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

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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 hydroxyoxoenamine form, but leads instead to 2-amino-2-trifluoro(trichloro)methyl-5,6-benzo-4-chromanones.

Earlier[1] 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-hydroxyoxoenamines.

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.†

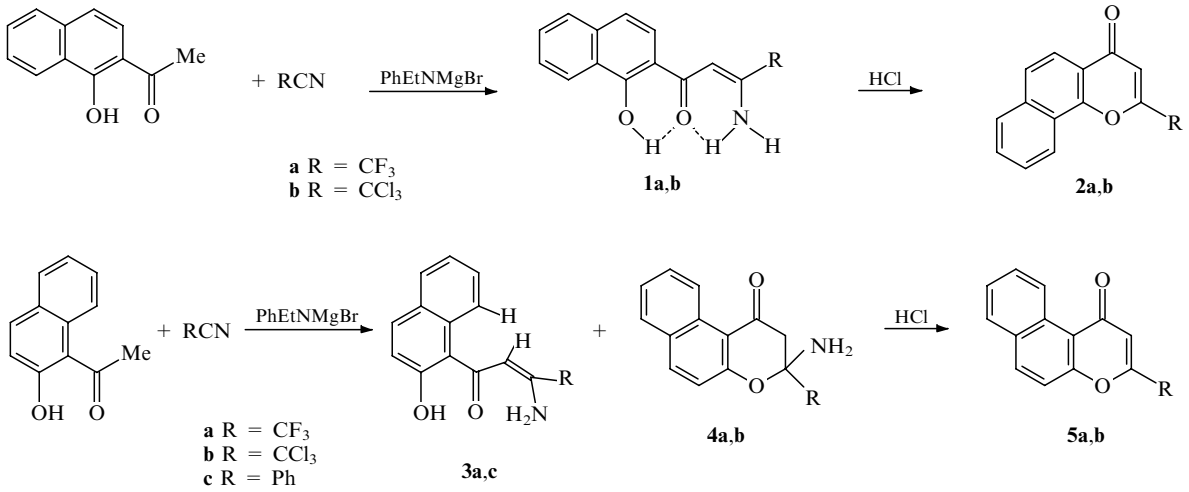
In contrast to the interaction of 2-acetylnaphth-1-ol with trihaloacetonitriles, condensation of 1-acetylnaphth-2-ol with trifluoroacetonitrile unexpectedly yielded the mixture of ring-chain isomers **3a**, **4a**. To explain the preparation of compound **4a** one can propose that in this case formation 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-trifluoromethyl-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 $C_{14}H_{10}F_3NO_2$: C 59.79; H 3.58%. IR ν/cm^{-1}: 3505 (NH_2), 1625, 1570, 1530 (NH_2, C=C–C=O); ^{1}H NMR ($CDCl_3$) δ 6.28 (s, 1H, =CH), 7.2–8.5 (m, 8H, arom. protons, NH_2), 14.47 (s, 1H, OH). Compound **1b**: yield 40%, mp 129–130 °C (ethanol). Found: C 50.76; H 3.03. Calc. for $C_{14}H_{10}Cl_3NO_2$: C 50.86; H 3.05%. IR ν/cm^{-1}: 3490 (NH_2), 1610, 1570, 1520 (NH_2, C=C–C=O); ^{1}H NMR ($CDCl_3$) δ 6.71 (s, 1H, =CH), 7.2–8.5 (m, 8H, arom. protons, NH_2), 14.49 (s, 1H, OH). Compound **2a**: yield 78%, mp 117–118 °C (ethanol). Found: C 63.74; H 2.86. Calc. for $C_{14}H_7F_3O_2$: C 63.65; H 2.67%. IR ν/cm^{-1}: 1670 (C=O); ^{1}H NMR ($CDCl_3$) 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 $C_{14}H_7Cl_3O_2$: C 53.63; H 2.25%. IR ν/cm^{-1}: 1645 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 1H, =CH), 7.7–8.6 (m, 6H, arom. protons).

‡ Compound **3a**: yield 25%, mp 80–82 °C. ^{1}H NMR δ 6.26 (s, 1H, =CH), 7.1–8.2 (m, 8H, arom. protons, NH_2), 11.90 (s, 1H, OH). Compound **3c**: yield 6%, mp 128–129 °C (benzene). Found: C 78.48; H 5.16. Calc. for $C_{19}H_{15}NO_2$: C 78.87; H 5.23%. IR ν/cm^{-1}: 3450 (NH_2), 1605, 1550, 1520 (NH_2, C=C–C=O); ^{1}H NMR δ 5.6, 10.3 (broad s, 2H, NH_2), 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 $C_{14}H_{10}F_3NO_2$: C 59.79; H 3.58%. IR ν/cm^{-1}: 3470, 3380 (NH_2), 1670 (C=O), 1625, 1600, 1570, 1515 (NH_2, arom.); ^{1}H NMR δ 2.48 (s, 2H, NH_2), 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 $C_{14}H_{10}Cl_3NO_2$: C 50.86; H 3.05%. IR ν/cm^{-1}: 3420, 3350 (NH_2), 1660 (C=O), 1610, 1590, 1560, 1500 (NH_2, arom.); ^{1}H NMR δ 2.57 (s, 2H, NH_2), 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 $C_{14}H_7F_3O_2$: C 63.65; H 2.67%. IR ν/cm^{-1}: 1660 (C=O), 1625, 1590, 1570 (C=C, arom.); ^{1}H 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 $C_{14}H_7Cl_3O_2$: C 53.63; H 2.25%. IR ν/cm^{-1}: 1650 (C=O), 1620, 1600, 1575 (C=C, arom.); ^{1}H 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.

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