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GENERATION OF 10-THIAANTHRACENES BY THE REACTION OF AN ARYLLITHIUM WITH THIOXANTHYLIUM SALTS

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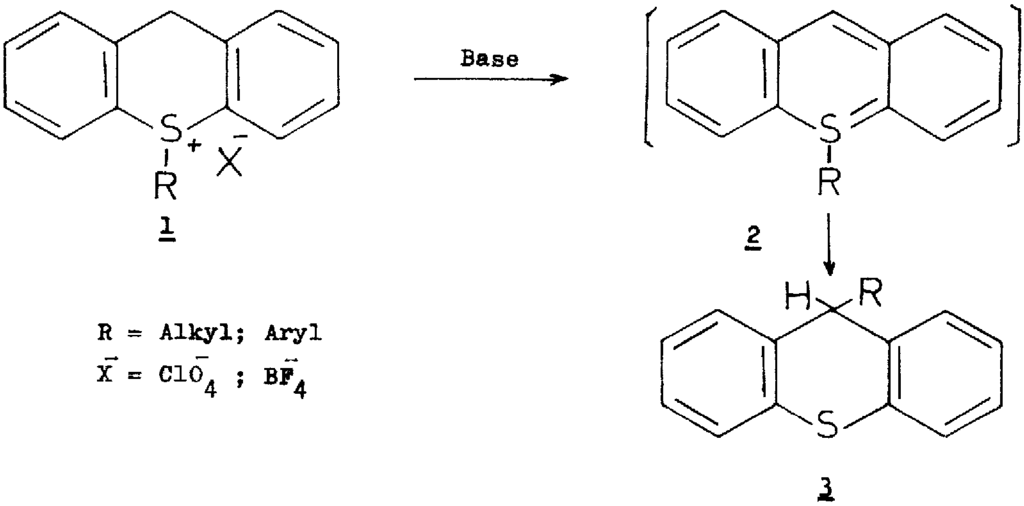
It has been reported that the reaction of phenyllithium with thioxanthylium perchlorates would yield the stable, red-brown, 10-thiaanthracenes.^{1,2} However, the recent reinvestigation by Mislow and coworkers proved that the products of these reactions are oligomeric materials of undetermined structure, rather than the stable 10-thiaanthracenes claimed earlier.^{3} These workers examined the reaction of 10-alkyl- and 10-arylthioxanthenium salts, 1, with strong bases and established that the thiaanthracenes, 2, are inherently unstable red-violet species which display an absorption band near 500 nm and which readily undergo rearrangement to the corresponding thioxanthenes 3. In the present investigation, we wish to report the generation of 10-thiaanthracenes and isolation of monomeric products from the reaction of an aryllithium with thioxanthylium salts.

