Preparation of 4-thia-10*b*-azaindeno[2,1,7-*lma*]fluorenes

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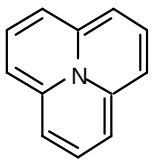
Dedicated to our good friend Douglas Lloyd to mark the occasion of his 80th birthday

Abstract

The salt **2** condenses with dimethylformamide in acetic anhydride giving the Vilsmeier salt **3**. This is cyclised to the parent 4-thia-10*b*-azaindeno[2,1,7-*lma*]fluorene **4** by triethylamine in dimethylformamide. When the salt **2** is heated in acetic anhydride in the presence of triethylamine the green thiacyclazine derivative **5** is isolated.

Introduction

Cycl[3.3.3]azine **1** and its derivatives have been studied extensively[1] in connection with their structural relationship to the phenalenyl cation, anion and radical (C^+, C^-, $C^\bullet$ respectively in place of N in **1**).[2] Numerous novel heterocyclic systems are possible, but as yet unknown, in which a =CH– or –CH=CH– moiety in **1** is replaced by a heteroatom unit. We report here syntheses of sulfur-containing analogues of **1**, in which a –CH=CH– moiety is replaced by sulfur, starting from the indeno[2,1-*d*]pyrido[2,1-*b*]thiazolium salt **2**.



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Results and Discussion

The salt **2** was prepared by condensation of 6-methyl-2-thiopyridone with 1-bromoindan-2-one followed by cyclisation of the resulting 2-(1,2-dihydro-2-oxoinden-1-ylthio)-6-methylpyridinium

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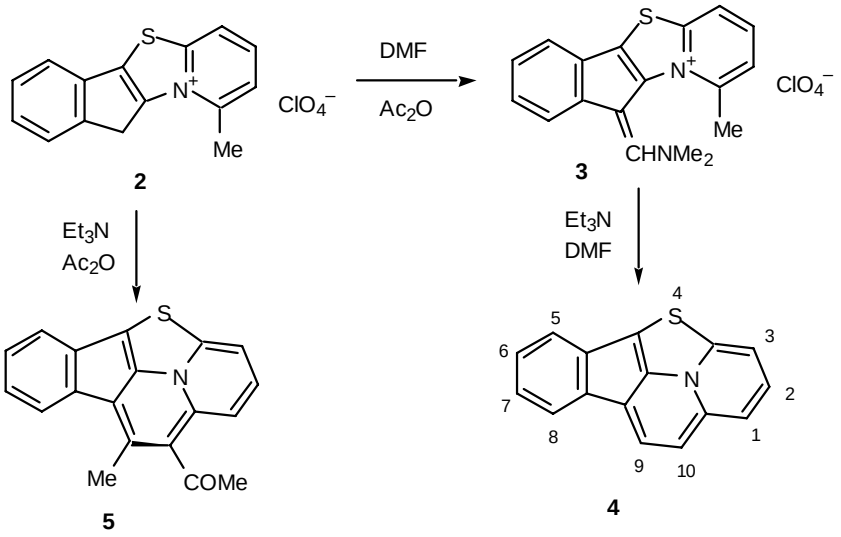
bromide with phosphorus pentachloride in nitromethane, according to the procedure described[3] for preparation of the salt **2** lacking the methyl group.



The salt **2** condensed with dimethylformamide in acetic anhydride giving, under optimum conditions, a mixture of the starting salt and the Vilsmeier salt **3** in a molar ratio of 6:4. The Vilsmeier salt **3** was cyclised to the parent 4-thia-10*b*-azaindeno[2,1,7-*lma*]fluorene **4** by triethylamine in dimethylformamide. When the salt **2** was heated in acetic anhydride in the presence of triethylamine the initially formed red solution rapidly turned green and the green thiacyclazine derivative **5** was isolated.

