

Condensation of acetylnaphthols with trifluoro- and trichloro-acetonitriles. The first example of ring-chain isomerism in the aromatic β -hydroxyoxoamine series

Vyacheslav Ya. Sosnovskikh

Department of Chemistry, A. M. Gor'ky Ural State University, 620083 Ekaterinburg, Russian Federation. Fax: +7 343 246 0228

In contrast to 2-acetylnaphth-1-ol, condensation of 1-acetylnaphth-2-ol with trifluoro- and trichloro-acetonitriles does not stop at ring-opening of the hydroxyoxoamine form, but leads instead to 2-amino-2-trifluoro(trichloro)methyl-5,6-benzo-4-chromanones.

Earlier¹ we showed that the interaction of 2-hydroxyacetophenone with trifluoro- and trichloro-acetonitriles in the presence of *N*-ethylanilinomagnesium bromide proceeds via nucleophilic addition of enolate anion to an activated nitrile group and leads to the corresponding β -hydroxyoxoamines.

Continuing our study of this reaction, we have found that 2-acetylnaphth-1-ol behaves analogously to 2-hydroxyacetophenone and gives 3-amino-1-(1-hydroxy-2-naphthyl)-4,4,4-trifluoro(trichloro)but-2-en-1-ones **1a,b**, which exist as *Z*-isomers with a coplanar *s-cis*, *s-cis*-conformation stabilized by intramolecular hydrogen bonds involving amino and hydroxy group hydrogen atoms.² Acidic hydrolysis of these compounds gives 2-trifluoro(trichloro)methyl-7,8-benzo-4-chromones **2a,b** in high yields.[†]

In contrast to the interaction of 2-acetylnaphth-1-ol with trihaloacetonitriles, condensation of 1-acetylnaphth-2-ol with trifluoroacetonitrile unexpectedly yielded the mixture of ring-chain isomers **3a, 4a**. To explain the preparation of compound **4a** one can propose that in this case formation of the coplanar conformer becomes impossible because of the unfavourable interaction between the peri-hydrogen and aminoenone system which is forced to turn out from the plane of the naphthalene ring. This causes a weakening of the intramolecular hydrogen

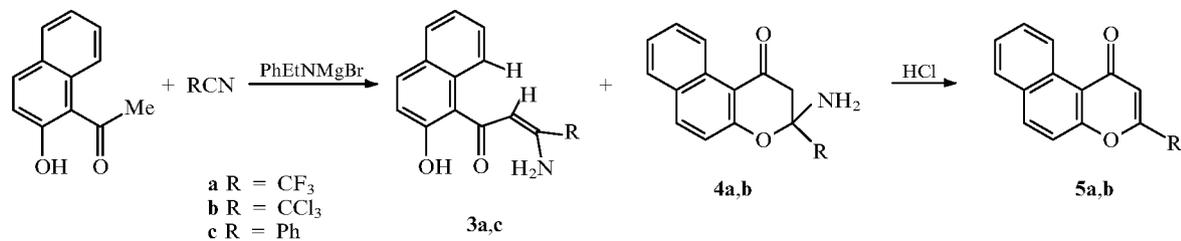
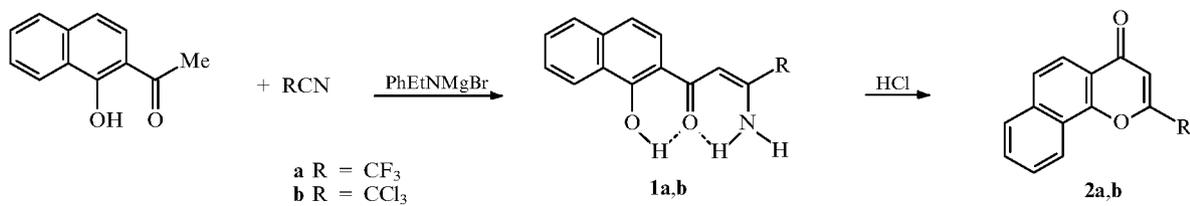
bond in the ketol fragment and increases the conformational mobility of the molecule.

As a result the reaction of 1-acetylnaphth-2-ol with trifluoroacetonitrile gave a 25% yield of the product which consisted of 90% 3-amino-1-(2-hydroxynaphth-1-yl)-4,4,4-trifluorobut-2-en-1-one **3a** and 10% 2-amino-2-trifluoro-methyl-5,6-benzo-4-chromanone **4a**. After recrystallisation from ethanol it contained only 5% of ring-opened form **3a** and 95% of cyclic form **4a**. Repeated recrystallisation from ethanol gave the pure compound **4a**.

