# Anodic co-oxidation of urazole and ferrocenes: first trapping of cyclopentadienols

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**Cyclopentadien-5-ols, the major products resulting from decomposition of some ferrocenium cations by molecular oxygen, are regio- and stereo-selectively trapped by 4-phenyl-1,2,4-triazoline-3,5-dione.**

In oxygenated organic solvents, ferrocenium cations are unstable[1] and can easily be used for generating substituted cyclopentadienes in the presence of very reactive dienophiles. The strong dienophilic character of cyclic α-carbonyl azo compounds is well known.[2–6] These are generally prepared by chemical oxidation of the corresponding hydrazino compounds using lead(IV) acetate[7,8] or *tert*-butyl hypochlorite.[9–11] We report herein the co-oxidation of ferrocenes and a triazolidinedione (urazole) in a flow cell fitted with a graphite felt porous anode.[12] Electrolyses were performed in acidified MeCN (2% $H_2SO_4$); solid sodium carbonate and oxygen were added to the solution of triazolinedione and ferrocenium cations at the outlet of the cell. Decomposition of ferrocenium cations proceeded *via* unexpected cyclopentadien-5-ols as major products which were trapped *in situ* with 4-phenyl-1,2,4-triazoline-3,5-dione (Scheme 1). To the best of our knowledge, this reaction has never been reported before. Theoretical calculations show that the three cyclopentadienol isomers should be very unstable.[13] Previously, cyclopentadienol has only been postulated as an intermediate during a thermal retro-Diels–Alder reaction.[14]

Decomposition of ferrocenium cation **1a** in the presence of triazolinedione **2** was complete after 1 h and gave a mixture of **3a** and **4a**. The yield of **3a** increased as the molar ratio triazolinedione : ferrocenium cation increased, whereas the yield of **4a** was practically unchanged (Table 1). The $^1$H and $^{13}$C NMR spectra of **3a** show a regio- and stereo-selective addition. X-Ray analyses show that **3a** results from an *exo* addition (Fig. 1) and **4a** from an *endo* addition. Compound **4a** is identical to the Diels–Alder adduct prepared by a different method using **2** and freshly distilled cyclopentadiene.[8]

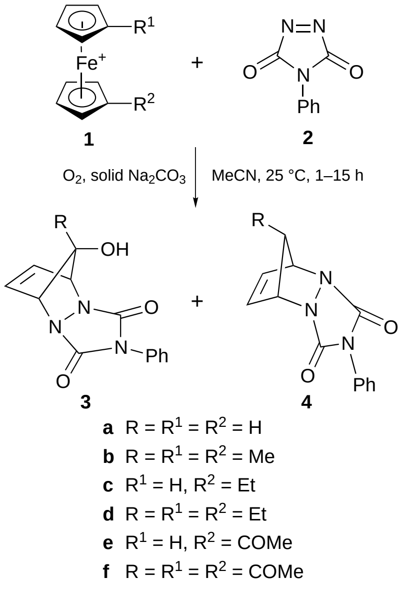
1,1′-Dialkylated ferrocenium cations **1b** and **1d** decomposed more slowly than **1a** and gave, after reaction with **2**, compounds **3b** and **3d** respectively. The $^1$H and $^{13}$C NMR spectra of **3b** and **3d** and the X-ray analysis of **3b** (Fig. 2) indicate a regioselective *exo*-addition like that for **3a**. After decomposition of mono-alkylated ferrocenium cation **1c** and reaction with **2**, a mixture of **3a** and **3d** was isolated. Compounds **3a** and **3d** were separated by column chromatography. Adduct **4a** was not detected.

The rate of decomposition of acetylferrocenium **1e** and 1,1′-diacetylferrocenium **1f** was much faster. Thus **1f** gave a mixture of unidentified products and **1e** gave **3a** in poor yield (12%).

**Table 1** Composition of mixtures from decomposition of ferrocenium cations **1** in the presence of 4-phenyl-1,2,4-triazoline-3,5-dione **2**

| Substrates (molar ratio) | Products (% yield[a]) |
|---|---|
| **1a** + **2** (1 : 1) | **3a** (46) + **4a** (12) |
| **1a** + **2** (1 : 2) | **3a** (69) + **4a** (14) |
| **1a** + **2** (1 : 3) | **3a** (80) + **4a** (15) |
| **1b** + **2** (1 : 2) | **3b** (41) |
| **1c** + **2** (1 : 2) | **3a** (24) + **3d** (45) |
| **1d** + **2** (1 : 2) | **3d** (52) |
| **1e** + **2** (1 : 2) | **3a** (12) |
| **1f** + **2** (1 : 2) | — |

[a] Calculated from initial ferrocene.



