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Unusual Diels—Alder reaction of 7,12-ethenoquinolino[6,7-*f*]quinoline derivatives

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Earlier[1,2] during synthesis of 2-spiroannulated 1,2,3,4-tetrahydroquinolines, original spiro structures **1** with the framework of 7,12-ethenoquinolino[6,7-*f*]quinoline (Scheme 1) have been isolated and characterized.

The study of chemical transformations of polycycles **1** revealed unusual reluctance of endocyclic C=N bonds. For instance, they were not involved into the reduction ($NaBH_4$ in boiling methanol or ethanol, $LiAlH_4$ in diethyl ether or THF), the Grignard (MeMgI in diethyl ether or THF), or oxidation (Na_2WO_4/H_2O_2) reactions characteristic of azomethines. These facts, probably, can be explained by steric hindrance, which is created by the rigid bicyclic framework, as well as the cycloalkane substituents at α-position to the nitrogen atoms of the molecule.

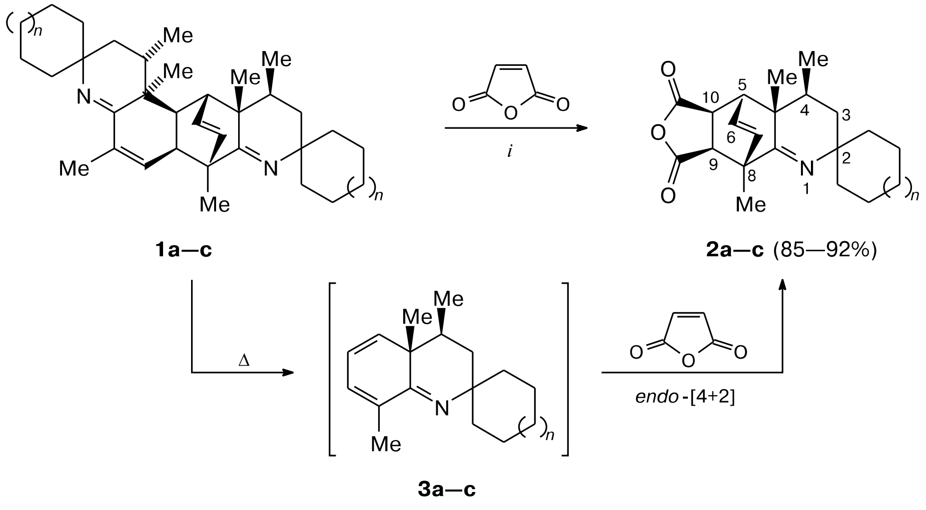
Maleic anhydride does not react with the imine fragments either. Instead of usual acylation products at the nitrogen atom, after heating of 7,12-ethenoquinolino-[6,7-*f*]quinolines **1** with an excess of maleic anhydride the earlier unknown spiroheterocycles, 5,8-ethenoquinolines **2** (see Scheme 1), were isolated in high yields.

We suggest that the reaction proceeds through the 2,3,4,4a-tetrahydroquinoline intermediates **3**, which result from the retro-diene cleavage of the starting polycycles **1** on heating. Such unstable dienes **3** are trapped by the dienophile, which leads to the *endo*-adducts of [4+2] cycloaddition **2**.

Configurations of new asymmetric centers (at the C(9) and C(10) atoms) were established from the data of correlation NMR spectroscopy. In particular, the two-dimensional NOESY spectrum exhibits an intensive cross-peak between the proton H(4) and H(10) signals, which indicates their closeness in space.

Note that the intermediate 2,3,4,4a-tetrahydroquinolines **3** are virtually unknown in the literature, there are only several reports on their formation in low yields as the intermediate products in the synthesis of 1,2,3,4-tetrahydroquinolines.[3—5]

Scheme 1



i. *o*-$C_6H_4Me_2$, Δ, 3 h

n = 0 (**a**), 1 (**b**), 2 (**c**)

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Synthesis of 5,8-ethenoquinolines 2. A mixture of polycycle **1** (1.0 g, ~2.0 mmol) and maleic anhydride (0.42 g, 4.30 mmol) in *o*-xylene (15 mL) was refluxed for 3 h. Xylene was evaporated at reduced pressure, the residue, a yellow oil, was triturated with diethyl ether (10 mL). A powder obtained was filtered off, washed with diethyl ether (2×10 mL), and recrystallized from hexane—EtOAc mixture to obtained adducts **2** as clear stretched prisms.

(4*R,4a*R**,5*S**,8*R**,9*R**,10*R**)-4,4a,5,8-Tetrahydro-4,4a,8-trimethyl-3*H*-spiro[5,8-ethenoquinoline-2,1´-cyclopentane]-9,10-dicarboxylic acid anhydride (2a).** The yield was 87%, m.p. 197—199 °C. Found (%): C, 73.15; H, 7.43; N, 4.29. $C_{20}H_{25}NO_3$. Calculated (%): C, 73.37; H, 7.70; N, 4.28. IR, ν/cm^{-1} (KBr): 1660 (N=C, C=C); 1779, 1842 (C=O). MS, *m/z* (I_{rel} (%)): 328 (4), 327 $[M]^+$ (26), 229 (22), 228 (6), 215 (11), 214 (68), 188 (17), 187 (100), 186 (12), 172 (5), 158 (18), 148 (12), 145 (12), 144 (13), 130 (8), 119 (7), 109 (8), 91 (18), 82 (18), 67 (22). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.77 (s, 3 H, Me(4a)); 0.92 (d, 3 H, Me(4), *J* = 6.1 Hz); 1.5—1.6 (m, 3 H, H(4), H(3)); 1.59 (s, 3 H, Me(8)); 2.77 (d, 1 H, H(9), *J* = 8.6 Hz); 3.23 (m, 1 H, H(5), *J* = 6.4 Hz, *J* = 3.1 Hz, *J* = 1.5 Hz); 3.35 (dd, 1 H, H(10), *J* = 3.1 Hz, *J* = 8.6 Hz); 6.14 (dd, 1 H, H(6), *J* = 1.5 Hz, *J* = 8.4 Hz); 6.37 (dd, 1 H, H(7), *J* = 6.4 Hz, *J* = 8.4 Hz); 1.5—1.9 (m, 8 H, H of cyclopentane). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 172.8, 170.1 (both s, C=O); 171.7 (C(8a)); 135.3 (C(6)); 132.9 (C(7)); 66.3 (C(2)); 51.3 (C(9)); 46.1 (C(8)); 41.9 (C(5)); 41.6 (C(4a)); 41.4 (C(10)); 38.5 (C(3)); 31.3 (C(4)); 43.2, 42.1, 23.8, 23.7 (all t, C of cyclopentane); 16.9 (Me(8)); 16.7 (Me(4a)); 14.5 (Me(4)).

References

1. V. V. Kouznetsov, F. I. Zubkov, E. V. Nikitina, L. D. A. Duarte, *Tetrahedron Lett.*, 2004, **45**, 1981.
2. F. I. Zubkov, E. V. Nikitina, V. V. Kouznetsov, L. D. A. Duarte, *Eur. J. Org. Chem.*, 2004, 5064.
3. H. Posson, J.-P. Hurvois, C. Moinnet, *Synlett*, 2000, 209.
4. L. W. Deady, R. D. Topsom, R. E. J. Hutchinson, J. Vaughan, G. J. Wright, *Tetrahedron Lett.*, 1968, 1773.
5. R. Fusco, F. Sannicoly, *Khim. Geterotsikl. Soedin.*, 1978, 504 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1978, **14**, 413].

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