The condensation product of 1-acetylnaphth-2-ol with trichloroacetonitrile cyclized much faster and we were able to isolate it in the cyclic form **4b**. Treatment of compounds **4a,b** with concentrated hydrochloric acid gave the 2-trifluoro(trichloro)methyl-5,6-benzo-4-chromones **5a,b** in almost quantitative yield.[‡]

[†] Compounds **1, 3, 4** were prepared by the procedure in ref. 3. Compound **1a**: yield 24%, mp 127–128 °C (hexane). Found: C 60.05; H 3.77. Calc. for C₁₄H₁₀F₃NO₂: C 59.79; H 3.58%. IR ν/cm^{-1} : 3505 (NH₂), 1625, 1570, 1530 (NH₂, C=C–C=O); ¹H NMR (CDCl₃) δ 6.28 (s, 1H, =CH), 7.2–8.5 (m, 8H, arom. protons, NH₂), 14.47 (s, 1H, OH). Compound **1b**: yield 40%, mp 129–130 °C (ethanol). Found: C 50.76; H 3.03. Calc. for C₁₄H₁₀Cl₃NO₂: C 50.86; H 3.05%. IR ν/cm^{-1} : 3490 (NH₂), 1610, 1570, 1520 (NH₂, C=C–C=O); ¹H NMR (CDCl₃) δ 6.71 (s, 1H, =CH), 7.2–8.5 (m, 8H, arom. protons, NH₂), 14.49 (s, 1H, OH). Compound **2a**: yield 78%, mp 117–118 °C (ethanol). Found: C 63.74; H 2.86. Calc. for C₁₄H₇F₃O₂: C 63.65; H 2.67%. IR ν/cm^{-1} : 1670 (C=O); ¹H NMR (CDCl₃) δ 6.86 (s, 1H, =CH), 7.6–8.5 (m, 6H, arom. protons). Compound **2b**: yield 75%, mp 164–165 °C (ethanol). Found: C 53.50; H 2.38. Calc. for C₁₄H₇Cl₃O₂: C 53.63; H 2.25%. IR ν/cm^{-1} : 1645 (C=O); ¹H NMR (CDCl₃) δ 7.15 (s, 1H, =CH), 7.7–8.6 (m, 6H, arom. protons).

[‡] Compound **3a**: yield 25%, mp 80–82 °C. ¹H NMR δ 6.26 (s, 1H, =CH), 7.1–8.2 (m, 8H, arom. protons, NH₂), 11.90 (s, 1H, OH). Compound **3c**: yield 6%, mp 128–129 °C (benzene). Found: C 78.48; H 5.16. Calc. for C₁₉H₁₅NO₂: C 78.87; H 5.23%. IR ν/cm^{-1} : 3450 (NH₂), 1605, 1550, 1520 (NH₂, C=C–C=O); ¹H NMR δ 5.6, 10.3 (broad s, 2H, NH₂), 6.16 (s, 1H, =CH), 7.1–8.4 (m, 11H, arom. protons), 12.05 (s, 1H, OH). Compound **4a**: yield 25%, mp 121–122 °C (ethanol). Found: C 59.66; H 3.42. Calc. for C₁₄H₁₀F₃NO₂: C 59.79; H 3.58%. IR ν/cm^{-1} : 3470, 3380 (NH₂), 1670 (C=O), 1625, 1600, 1570, 1515 (NH₂, arom.); ¹H NMR δ 2.48 (s, 2H, NH₂), 2.90, 3.30 (dd, 2H, H_A, H_B, *J* = 16.2 Hz), 7.1–8.0 (m, 5H, arom. protons), 9.35 (d, 1H, peri-H). Compound **4b**: yield 34%, mp 157–158 °C (ethanol). Found: C 51.02; H 3.23. Calc. for C₁₄H₁₀Cl₃NO₂: C 50.86; H 3.05%. IR ν/cm^{-1} : 3420, 3350 (NH₂), 1660 (C=O), 1610, 1590, 1560, 1500 (NH₂, arom.); ¹H NMR δ 2.57 (s, 2H, NH₂), 3.11, 3.65 (dd, 2H, H_A, H_B, *J* = 16.1 Hz), 7.1–8.0 (m, 5H, arom. protons), 9.39 (d, 1H, peri-H). Compound **5a**: yield 87%, mp 119–120 °C (ethanol). Found: C 63.54; H 2.93. Calc. for C₁₄H₇F₃O₂: C 63.65; H 2.67%. IR ν/cm^{-1} : 1660 (C=O), 1625, 1590, 1570 (C=C, arom.); ¹H NMR δ 6.84 (s, 1H, =CH), 7.5–8.2 (m, 5H, arom. protons), 9.8–9.9 (m, 1H, peri-H). Compound **5b**: yield 84%, mp 142–143 °C (ethanol). Found: C 53.69; H 2.35. Calc. for C₁₄H₇Cl₃O₂: C 53.63; H 2.25%. IR ν/cm^{-1} : 1650 (C=O), 1620, 1600, 1575 (C=C, arom.); ¹H NMR δ 7.13 (s, 1H, =CH), 7.5–8.2 (m, 5H, arom. protons), 9.9–10.0 (m, 1H, peri-H).



The cyclisation of **3** to **4** is the first example of ring-chain isomerism in the aromatic β -hydroxyoxoenamine series.

It should be noted that the reaction with benzonitrile ceases with the formation of a compound **3c** which exists only in the ring-opened form.

References

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