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SHORT COMMUNICATIONS

First Example of [3,3]-Sigmatropic Rearrangement in the Series of 2-(Prop-2-yn-1-ylsulfanyl)-1,4,5,6,7,8-hexahydroquinolines

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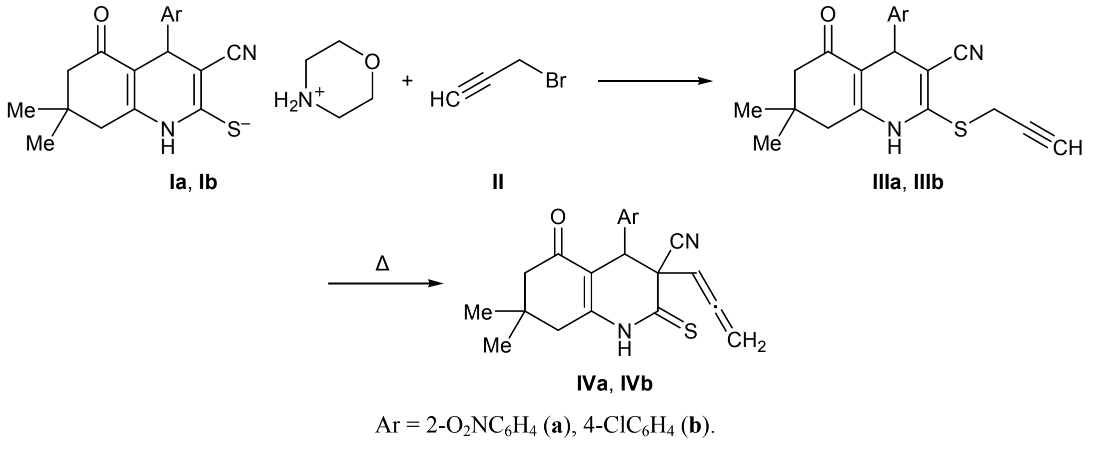
We previously revealed [3,3]-sigmatropic rearrangement of 2-allylsulfanyl(selanyl)-substituted 1,4-dihydropyridines and 1,4,5,6,7,8-hexahydroquinolines into 3-allyl-2-thioxo(selenoxo)-1,2,3,4-hexahydropyridines and 3-allyl-2-thioxo-1,2,3,4,5,6,7,8-octahydroquinolines [1]. [3,3]-Sigmatropic rearrangement of 3-(prop-2-yn-1-ylsulfanyl)-substituted carbo- and heterocycles usually results in formation of fused 2-methylthiophene or thiopyran derivatives [2].

In the present communication we report for the first time on the alkylation of morpholinium 4-aryl-3-cyano-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-2-thiolates **Ia** and **Ib** with prop-2-yn-1-yl bromide (**II**) with formation of 4-aryl-7,7-dimethyl-5-oxo-2-(prop-2-yn-1-ylsulfanyl)-1,4,5,6,7,8-hexahydroquinoline-3-carbonitriles **IIIa** and **IIIb** which underwent regioselective [3,3]-sigmatropic rearrangement into 4-aryl-7,7-dimethyl-5-oxo-3-(propa-1,2-dien-1-yl)-2-thioxo-1,2,3,4,5,6,7,8-octahydroquinoline-3-carbonitriles **IVa** and **IVb** on heating in boiling ethanol. The structure of compound **IVa** was determined by X-ray analysis, which will be reported elsewhere.

Morpholinium 3-cyano-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-2-thiolate (**Ia**) and morpholinium 4-(4-chlorophenyl)-3-cyano-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-2-thiolate (**Ib**) were synthesized according to the procedure described in [3].

7,7-Dimethyl-4-(2-nitrophenyl)-5-oxo-2-(prop-2-yn-1-ylsulfanyl)-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (IIIa). Prop-2-yn-1-yl bromide (**II**), 0.09 ml (1.2 mmol), was added at 25°C to a suspension of 0.5 g (1.13 mmol) of morpholinium salt **Ia** in 10 ml of ethanol. The mixture was stirred for 3 h, and the precipitate was filtered off and washed with ethanol and hexane. Yield 0.36g (81%), yellow powder, mp 133°C. IR spectrum, ν, cm^{-1}: 3442 (NH), 2209 (C≡N), 1614 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.80 s and 0.98 s (3H each, Me), 1.92 d and 2.14 d (1H each, 6-H, ^2J = 16.0 Hz), 2.36 d and 2.41 d (1H each, 8-H, ^2J = 16.0 Hz), 3.41 s (1H, ≡CH), 3.97 s (2H, SCH_2), 5.28 s (1H, 4-H), 7.44 t (1H, H_{arom}, J = 8.0 Hz), 7.54 d (1H, H_{arom}, J = 8.0 Hz), 7.70 t (1H, H_{arom}, J = 8.0 Hz), 7.80 d (1H, H_{arom}, J = 8.0 Hz), 9.86 br.s (1H, NH).



Ar = 2-$O_2NC_6H_4$ (**a**), 4-ClC_6H_4 (**b**).

Mass spectrum, *m*/*z* (I_{rel}, %): 395 (1) $[M + 2]^+$, 394 (1) $[M + 1]^+$, 393 (5) $[M]^+$, 376 (45), 320 (71), 290 (34), 261 (18), 203 (14), 162 (24), 83 (100), 39 (93) $[CH_2C{\equiv}CH]^+$. Found, %: C 64.02; H 4.75; N 10.49. $C_{21}H_{19}N_3O_3S$. Calculated, %: C 64.10; H 4.87; N 10.68.