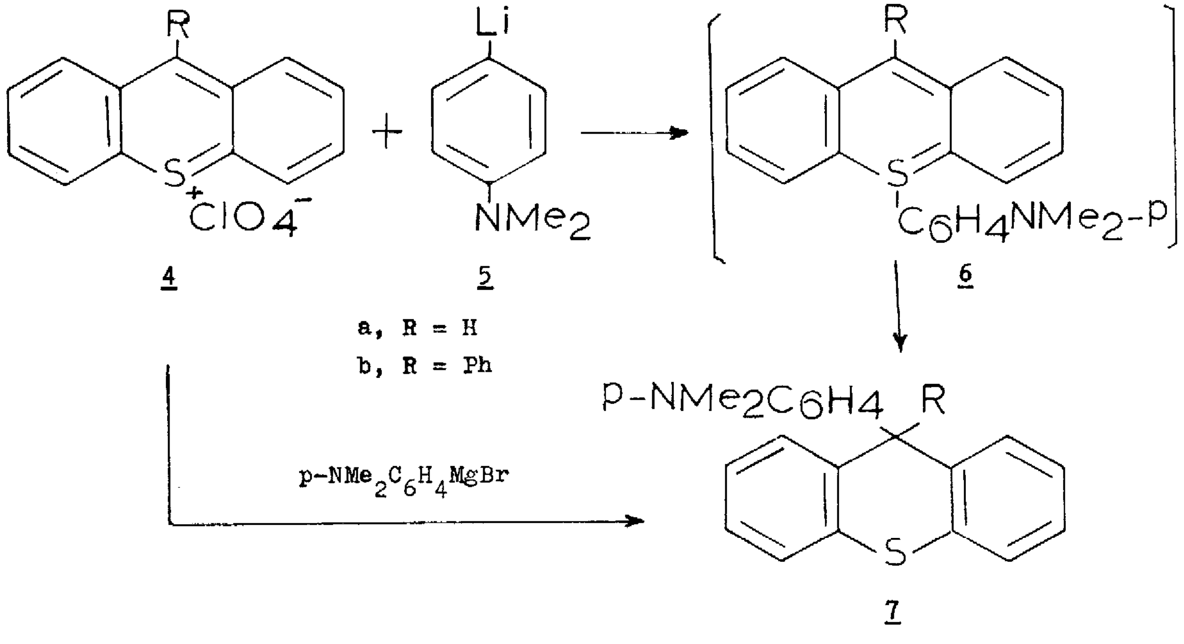


R = Alkyl; Aryl

$\bar{X}$ = $Cl\bar{O}_4$; $B\bar{F}_4$

In a previous study, we showed that the electron donating groups on substitutions attached to sulfur atom increases the stability of thiabenzenes.[4] On the basis of this observation we have now decided to determine the effect of electron-donating p-dimethylamino group on stability of thiaanthracenes[5] and inhibition of pathways leading to the red-brown oligomers.[3] Unlike the reaction of phenyllithium with thioxanthylium perchlorate 4a,[1,2] addition of p-dimethylaminophenyllithium,[6] 5, to 4a under nitrogen stream at -60° produced the red-violet, ether-soluble, intermediate 6a which exhibited an absorption band near 500 nm (ether) typical of other thiaanthracenes. After quenching the reaction mixture with ammonium chloride, the color of the solution gradually changed to dark orange, and the absorption completely disappeared. Work-up of the resulting mixture afforded the white crystalline 9-(p-dimethylaminophenyl)-10-thioxanthene 7a in 15.5% yield: mp 145-146°; ir (CCl_4) 3010, 2840, 2730, 1575, 1440, 1420, 1320, 1255, 1180, 1139, 1045, 1020, 935, 683, 644 cm^{-1}; uv (EtOH) λmax (log ϵ) 214 (4.67), and 270 nm (4.51); NMR ($CDCl_3$) δ 2.82 (s, 6H, NCH_3), 5.18 (s, 1H, H-9), and 6.44-7.52 (m, 12H, ArH); mass spectrum m/e (rel intensity) 319 (3.26, P+2), 318 (12.29, P+1), 317 (50.95, P), 316 (60.76), 315 (100), 314 (63.70), 301 (47.04), 274 (51.40), 273 (21.95), 272 (51.35), 241 (35.28), 200 (33.71), 199 (52.92), 198 (92.19), 197 (52.95), 196 (27.44), 164 (50.96), 160 (50.96), 153 (47.04), 120 (17.64), 119 (15.68), 118 (13.72), 105 (9.80), 91 (9.8), 77 (15.68).

The compound 7a could also be prepared by the reaction of 4a with p-dimethylaminophenylmagnesium bromide[7] under nitrogen in 70% yield. The mp and the spectral data of the product were the same as that of the phenyllithium reaction.



a, R = H
b, R = Ph

Treatment of 9-phenyl-10-thioxanthylium perchlorate 4b[1] with 5 in ether under nitrogen atmosphere at -60° also gave the red-violet intermediate 6b with the characteristic thiaanthracene absorption maximum in the visible rigion, λmax ca. 505 nm (ether). After fading the violet color to dark orange, the white crystalline 9-phenyl-9-(p-dimethylaminophenyl)-10-thioxanthene 7b was isolated in 5% yield: mp 210-211°; ir (CCl_4) 3010, 2840, 2740, 1576, 1430, 1423, 1325, 1148, 1122, 1045, 1030, 938, 690, 630 cm^{-1}; uv (EtOH) λmax (log ε) 222 (4.66), and 271 (4.61); NMR ($CDCl_3$) δ 2.90 (s, 6H, NCH_3), and 6.6-7.5 (m, 17H, ArH); mass spectrum m/e (rel intensity) 395 (6.66, P+2), 394 (27.33, P+1), 393 (86.65, P), 392 (98.99), 391 (18.33), 318 (23.33), 317 (71.65), 316 (100), 301 (69.99), 274 (64.32), 273 (98.32), 272 (33.99), 271 (86.65), 257 (16.66), 236 (26.66), 197 (23.66), 196 (23.33), 184 (9.99), 153 (20.99), 152 (53.99), 120 (6.66), 77 (13.33).

The reaction of 4b with p-dimethylaminophenylmagnesium bromide gave a crystalline solid in 30% yield to which we assigned structure 7b based on mp and spectral data.

In conclusion, the appearance of the characteristic absorption band near 500 nm and the formation of thioxanthenes 7a-b from reaction of p-dimethylaminophenyllithium with thioxanthylium perchlorates 4a-b clearly signifies that at least part of the thioxanthenes are formed from the initially formed thiaanthracenes 6a-b; furthermore, our resuls show that the electron-donating p-dimethylamino group inhibits pathways leading to the formation of oligomeric materials.

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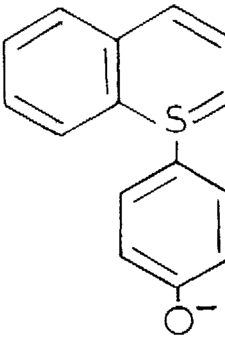

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