.40 (s, 20 H, Cp). MS (FAB), *m/z*: **1a** — 1181 $[M+H]^+$; **2a** — 1108 $[M^+]$; **3a** — 1292 $[M^+]$.

Samples **1a—3a** used for determination of K_{st} were additionally purified by column chromatography on Al_2O_3 (Brockmann II activity, benzene), reprecipitated from saturated solutions in benzene or chloroform with cooled hexane, and dried *in vacuo*. The K_{st} values for the extraligand complexes of compounds **1a—3a** with Im and that for zinc tetraphenylporphyrinate (**4**) (taken as the standard) were obtained by the method of spectrometric titration in benzene at two wavelengths and at 25 °C on a Specord UV-VIS instrument.

The formation of extracomplexes (EC) is accompanied by a bathochromic shift of all absorption bands of the porphyrin chromophore and by a change in their relative intensities. As the metallocomplex (MC) : Im ratio changes in the range from 1 : 0.1 to 1 : 500, several isobestic points are observed in the spectra of the mixtures. They are indicative of the formation of monoligand EC in the solution and existence of an equilibrium of the type:

$$\mathrm{MC} + \mathrm{Im} \overset{K_{st}}{\rightleftharpoons} \mathrm{EC}.$$

The obtained value of $K_{st} = (3.0\pm0.6)\cdot10^4$ for compound **4** at 550 and 570 nm is in good agreement with the data reported previously for the EC of **4** with related extraligands.[4,5] The K_{st} values $(3.8\pm0.9)\cdot10^4$ and $(3.0\pm0.7)\cdot10^4$ for complexes **2a** (at 436 and 684 nm) and **3a** (at 647 and 667 nm), respectively, appeared to be close to each other and to that of **4**. In contrast to this, the stability of the extraligand complex **1a** with Im exceeds the above mentioned values of K_{st} by two orders of magnitude and equals $(7.7\pm0.5)\cdot10^6$ (at 586 and 650 nm).

Thus, as could be expected, the stability of complexes of the donor extraligand with the acceptor Zn atom in the studied metalloporphyrins increases as the electron-withdrawing character of *meso*-substituents increases and principally corresponds to the increase in the values of σ_i constants for these substituents: −0.05 (Fc), ±0.05 (Ph), 0.04 (Rc), and 0.17 (Cy).[6,7]

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