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SYNTHESIS OF PARTIALLY HYDROGENATED SULFUR-CONTAINING QUINOLINES

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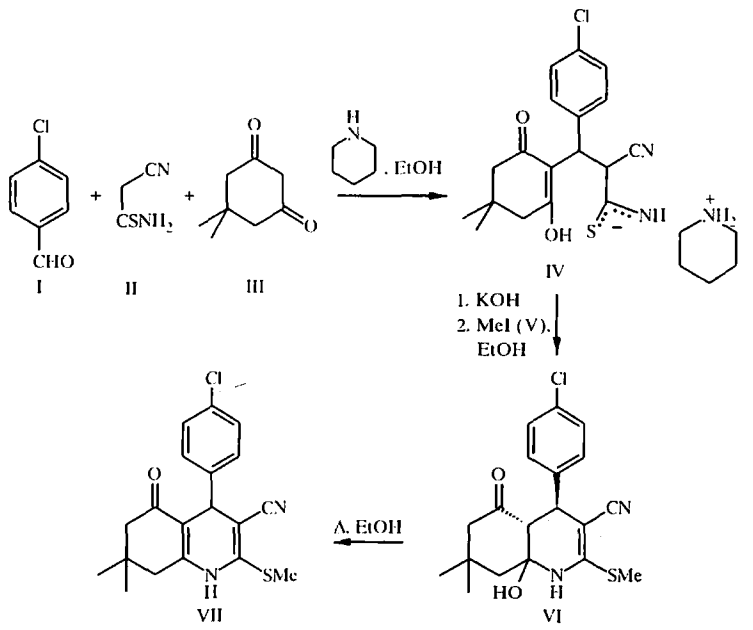
Reactions of arylmethylenecyanothioacetamides with dimedone and reactions of aromatic aldehydes with cyanothioacetamide and dimedone in the presence of secondary amines, leading to formation of substituted ammonium 2-(1-aryl-2-cyanoethyl-2-thiocarbamoyl-)-5,5-dimethyl-3-oxo-1-cyclohexen-1-olates have been described. It has been shown that the latter undergo ring closure to the corresponding hexahydroquinoline-2-thiolates [1-3].

For the first time we have been able to detect the formation of an intermediate 8a-hydroxy-1,4,4a,5,6,7,8,8a-octahydroquinoline. By condensation of 4-chlorobenzaldehyde (I), cyanothioacetamide (II), and dimedone (III) in ethanol in the presence of piperidine (~20°C), we obtained the Michael adduct IV, which upon successive treatment with a 10% aqueous solution of KOH and methyl iodide (V) converted to the previously unknown octahydroquinoline VI, which when heated briefly is dehydrated with formation of the corresponding sulfide, a derivative of hexahydroquinoline VII.



Piperidinium Salt of 5,5-Dimethyl-3-oxo-2-[1-(4-chlorophenyl)-2-cyanoethyl-2-thiocarbamoyl]-1-cyclohexen-1-ol (IV). Yield 92%; mp 187-189°C. IR spectrum: 3150-3270 (NH, + NH_2, OH), 2240 (CN), 1710 cm^{-1} (CO). PMR spectrum (DMSO-d_6): 0.93 (6H, br. s, 2Me); 1.60 (6H, m, $(CH_2)_3$); 1.93 (4H, br. s, $C_{(4)}H_2$

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and $C_{(6)}H_2$); 2.98 (4H, m, $N(CH_2)_2$); 5.03 (1H, d, ^3J = 11.9 Hz, $C_{(2)}H$); 5.85 (1H, d, ^3J = 11.9 Hz, $C_{(1)}H$); 7.13 and 7.49 (4H, both d, ^3J = 8.2 Hz, Ar); 7.22 (1H, br. s, OH or NH); 9.4 ppm (1H, br. s, NH or OH). Found, %: C 61.51; H 6.85; N 9.18; S 7.24. $C_{23}H_{30}ClN_3O_2S$. Calculated, %: C 61.66; H 6.75; N 9.38; S 7.16.

4-(4-Chlorophenyl)-3-cyano-8a-hydroxy-7,7-dimethyl-2-methylthio-5-oxo-1,4,4a,5,6,7,8,8a-octahydroquinoline (VI). Yield 75%; mp 285-287°C. IR spectrum: 3270-3390 (NH, OH), 2195 (CN), 1725, 1740 cm^{-1} (CO). PMR spectrum (DMSO-d_6): 0.9 and 1.03 (6H, both s, 2Me); 1.87 and 2.25 (2H, both d, ^2J = 13 Hz, $C_{(8)}H_2$); 2.46 (2H, s, $C_{(6)}H_2$); 2.53 (3H, s, SMe); 3.01 (1H, d, ^3J = 12.2 Hz, $C_{(4a)}H$); 3.37 (1H, d, ^3J = 12.2 Hz, $C_{(4)}H$); 5.75 (1H, s, OH); 7.18 and 7.41 (4H, both d, ^3J = 8.1 Hz, Ar); 7.73 ppm (1H, s, NH). Found, %: C 60.42; H 5.43; N 7.54; S 8.34. $C_{19}H_{21}ClN_2O_2S$. Calculated, %: C 60.55; H 5.62; N 7.43; S 8.51.

4-(4-Chlorophenyl)-3-cyano-7,7-dimethyl-2-methylthio-5-oxo-1,4,5,6,7,8-hexahydroquinoline (VII). Yield 89%; mp 281-283°C. IR spectrum: 3265-3381 (NH), 2190 (CN), 1740, 1753 cm^{-1} (CO). PMR spectrum (DMSO-d_6): 0.9 and 1.03 (6H, both s, 2Me); 2.03 and 2.32 (2H, both d, ^2J = 13.3 Hz, $C_{(8)}H_2$); 2.45 (2H, s, $C_{(6)}H_2$); 2.52 (3H, s, SMe); 4.50 (1H, s, $C_{(4)}H$); 7.19 and 7.43 (4H, both d, ^3J = 8.2 Hz, Ar); 9.66 ppm (1H, s, NH). Found, %: C 63.42; H 5.44; N 7.57; S 8.99. $C_{19}H_{19}ClN_2OS$. Calculated, %: C 63.59; H 5.34; N 7.81; S 8.93.

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