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LETTERS TO THE EDITOR

THE REACTION OF 2,5-BIS[(DIMETHYLAMINO)-METHYL]HYDROQUINONE AND 3-(DIMETHYLAMINO)-2-CYCLOHEXEN-1-ONES

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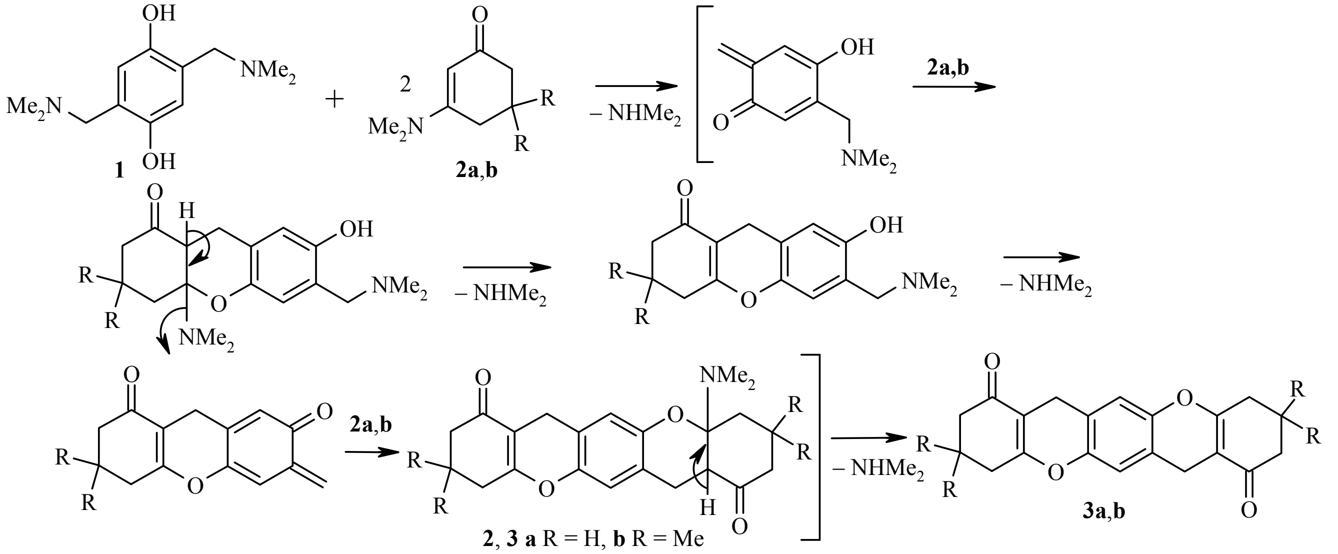
There have been a few examples reported for reactions of *o*-methylenequinones with enamines leading to chromans or 4H-chromenes [1-3]. We have shown that the reaction of 2,5-bis[(dimethylamino)methyl]-hydroquinone (**1**) with enamines **2a** and **2b** gives the previously unreported 2,3,4,7,9,10,11,14-octahydrochromeno[2,3-*b*]xanthene system. This is a tandem reaction involving the intermediate formation of *o*-methylenequinone from Mannich base **1**, subsequent cycloaddition involving enamines **2a** and **2b** as dienophiles, and elimination of a molecule of dimethylamine.



2, **3** **a** R = H, **b** R = Me

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The IR spectra were taken on a Shimadzu FTIR-8400S spectrometer for KBr pellets. The ^{1}H NMR spectra were taken on a Bruker AM 400 spectrometer at 400 MHz in DMSO-d_6 with TMS as the internal standard. The mass spectra were taken on a Finnigan Trance DSQ mass spectrometer with ionizing electron energy 70 eV. The elemental analysis was carried out on an automatic Euro-Vector EA-3000 CHNS-analyzer.

2,5-Bis[(dimethylamino)methyl]hydroquinone (1) was obtained according to Caldwell [4], while **3-(dimethylamino)-2-cyclohexen-1-one (2a) and 5,5-Dimethyl-3-(dimethylamino)-2-cyclohexen-1-one (2b)** were obtained according to Kowalski [5].

2,3,4,7,9,10,11,14-Octahydrochromeno[2,3-*b*]xanthene-1,8-dione (3a). A mixture of Mannich base **1** (1.0 g, 4.46 mmol) and enamine **2a** (1.24 g, 8.92 mmol) in DMF (15 ml) was heated at reflux for 3 h and then cooled. The precipitate formed was filtered off and recrystallized from DMF to give 1.02 g (71%) dione **3a** light-beige crystals with mp 279-280°C. IR spectrum, ν, cm^{-1}: 2947, 2893, 2839 (CH_2), 1651 (C=O), 1504, 1458, 1435, 1381, 1238, 1200, 1184, 1153, 1122, 1061, 991, 879, 768, 598, 532. ^{1}H NMR spectrum, δ, ppm: 1.85-2.05 (4H, m, H-3, H-10); 2.35-2.55 (8H, m, H-2, H-4, H-9, H-11); 3.34 (4H, s, H-7, H-14); 6.95 (2H, s, H-6, H-13). Mass spectrum, *m/z* (I_{rel}, %): 322 $[M]^+$ (100), 321 $[M-H]^+$ (99), 304 $[M-H_2O]^+$ (10), 294 $[M-CO]^+$ (8), 293 $[M-H-CO]^+$ (11), 279 $[M-CO-CH_3]^+$ (9), 266 $[M-2CO]^+$ (58), 265 (40), 210 (16), 161 (19), 152 (21), 115 (15), 77 $[Ph]^+$ (14). Found, %: C 74.61; H 5.54. $C_{20}H_{18}O_4$. Calculated, %: C 74.52; H 5.63.

3,3,10,10-Tetramethyl-2,3,4,7,9,10,11,14-octahydrochromeno[2,3-*b*]xanthene-1,8-dione (3b) was obtained analogously to dione **3a** from Mannich base **1** (1.0 g, 4.46 mmol) and enamine **2b** (1.49 g, 8.92 mmol) in DMF (15 ml) as light orange-crystals with mp 287-288°C (DMF). The yield of dione **3b** was 82% (1.38 g). IR spectrum, ν, cm^{-1}: 2962, 2876, 2845 (CH_2, CH_3), 1651 (C=O), 1506, 1468, 1454, 1435, 1383, 1369, 1244, 1213, 1202, 1169, 1148, 1111, 1026, 1013, 868, 623, 609, 559. ^{1}H NMR spectrum, δ, ppm: 1.01 (12H, s, $4CH_3$); 2.23 (4H, s, $2CH_2$); 2.42 (4H, s, $2CH_2$); 3.45 (2H, s, H-7, H-14); 6.94 (2H, s, H-6, H-13). Mass spectrum, *m/z* (I_{rel}, %): 378 $[M]^+$ (100), 377 $[M-H]^+$ (29), 363 $[M-CH_3]^+$ (22), 350 $[M-CO]^+$ (4), 345 $[M-CH_3-H_2O]^+$ (5), 335 $[M-CH_3-CO]^+$ (12), 321 (6), 308 (14), 294 (17), 209 (7), 189 (9), 165 (5), 152 (8), 115 (7), 91 $[C_7H_7]^+$ (4), 83 (9), 77 $[Ph]^+$ (5). Found, %: C 76.17; H 6.92. $C_{24}H_{26}O_4$. Calculated, %: C 76.23; H 6.81.

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