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SHORT PAPER

Heterocycles derived from dichlorothiophene

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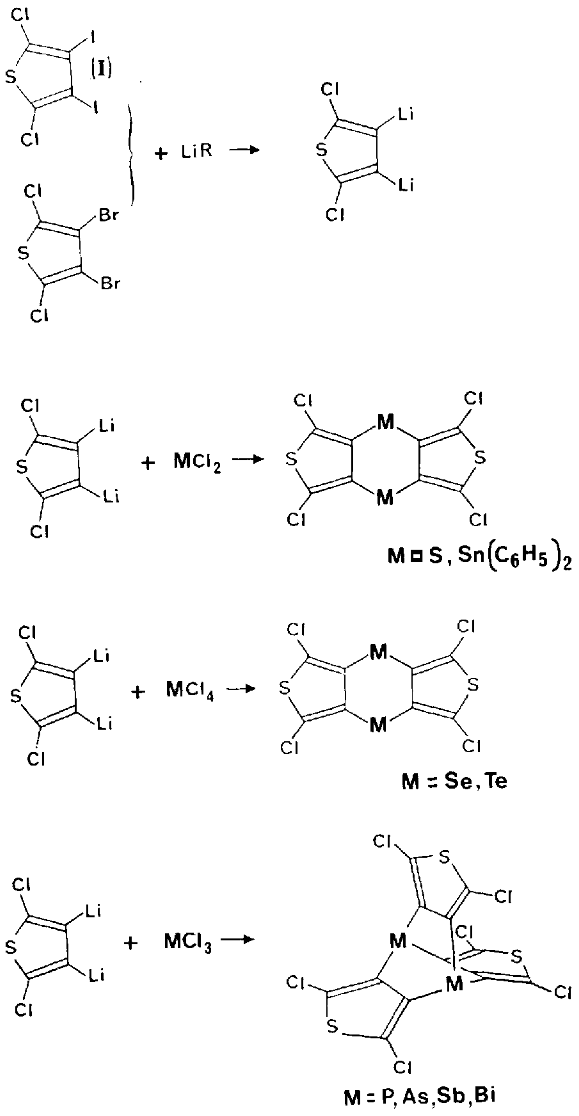
A number of new, air-stable heterocycles have been synthesized which contain 2,5-dichlorothiophene groups as the structure-forming units with sulphur, selenium, tellurium, phosphorus, arsenic, antimony, bismuth, tin and mercury acting as the hetero-atoms.