Experimental Section

10-Dimethylaminomethylene-1-methyl-10*H*-indeno[2,1-*d*]pyrido[2,1-*b*]thiazolium perchlorate (3). A mixture of the salt **2** (3.38 g, 10 mmol), dimethylformamide (11.55 mL, 0.15 mol) and acetic anhydride (100 mL) was boiled under reflux for 20 min. The resulting dark orange-brown solution was cooled and treated carefully with diethyl ether and the resulting brown precipitate (3.3 g) was filtered off, washed with ether and dried. This was shown by integration of its ^{1}H NMR spectrum to be a mixture of the starting material and the required Vilsmeier salt in a molar ratio of 6:4. The mixture was dissolved in dimethylformamide (50 mL), triethylamine (15 mL) was added, and the mixture was allowed to stand in an ice bath for 1 min. Water (250 mL) and methylene chloride (150 mL) were added and the mixture was shaken thoroughly and then filtered. The brown residue was washed sparingly with methylene chloride, followed by ethanol and finally ether, and dried. Recrystallisation from methanol/acetonitrile (9:1, 100 mL) with charcoal screening gave 10-dimethylaminomethylene-1-methyl-10*H*-indeno[2,1-*d*]pyrido[2,1-*b*]thiazolium perchlorate **3** (367 mg, 9%). A sample recrystallised from

methanol as orange needles. mp 198 ˚C (decomposed). Found: C, 55.2; H, 4.1; N, 7.4. $C_{18}H_{17}ClN_2O_4S$ requires C, 55.0; H, 4.4; N, 7.1%).

Cyclisation of the Vilsmeier salt 3. Triethylamine (16 mL) was added to a solution of the crude mixture from the previous reaction (10 mmol scale) in dimethylformamide (50 mL) and the mixture was boiled for 2 min. The resulting dark green solution was diluted with water and extracted with methylene chloride. The extracts were washed 6 times with water, dried (Na_2SO_4) and evaporated. The resulting solid residue was chromatographed on a column of alumina (3 × 33 cm) with methylene chloride as eluant. Evaporation of the dark green eluate gave a crystalline residue, which was dissolved in boiling benzene (50 cm^3). Boiling cyclohexane (50 mL) was then added. After filtration and cooling the product crystallised as dark green needle clusters (525 mg). The mother liquors were rechromatographed on a short column of alumina, the green eluates were evaporated and the residue recrystallised from cyclohexane (by displacement of methylene chloride) to give a further 200 mg of product. The total yield of 4-thia-10*b*-azaindeno[2,1,7-*lma*]fluorene **4** was 725 mg (29%). A sample recrystallised from cyclohexane as bronze plates. mp 150–152 ˚C. Found: C, 77.3; H, 3.9; S, 12.9. $C_{16}H_9NS$ requires C, 77.7; H, 3.7; S, 13.0%), Mass. 247. The mass spectrum showed the presence of an impurity containing chlorine (molecular weight 281).

Reaction of the salt 2 with acetic anhydride and triethylamine. Triethylamine (5.56 mL, 40 mmol) was added dropwise over 2 min to a boiling solution of the salt **2** (676 mg, 2 mmol) in acetic anhydride (40 mL). The resulting dark red solution was boiled for a further 2 min, its colour changing to green. The green solution was cooled, poured into water and allowed to stand overnight before being basified with sodium carbonate. The resulting suspension was extracted with methylene chloride. The dried extracts were evaporated and the residue was chromatographed on a column of alumina (3X20 cm) with methylene chloride/acetonitrile (5:1) as eluant. Evaporation of the green eluate yielded a dark green crystalline residue which, after recrystallisation from acetonitrile, gave *10-acetyl-9-methyl-4-thia-10b-azaindeno[2,1,7-lma]fluorene* **5** (176 mg, 29%) as dark green needles, mp 153–155 ˚C (Found: C, 74.9; H, 4.4; O, 4.4. $C_{19}H_{13}NOS$ requires C, 75.2; H, 4.3; O, 5.3%); λ_{max} (Nujol) 1633 cm^{-1} (C=O).

References

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