**Scheme 1**

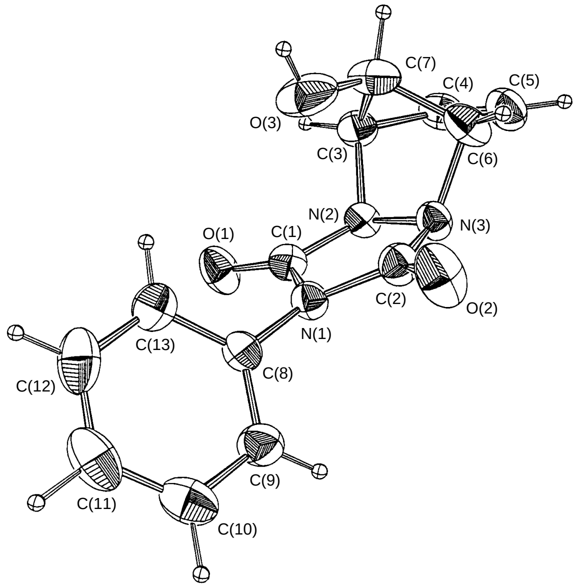


**Fig. 1** X-Ray structure of **3a**

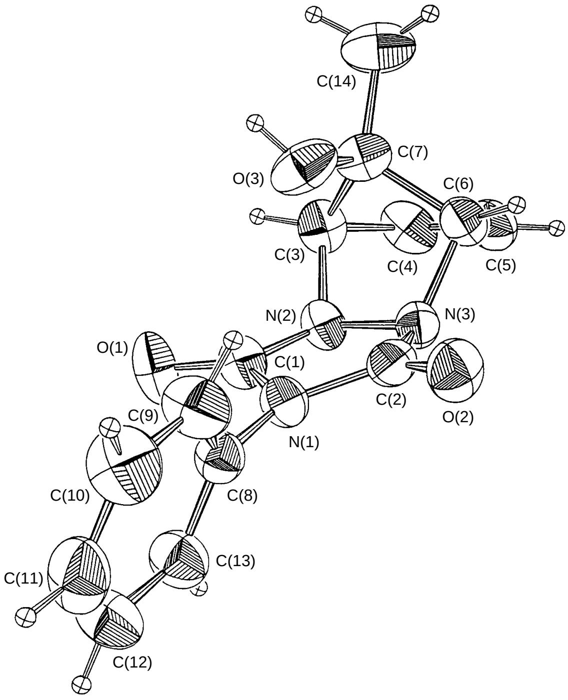


**Fig. 2** X-Ray structure of **3b**

Decomposition of ferrocenium cation is probably initiated *via* radical coupling with molecular oxygen as previously suggested.[1] After rearrangement and chemical evolution, cleavage of the iron and the formed cyclopentadienol ligand takes place, whereas only limited decomplexation of the second ligand (in case of **1a**) leads to free cyclopentadiene. To support this hypothesis, we note that the oxygen decomposition of ferrocenium cations in MeCN gave a brown precipitate characterised as an iron salt; elemental analyses of this salt showed the presence of one cyclopentadienyl ligand.[15]

## Footnotes

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† *Selected data* for **3a**, **3b** *and* **3d**. Satisfactory elemental analyses were obtained for these new compounds. For **3a**: mp 214 °C; $\nu(CH_2Cl_2)/cm^{-1}$ 1726 (CO); HRMS: *m/z* 241.084 ($M^+$); $\delta_H$ (300 MHz, $CD_3COCD_3$) −4.15 (dt, 1 H, C*H*OH), 4.80 (m, 2 H, CH), 5.65 (d, 1 H, OH), 6.53 (t, 2 H, =CH), 7.35–7.51 (m, 5 H, $C_6H_5$); $\delta_C$ (75 MHz, $CD_3COCD_3$) −69.14 (d, CH), 83.29 (d, CHOH), 134.00 (d, C=C), 160.34 (s, C=O), 133.73 (s), 126.86 (d), 128.68 (d), 129.62 (d) ($C_6H_5$). For **3b**: mp 213–214 °C; $\nu(CH_2Cl_2)/cm^{-1}$ 1724 (CO); HRMS: *m/z* 271.095 ($M^+$). $\delta_H$ (300 MHz, $CD_3COCD_3$) −1.40 (s, 3 H, $CH_3$), 3.36 (s, 1 H, OH), 4.63 (t, 2 H, CH), 6.50 (t, 2 H, =CH), 7.3–7.5 (m, 5 H, $C_6H_5$); $\delta_C$ (75 MHz, $CD_3COCD_3$) −17.57 (q, $CH_3$), 71.03 (d, CH), 90.26 (d, COH), 132.80 (d, C=C), 158.88 (s, C=O), 131.30 (s), 125.67 (d), 128.62 (d), 129.22 (d) ($C_6H_5$). For **3d** mp 197–198 °C; $\nu(CH_2Cl_2)/cm^{-1}$ 1725 (CO); HRMS: *m/z* 285.110 ($M^+$); $\delta_H$ (300 MHz, $CD_3COCD_3$) −0.98 (t, 3 H, $CH_3$), 1.71 (q, 2 H, $CH_2$), 3.34 (s, 1 H, OH), 4.67 (t, 2 H, CH), 6.48 (t, 2 H, =CH), 7.3–7.5 (m, 5 H, $C_6H_5$); $\delta_C$ (75 MHz, $CD_3COCD_3$) −9.29 (q, $CH_3$), 23.98 (t, $CH_2$), 69.89 (d, CH), 93.76 (s, COH), 132.46 (d, C=C), 158.93 (s, C=O), 131.35 (s), 125.70 (d), 128.59 (d), 129.21 (d) ($C_6H_5$).

‡ *X-Ray crystal data* for **3a**: $C_{13}H_{11}N_3O_3$: MW = 257.25, Orthorhombic, *Pbca*, $a$ = 11.386(2), $b$ = 12.706(2), $c$ = 16.275(3) Å, $V$ = 2354.4(7) Å$^3$, $Z$ = 8, $R$ = 0.030, $Rw$ = 0.029 for 1354 observations and 206 variables. For **3b**: $C_{14}H_{13}N_3O_3$: MW = 271.28, monoclinic, $P2_1/n$, $a$ = 16.440(8), $b$ = 8.490(7), $c$ = 9.580(4) Å, $\beta$ = 105.07(3)°, $V$ = 1291(1) Å$^3$, $Z$ = 4, $R$ = 0.036, $Rw$ = 0.034 for 1278 observations and 221 variables.

Data at 294 K were collected on an automatic diffractometer CAD4 Enrar-Nonius with graphite monochromatized Mo-Kα radiation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/484.

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