Keywords: Heterocycle, 3,4-dilithiodichlorothiophene, synthesis



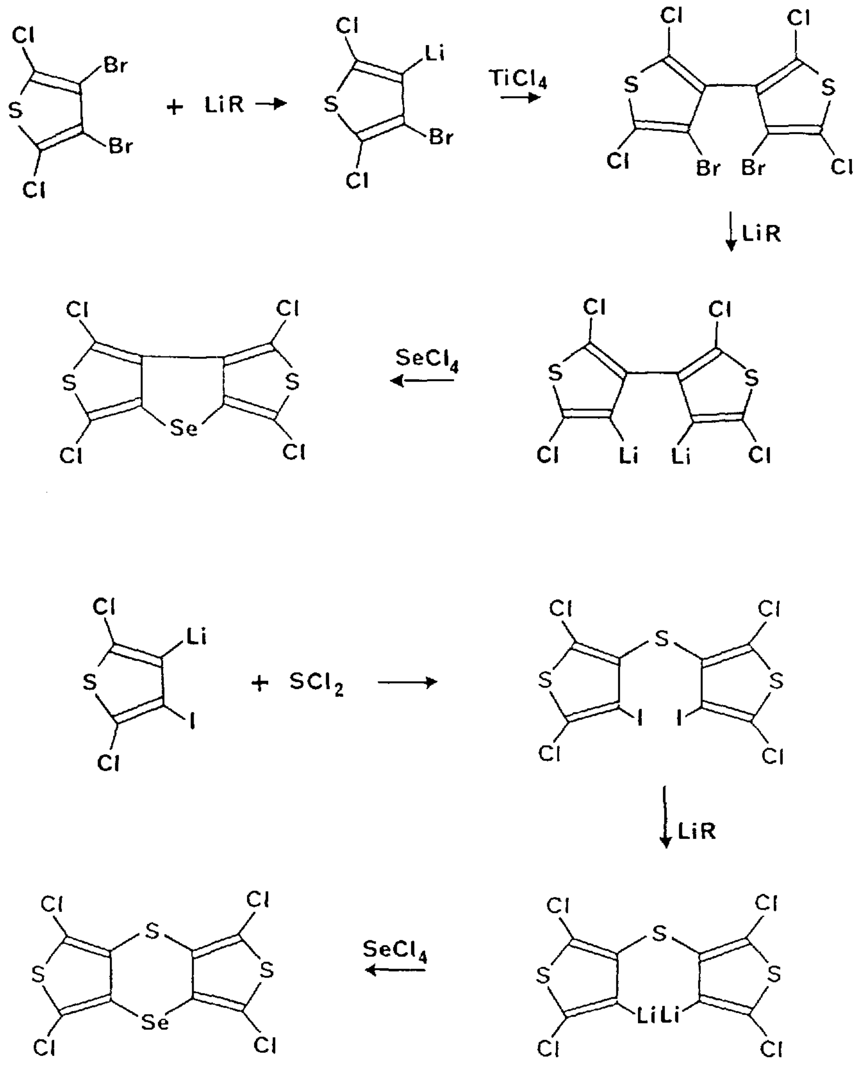
Scheme 1

INTRODUCTION AND DISCUSSION

Aromatic systems containing two lithium atoms in positions *ortho* to each other are rather difficult to prepare[1] and hence heterocycles derived from arenes have often to be prepared by either direct synthesis or transmetallations using organomercurials.[2] By blocking the reactive 2,5-positions of thiophene with chlorine substituents we have been able to carry out a high-yield synthesis of 3,4-dilithio-3,5-dichlorothiophene and use it to make a variety of heterocycles as shown in Scheme 1.

Aryne formation often occurs at very low temperatures with 1-lithio-2-haloarene systems whereas 2-lithio-4-halo-2,5-dichlorothiophenes are sufficiently stable to allow the stepwise build-up of other heterocyclic derivatives (Scheme 2).

Attempts to use 3,4-diiodo-2,5-dichlorothiophene (**I**) in direct synthesis failed due to thermal instability of the thiophene ring system at the temperatures (>220°C) required for reaction. Typically, sulphur and **I** gave a black, carbon-like residue, iodine and sulphur chlorides on being heated overnight in a sealed tube at 220°C. There appears to be no reason why similar heterocycles to those described above contain-



Scheme 2

ing furan, selenophene or tellurophene rings should not be made by the same procedures; positional isomers would occur, of course, if 2,3-dilithiothiophene derivatives were used in any of the above syntheses.

EXPERIMENTAL

All the reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen; before the addition of 1.6 mol dm^{-3} butyllithium in hexane the reaction vessels were cooled to the temperature of a toluene slush-bath (−95 °C). The 2,5-dichloro-3,4-diiodothiophene and 2,5-dichloro-3,4-dibromothiophene startiong materials were prepared in high yield by the method described by McOmie.[3] Analytical and infrared details for the products are given in Tables 1 and 2.

