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LETTERS TO THE EDITOR

SYNTHESIS OF 2-ALKYLTHIO-4'-OXO-5,5-PENTAMETHYLENESPIRO-[1-PYRROLINE-3,1'-CYCLOHEXADIENES]

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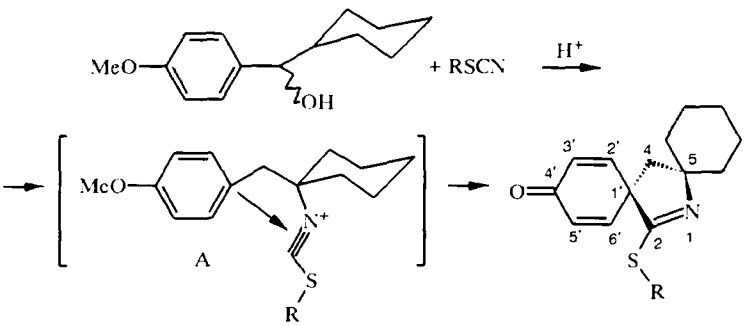
Earlier we proposed a method for obtaining 5,5-dimethyl-2-methylthio-4'-oxospiro[1-pyrroline-3,1'-cyclohexadienes] [1, 2]. We established that reaction of 4-methoxyphenylcyclohexylcarbinol with alkylthiocyanates RSCN (R = Me, $PhCH_2$) under Ritter reaction conditions leads to the dispirotricyclic system 2-alkylthio-4'-oxo-5,5-pentamethylenespiro[1-pyrroline-3,1'-cyclohexadiene] (**1**). To avoid the diene–phenol rearrangement, we carried out the reaction at -10°C to -15°C and a mole ratio of conc. H_2SO_4 : carbinol of ~4.5 : 1. During the reaction, isomerization of the secondary cyclohexyl-*p*-methoxyphenyl carbenium ion formed occurs, to the more stable tertiary pentamethylene-*p*-methoxybenzyl carbocation. Obviously, *ipso* attack in intermediate A is due to the electron-donor properties of the MeO group in the *para* position of the aromatic ring, as was described for analogous reactions in the alicyclic series [3-5].

Spiropyrroline systems were postulated earlier as intermediates in synthesis of methoxy-substituted isoquinolines [6,7], but none had been isolated. In our case, probably the sulfur atom of the functional group affects the increase in stability of compounds **1**. The insignificant yield of compounds **1a,b** is probably due to side reactions of oligomerization of the starting carbinol under the reaction conditions.



1a R = Me, **b** R = CH_2Ph

2-Methylthio-4'-oxo-5,5-pentamethylenespiro[1'-pyrroline-3,1'-cyclohexadiene] (1a). A solution of *p*-methoxyphenyl(cyclohexyl)carbinol (5.5 g, 25 mmol) and methylthiocyanate (1.38 ml, 20 mmol) in CH_2Cl_2 (50 ml) at a temperature no higher than -15°C was added dropwise to 98% H_2SO_4 (6 ml, 110 mmol) with vigorous

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stirring. After 30 min, it was poured into a mixture of 150 g ice and 75 g NH_4Cl, stirred, and neutralized with conc. NH_4OH to pH ~8. The aqueous layer was separated and extracted with CH_2Cl_2 (2 × 20 ml). The combined organic layers were dried with anhydrous $MgSO_4$. Dichloromethane was distilled off and the residue was recrystallized from ether. Yield 14%; mp 104-106°C. IR spectrum (vaseline oil): 1660 (C=O), 1625 (C=C), 1585 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.92 (2H, d, 2,6-H); 6.23 (2H, d, 3,5-H); 2.35 (3H, s, SMe); 2.19 (2H, s, CH_2); 1.34-1.83 (10H, m, $(CH_2)_5$). Found, %: C 69.12; H 7.40; N 5.25. $C_{15}H_{19}NOS$. Calculated, %: C 68.93; H 7.33; N 5.36.

2-Benzylthio-4-oxo-5,5-pentamethylenespiro[1-pyrroline-3,1'-cyclohexadiene] (1b). Obtained similarly from *p*-methoxyphenylcyclohexylcarbinol (5.5 g, 25 mmol), benzylthiocyanate (2.98 g, 20 mmol) and conc. H_2SO_4 (6 ml) in CH_2Cl_2 (50 ml). Yield 17%; mp 140-142°C. IR spectrum (vaseline oil): 1655 (C=O), 1625 (C=C), 1585 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ: 7.23-7.48 (5H, m, Ph); 6.90 (2H, d, 2,6-H); 6.22 (2H, d, 3,5-H); 4.72 (2H, s, SCH_2); 2.19 (2H, s, 4'-CH_2); 1.40-1.85 (10H, m, $(CH_2)_5$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 184.14 (C=O); 164.31 (C=C); 150.55 ($C_{(2,6)}$); 137.48, 128.98, 128.70, 128.28, 128.21, 127.08 (Ph), ($C_{(3,5)}$); 77.75 ($C_{(1)}$; 60.98 ($C_{(5)}$); 45.77 ($C_{(4)}$); 34.63, 26.00, 23.00 ($C_{cyclohexyl}$); the DMSO signal overlaps the SCH_2 signal. Mass spectrum, *m/z* (*I*, %): M^+ 337 (1); 197 (11); 188 [M - $PhCH_2SCN$]$^+$ (28); 107 (40); 91 (100); 81 (30). Found, %: C 74.47; H 7.02; N 4.38. $C_{21}H_{23}NOS$. Calculated, %: C 74.74; H 6.87; N 4.15.

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