4-(4-Chlorophenyl)-7,7-dimethyl-5-oxo-2-(prop-2-yn-1-ylsulfanyl)-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (IIIb) was synthesized in a similar way from salt **Ib**. Yield 0.30 g (63%), light yellow powder, mp 145–147°C. IR spectrum, ν, cm^{-1}: 3448 (NH), 2202 (C≡N), 1610 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.89 s and 1.01 s (3H each, Me), 2.03 d and 2.21 d (1H each, 6-H, ^2J = 16.0 Hz), 2.42 s (2H, 8-H), 3.48 s (1H, ≡CH), 3.89 d and 3.99 d (1H each, SCH_2, ^2J = 16.0 Hz), 4.54 s (1H, 4-H), 7.23 d (2H, H_{arom}, J = 8.0 Hz), 7.37 d (2H, H_{arom}, J = 8.0 Hz), 9.76 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 21.40, 27.13, 29.13, 32.63, 50.46, 76.11, 78.90, 94.01, 108.10, 119.02, 128.87, 129.69, 131.98, 142.45, 144.02, 150.38, 194.93. Mass spectrum, *m*/*z* (I_{rel}, %): 384 (15) $[M + 2]^+$, 383 (14) $[M + 1]^+$, 382 (37) $[M]^+$, 381 (14) $[M - 1]^+$, 271 (100), 215 (12), 143 (2), 32 (5). Found, %: C 65.77; H 4.85; N 7.22. $C_{21}H_{19}ClN_2OS$. Calculated, %: C 65.87; H 5.00; N 7.32.

7,7-Dimethyl-4-(2-nitrophenyl)-5-oxo-3-(propa-1,2-dien-1-yl)-2-thioxo-1,2,3,4,5,6,7,8-octahydroquinoline-3-carbonitrile (IVa). A suspension of 0.3 g (0.76 mmol) of compound **IIIa** in 10 ml of ethanol was heated for 5 h under reflux. The precipitate was filtered off and washed with ethanol and hexane. Yield 0.255 g (85%), bright yellow powder, mp 165–167°C (from EtOH). IR spectrum, ν, cm^{-1}: 3460 (NH), 2247 (C≡N), 1649 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.89 s and 1.02 s (3H each, Me), 2.09 d and 2.23 d (1H each, 6-H, J = 16.0 Hz), 2.55 s (2H, 8-H), 5.12 s (1H, 4-H), 5.25–5.36 m (2H, $=CH_2$), 5.70 t (1H, =CH, ^4J = 4.0 Hz), 7.11 d (1H, H_{arom}, J = 8.0 Hz), 7.56 t (1H, H_{arom}, J = 8.0 Hz), 7.70 t (1H, H_{arom}, J = 8.0 Hz), 8.02 d (1H, H_{arom}, J = 8.0 Hz), 12.61 br.s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 393 (1) $[M]^+$, 376 (12), 320 (100), 290 (10), 164 (2), 120 (2), 83 (36). Found, %: C 64.00; H 4.65; N 10.52. $C_{21}H_{19}N_3O_3S$. Calculated, %: C 64.10; H 4.87; N 10.68.

4-(4-Chlorophenyl)-7,7-dimethyl-5-oxo-3-(propa-1,2-dien-1-yl)-2-thioxo-1,2,3,4,5,6,7,8-octahydroquinoline-3-carbonitrile (IVb) was synthesized in a similar way from compound **IIIb**. Yield 0.27 g (90%), bright yellow powder, mp 176–178°C. IR spectrum, ν, cm^{-1}: 3437 (NH), 2240 (C≡N), 1633 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.94 s and 1.04 s (3H each, Me), 2.15 d and 2.27 d (1H each, 6-H, ^2J = 16.0 Hz), 2.57 d (1H, 8-H, ^2J = 16.0 Hz; the other 8-H signal was obscured by the solvent signal), 4.26 s (1H, 4-H), 5.20–5.29 m (2H, $=CH_2$), 5.69 t (1H, =CH, ^4J = 4.0 Hz), 7.16 d (2H, H_{arom}, J = 8.0 Hz), 7.40 d (2H, H_{arom}, J = 8.0 Hz), 12.48 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 27.05, 27.91, 32.38, 38.57, 42.56, 49.66, 58.20, 81.43, 89.89, 113.49, 116.99, 128.49, 129.94, 132.61, 136.18, 148.33, 148.42, 194.52, 206.52. Mass spectrum, *m*/*z* (I_{rel}, %): 384 (41) $[M + 2]^+$, 383 (44) $[M + 1]^+$, 382 (100) $[M]^+$, 381 (64) $[M - 1]^+$, 326 (34), 271 (36), 162 (11), 127 (9), 83 (19). Found, %: C 65.75; H 4.82; N 7.23. $C_{21}H_{19}ClN_2OS$. Calculated, %: C 65.87; H 5.00; N 7.32.

The IR spectra were recorded in KBr on a Perkin–Elmer Spectrum One FIR spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-400 instrument at 400.397 and 101 MHz, respectively, using DMSO-d_6 as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1321 mass spectrometer with direct sample admission into the ion source. The melting points were determined on a Kofler hot stage. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using acetone–hexane (3 : 5) as eluent; spots were visualized by treatment with iodine vapor or under UV irradiation.

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