Preparation of $(C_4SCl_2)S_2$

To a cold, stirred solution of 15.5 cm^3 butyllithium in 150 cm^3 of dry ether was added an ethereal solution of 2,5-dichloro-3,4-di-iodothiophene (5 g, 12 mmol,

Table 1 Analytical data for the various heterocycles

Formula	M.p. (°C)	Found (Calculated) (%)		
		C	S	H
$(C_4Cl_2S)_2\ S_2$	283.5–284.5	26.2 (26.2)	34.95 (35.1)	0.0 (0.0)
$(C_4Cl_2S)_2SeS$	272–273	23.4 (23.2)	23.75 (23.3)	—
$(C_4Cl_2S)_2Se_2$	375–276	21.3 (20.9)	14.4 (13.9)	—
$(C_4Cl_2S)_2Te_2$	246–247	17.3 (17.2)	11.8 (11.5)	—
$(C_4Cl_2S)_2TeS$	239–240	21.05 (20.8)	20.6 (20.8)	—
$(C_4Cl_2S)_3P_2$	>360	28.5 (28.0)	18.6 (18.7)	—
$(C_4Cl_2S)_3As_2$	>360	23.9; 23.1 (23.9)	15.3 (15.95)	0.1 (0.0)
$(C_4Cl_2S)_3Sb_2$	356–358(d)	20.8 (20.7)	13.7 (13.8)	—
$(C_4Cl_2S)_3Bi_2$	322–323(d)	16.95 (16.6)	10.9 (11.0)	—
$3,3'-Br_2(C_4Cl_2S)_2$	141–142	21.0; 21.1 (20.8)	14.1 (13.9)	0.1, 0.1 (0.0)
$3,3'-I_2(C_4Cl_2S)_2$	125–126	17.7 (17.3)	11.8 (11.5)	0.0 (0.0)
$(C_4Cl_2S)_2S$	210–211	28.7 (28.7)	28.6 (28.7)	—
$(C_4Cl_2S)_2Se$	206–207	25.3 (25.2)	16.4 (16.8)	—
$(C_4Cl_2SHg)_x$	>360	13.8, 13.8 (13.65)	9.1 (9.1)	0.0 (0.0)
$(C_4Cl_2S)_2[Sn(C_6H_5)_2]_2$	293–294	45.1 (45.35)	7.4 (7.6)	2.4 (2.4)

in 30 cm^3 ether); after 20 min sulphur dichloride (1.3 g, 12.6 mmol) was dripped in and stirring continued for a further 30 min. The mixture was then allowed to warm up slowly to room temperature and was stirred for 60 min. The filtered precipitate was washed thoroughly with ether, taken up in toluene (100 cm^3) and boiled with charcoal before filtration and crystallization; yield 1.55 g of colourless, needle-shaped crystals (35%), m.p. 283.5–284.5°C. The analytical sample was washed thoroughly with hexane and dried overnight at 90°C in an oven. A similar procedure was followed for the other heterocycles; the analytical data are given in Table 1.

Table 2 Representative infrared spectra (Nujol mulls, cm^{-1})

$(C_4Cl_2S)_2S_2$	315m; 405w; 425w; 489m; 783m; 891m; 1067s; 1241w; 1278s; 1420w; 1505sh; 1512s.
$(C_4Cl_2S)_2SSe$	264wb; 312w; 487w; 758vw; 764vw; 783m; 871w; 890m; 1051m; 1066s; 1276m; 1410w; 1419vw; 1494w; 1501sh; 1511s.
$(C_4Cl_2SHg)_x$	261m; 294m; 361w; 815vw; 1009vs; 1384s; 1397m.
$(C_4Cl_2S)_3P_2$	332m; 362s; 423m; 443vs; 527s; 762w; 856wb; 1049sh; 1060vs; 1223sh; 1231m; 1428vs; 1509s.
$(C_4Cl_2S)_3Sb_2$	264s; 281wsh; 369m; 735wb; 818vw; 966vw; 1020vs; 1069vwb; 1192w; 1210w; 1392vs.
$3,3'-I_2(C_4Cl_2S)_2$	365w; 391w; 499w; 506w; 583m; 591m; 607w; 657m; 702w; 761m; 801m; 826m; 937m; 1036s; 1080w; 1237w; 1314w; 1404m; 1544mb.
$(C_4Cl_2S)_2S$	382w; 479m; 657w; 765m; 840w; 933s; 1034sh; 1046m; 1111s; 1263m; 1502w; 1577mb.

