Substitution of 6a-Thiathiophthens and Related Compounds with Arenediazonium Fluoroborates: Rearrangement into Novel Heterocyclic Systems

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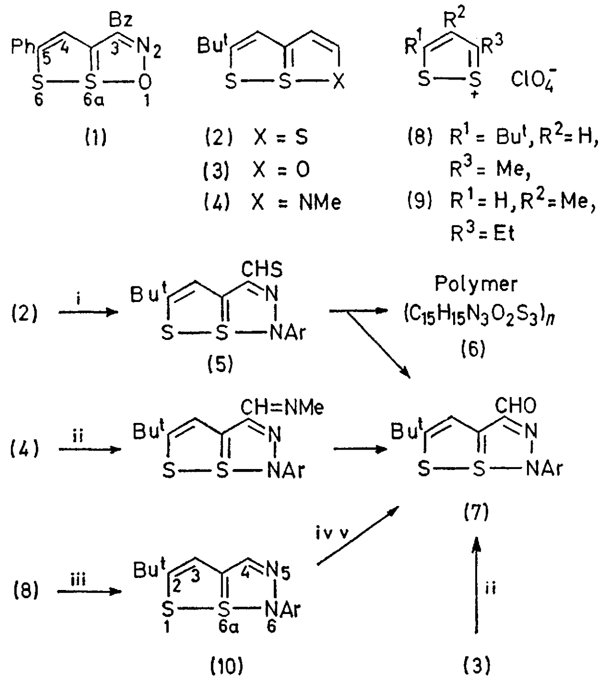
Summary 6a-Thiathiophthens and related compounds couple with arenediazonium fluoroborates with accompanying rearrangement into derivatives of novel hypervalent heterocyclic systems.

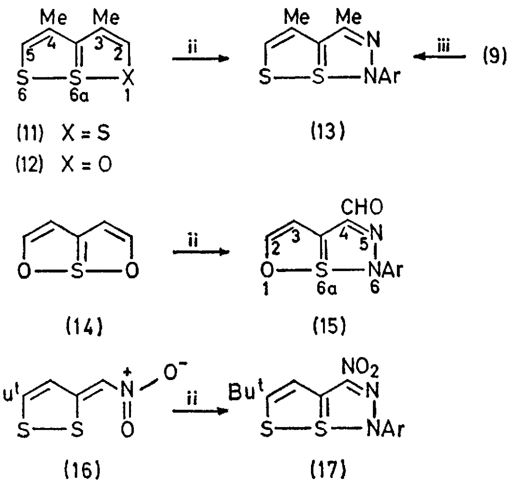
Electrophilic bromination[1] and Vilsmeier formylation[2] of 6a-thiathiophthens proceed normally to give 3-bromo- and 3-formyl-6a-thiathiophthens, respectively. However, nitrosation of 2,5-diphenyl-6a-thiathiophthen gives the oxadithia-azapentalene (**1**),[1] rearrangement and partial desulphurisation accompanying the introduction of the nitroso-group. We report here an analogous rearrangement of 6a-thiathiophthens and related compounds into derivatives of new heterocyclic systems during substitution reactions with arenediazonium fluoroborates.



Ar = p-$NO_2 \cdot C_6H_4$

Reagents: i, $ArN_2{}^+BF_4{}^-$–MeCN–H_2O; ii, $ArN_2{}^+BF_4{}^-$–MeCN; iii, $ArN_2{}^+BF_4{}^-$–EtOH; iv, DMF–$POCl_3$, 60—80°; v, OH^-.

Treatment of 2-t-butyl-6a-thiathiophthen (**2**)[2b] with p-nitrobenzenediazonium fluoroborate in aqueous acetonitrile at room temperature gave a sparingly soluble reddish brown powder (**6**) (16%) of composition $(C_{15}H_{15}N_3O_2S_3)_n$ together with the aldehyde (**7**) (22%). These products arise from the transient intermediate thioaldehyde (**5**), part of which polymerises in the well known manner of thioaldehydes, part being hydrolysed to give the aldehyde (**7**). The aldehyde (**7**), orange-red needles, m.p. 187—187·5°, ν(C=O) (KBr) 1680 cm^{-1}, δ (100 MHz; $CDCl_3$; Me_4Si internal reference) 1·53 (9H, Bu^t), 7·95 (2H, m, 2 × *ortho*-H), 8·29 (2H, m, 2 × *meta*-H), 9·24 (1H, 3-H), and 10·24 (1H, CHO), was also formed in high yield in the reactions of p-nitrobenzenediazonium fluoroborate with the oxadithiapentalene (**3**)[3] (98%) and the dithia-azapentalene (**4**)[4] (83%). In an alternative, 'non-rearrangement' synthesis, coupling of the dithiolium perchlorate (**8**)[2a] with p-nitrobenzene diazonium fluoroborate in ethanol gave the dithiadiazapentalene (**10**) (35%), deep red spars, m.p. 267—268°, δ 1·47 (9H, Bu^t), 7·79 (1H, 3-H), 7·90 (2H, m, 2 × *ortho*-H), 8·27 (2H, m, 2 × *meta*-H) and 8·41 (1H, 4-H), Vilsmeier formylation of which afforded the aldehyde (**7**) (18%) Reaction (**8**) → (**10**) exemplifies a general method of preparation of 1,6a-dithia-5,6-diazapentalenes, a novel class of hypervalent[5] heterocyclic compounds of the 6a-thiathiophthen type.



Reagents ii *and* iii *as before.*

Coupling of p-nitrobenzenediazonium fluoroborate with the thiathiophthen (**11**),[3] in which the reactive 3(4)-position is blocked, proceeded with elimination of the potential thioformyl group and gave the dithiadiazapentalene (**13**) (14%). The oxadithiapentalene (**12**)[3] also gave compound (**13**) (83%) by deformylation. The dithiadiazapentalene (**13**), red needles, m.p. 208·5—209°, was obtained directly (95%) by the reaction of the dithiolium perchlorate (**9**)[4] with p-nitrobenzenediazonium fluoroborate in ethanol. The ready tendency of 6a-thiathiophthens, 1-oxa-6,6a-dithiapentalenes, and 1,6a-dithia-6-azapentalenes to rearrange into 1,6a-dithia-5,6-diazapentalenes, involving where necessary (thio)formyl group elimination, indicates that a strong S(6a)–N(6) bonding interaction exists in the 1,6a-dithia-5,6-diazapentalene system.

Rearrangement also accompanied the coupling of p-nitrobenzenediazonium fluoroborate with 1,6-dioxa-6a-thiapentalene (**14**).[6] The product (**15**) (24% conversion), yellow needles, m.p. 254—257°, ν(C=O) (KBr) 1682 cm^{-1}, δ 7·96 (2H, m, 2 × *ortho*-H), 8·09 (1H, d†, 3-H), 8·41 (2H, m, 2 × *meta*-H), 9·44 (1H, d†, 2-H), and 10·24 (1H, CHO), is the first reported member of the 1-oxa-6a-thia-5,6-diazapentalene system. The nitro-compound (**17**), red needles, m.p. 230—231°, was also obtained (91%) by treatment of the dithiole (**16**)[7] with *p*-nitrobenzenediazonium fluoroborate.

Satisfactory analytical data were obtained for all new compounds.

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† Spectrum obtained using 'Computer of Averaged Transients'; *J* value not determined.

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