Synthesis of Condensed Bicyclic Thiophene Derivatives from Diyne Systems

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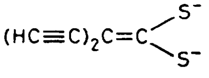
Metallation of the acetylenes $\mathrm{MeC{\equiv}CR}$ (R = $\mathrm{C{\equiv}C{-}SiMe_3}$, $\mathrm{C{\equiv}CMe}$, $\mathrm{C{\equiv}C{-}SMe}$, $\mathrm{C{\equiv}C{-}Nalkyl_2}$, $\mathrm{S{-}C{\equiv}CSiMe_3}$, $\mathrm{S{-}C{\equiv}C{-}Me}$) with $\mathrm{BuLi{\cdot}Bu^tOK}$, followed by the successive addition of carbon disulphide, t-butyl alcohol, and hexamethylphosphoric triamide gives thieno[2,3,-*b*]thiophene, thieno-1,4-dithi-ine, and some of their derivatives in reasonable yields.

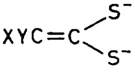
The thiophene ring is opened by strong bases in a polar medium.[1–3] Extension of the reaction to thieno[2,3-*b*]thiophene would be expected to give system A. Conversely, compounds of type A might be synthetic precursors to thienothiophenes; it is already known that 1,3-diynes and H_2S give thiophene.[4] The active methylene compounds $\mathrm{XYCH_2}$ react with CS_2 in the presence of bases to give the enedithiolates B.[5,6] By analogy, diynes of type (**1**) (Scheme 1) could give the system present in A on successive deprotonation, reaction with CS_2, and a second deprotonation. Accordingly, the reactions outlined in Scheme 1 were tried as a possible synthesis of thieno[2,3-*b*]thiophenes.

BuLi 0·10) mol) in 70 ml of hexane was added to 0.12 mol of $\mathrm{Bu^tOK}$ in 100 ml tetrahydrofuran (THF) at −100 °C. To this solution (at −80 °C) was added 0.05 mol of the diyne (**1**), followed (at −100 °C) by CS_2 (0.07 mol), to give a dark brown reaction mixture. To this was added, at −30 °C, 0.10 mol of t-butyl alcohol and 50 ml of hexamethylphosphoric triamide (HMPT). After warming the mixture for 30 min at 30 °C,



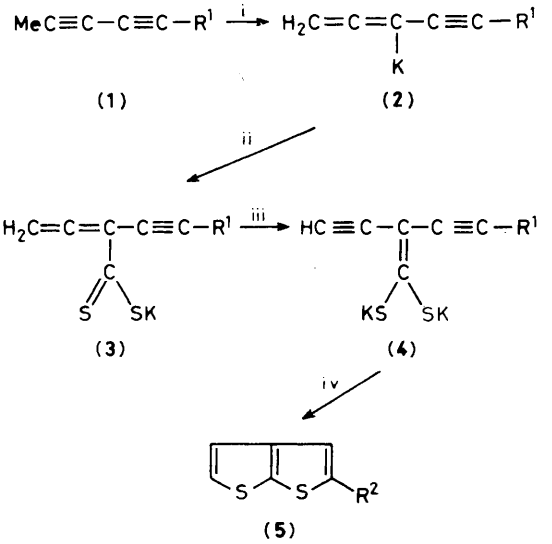
$\mathrm{(HC{\equiv}C)_2C{=}C(S^-)_2}$

A



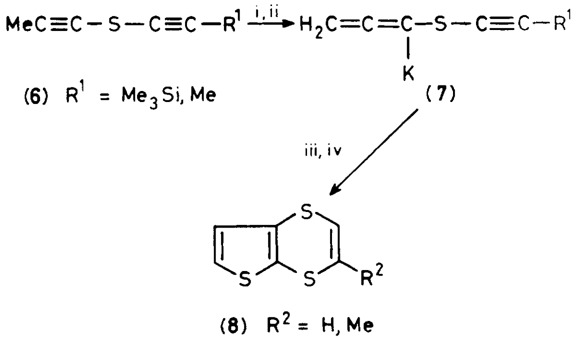
$\mathrm{XYC{=}C(S^-)_2}$

B



R^1 = $\mathrm{Me_3Si}$, alkyl, $\mathrm{N(alkyl)_2}$, S(alkyl)
R^2 = H, alkyl, $\mathrm{N(alkyl)_2}$, S(alkyl)

Scheme 1. i, $\mathrm{BuLi{\cdot}Bu^tOK}$, THF–hexane; ii, CS_2, −100 °C; iii, (**2**); iv, $\mathrm{Bu^tOH}$, HMPT.



Scheme 2. i, Bu^{t}OK–THF, −90 °C; ii, BuLi–hexane, −90 °C; iii, CS_2, −100 °C; iv, Bu^{t}OH, HMPT, −30 to 30 °C.

water was added and the pure (^{1}H n.m.r. spectra, g.l.c.) products were isolated by extraction (diethyl ether–pentane 1 : 1) and subsequent distillation at <0.5 mmHg. If R^1 = $SiMe_3$, the parent compound (**5**; R=H) was isolated. The purity and identity of (**5**) were determined by g.l.c. and comparison with reported data (b.p., ^{1}H n.m.r.).[7] We assume that the $SiMe_3$ group has been split off from C≡C by the t-butoxide group at some intermediate stage.

In analogy with Scheme 1 the unknown thieno-1,4-dithi-ine (**8**; R^2=H) and the methyl derivative (**8**; R^2=Me) could be obtained in *ca.* 40% yield from the diynes (**6**) (Scheme 2, R^1 = $SiMe_3$, Me, respectively).

We suggest that the modest yield (*ca.* 40%) of (**5**) from (**1**) is the result of the removal of 50% of (**2**), the latter acting as a proton abstractor in the conversion of (**3**) into (**4**) (Scheme 1). The rather low yield of (**8**) from (**6**) (Scheme 2) can be explained in a similar way.

Thienothiophene, used by Wijnberg *et al.*[8] as the starting compound in the synthesis of heterohelicenes, has been prepared by Gronowitz and Persson,[7] starting from 3-bromothiophene.

The starting compounds for our synthesis of (**5**) and (**8**) are easily accessible.[9–11]

Received, 24th May 1983; Com. 669

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