Preparation of $(C_4SCl_2)SSe$

Butyllithium (10.1 cm^3) was added to a cold ethereal solution (−70°C) of 2,5-dichloro-3,4-dibromothiophene (5 g, 16 mmol, in 200 cm^3 of dry ether) and stirring continued for 45 min. Sulphur dichloride (0.63 g, 5.8 mmol) was added to the white slurry and the mixture stirred for 30 min at −70°C before the addition of a further 10.1 cm^3 of butyllithium; the temperature was then reduced by replacing the cold bath with a toluene-slush bath (−95°C) and 1.8 g, 8.1 mmol of selenium tetrachloride ($SeCl_4$) added to the reaction flask. Stirring was carried out for 30 min before the temperature was allowed slowly to rise to ambient and stirring continued for 1 h. After removal of solvent the solid product was dissolved in toluene (100 cm^3) boiled with charcoal and the filtered solution set aside to crystallize. Colourless, needle-shaped crystals (1.5 g; 25%) were obtained; the corresponding tellurium derivative was

Preparation of 3,3′-$I_2(C_4Cl_2S)_2$

To a cold, stirred, ether solution of 2,5-dichloro-3,4-diiodothiophene (5 g, 12 mmol, in 150 cm^3 of ether) was added 8 cm^3 of butyllithium in a dropwise manner over a period of 5 min. After 30 min, titanium tetrachloride ($TiCl_4$) (4.7 g, 13.6 mmol,) was added to the white slurry, when a purple–red slurry was obtained; this was stirred for 60 min. The reaction mixture was allowed to warm up slowly to room temperature and stirring continued for 2 h; the solid originally obtained gradually dissolved as the mixture darkened until it was black–red in colour. At this point distilled water (150 cm^3) was added slowly with vigorous stirring to give a clear, yellow organic layer above a voilet aqueous phase. The organic layer and two washings (50 cm^3 of ether) were dried over magnesium sulphate, filtered and refluxed with charcoal. Removal of solvent gave a yellow–brown solid which was recrystallized from boiling methanol to give 2.0 g (30%) of pale yellow, granular crystals, m.p. 125–126°C. The corresponding bromide was obtained by a similar procedure starting from 2,5-dich-loro-3,4-dibromothiophene. Both the di-iodide and the dibromide could be lithiated readily at low temperatures with butyllithium: treatment of the dilithiated compound with either sulphur dichloride (SCl_2) or selenium tetrachloride ($SeCl_4$) gives the heterocycles $(C_4Cl_2S)_2S$ and $(C_4Cl_4S)_2Se$ shown in Scheme 1.

The molecular weights of all the synthesized products were checked using mass spectrometry, except for $Bi_2(C_4Cl_2S)_3$ where the parent ion could not be detected. In all other cases, the isotopomeric pattern of the molecular ions was in agreement with that expected for species containing either four or six chlorine atoms. The mercurials were too involatile to record conventional mass spectra; the tetramer and trimer, $(C_4Cl_2SHg)_x$: $x = 3, 4$, were detected in a Laser Induced Mass Spectrum (LIMA) kindly recorded by Miss A. Waddilove of our Physics Department. This laser-induced mass spectrum recorded the negative ions and showed peaks for $(C_4Cl_2SHg)_4Cl^-$ and $(C_4Cl_2SHg)_3Cl^-$ plus other fragments. It is usual in this kind of spectrum to observe molecules and their fragments having appended Cl^- ions; we assume, therefore, without proof, that the $(C_4Cl_2SHg)_3Cl^-$ ion represents the existence of a true trimer molecule and is not due to a fragmentation ion of the tetramer.

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