Reaction of 1,3,4,6-Tetrakis(alkylthio)-2λ⁴δ²-thieno[3,4-*c*]thiophenes with Trifluoroacetic Acid and with Vilsmeier Reagent, and Synthesis of New 2λ⁴δ²-Thieno[3,4-*c*]thiophene Derivatives

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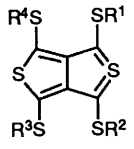
2λ⁴δ²-Thieno[3,4-*c*]thiophenes **1a**, **1c** and **1d** possessing t-butylthio substituents reacted with trifluoroacetic acid to give the thione derivatives **3a**, **3'c** and **3'd** through the intermediary formation of a proton adduct, 1*H*-thieno[3,4-*c*]thiophenium trifluoroacetates, followed by cleavage of the Bu^t–S bond. Treatment of the thione **3a** with sodium hydride and then an alkyl iodide gave 2λ⁴δ²-thieno[3,4-*c*]thiophenes **1c** and **5**–**7**. The reaction of 2λ⁴δ²-thieno[3,4-*c*]thiophenes **1a**–**e** with trifluoroacetic acid and water resulted in the formation of thieno[3,4-*c*]thiophen-1(3*H*)-ones **9**–**12**. Compounds **1a** and **1b** reacted with Vilsmeier reagent to give mono- and di-formyl-substituted 2λ⁴δ²-thieno[3,4-*c*]thiophenes **15a**, **15b** and **16b**. Furthermore, formyl-substituted derivatives **15a** and **16b** reacted with malononitrile, ethyl cyanoacetate, and *N*,*N*-dimethylhydrazine to give the condensed compounds **17**–**21**.

The 2λ⁴δ²-thieno[3,4-*c*]thiophene system involving 10π-electrons has attracted much attention because of its non-classical structure.[1] 1,3,4,6-Tetraphenyl-2λ⁴δ²-thieno[3,4-*c*]thiophene has been synthesized by acetic anhydride dehydration of 1,3,4,6-tetraphenyl-1*H*,3*H*-thieno[3,4-*c*]thiophene 2-oxide prepared by the reaction of 1,1,2,2-tetrabenzoylethane and phosphorus pentasulphide.[2] The formation of 2λ⁴δ²-thieno[3,4-*c*]thiophene[3] and 1,3-dimethyl- or 1,3-bis(methoxycarbonyl)-2λ⁴δ²-thieno[3,4-*c*]thiophene[4,5] was established by trapping with *N*-phenylmaleimide in the dehydration of the 1*H*,3*H*-thieno[3,4-*c*]thiophene 2-oxide and 4,6-dimethyl or 4,6-bis(methoxycarbonyl)-1*H*,3*H*-thieno[3,4-*c*]thiophene 2-oxide respectively. Recently we have prepared 1,3,4,6-tetrakis(alkylthio)-2λ⁴δ²-thieno[3,4-*c*]thiophenes by a one-step synthetic method using 2,3-bis(alkylthio)cyclopropenethiones as the starting materials.[6] The photoelectron spectral[7] and cyclic voltammetric[8] studies of these compounds have revealed that their electron-donating properties are similar to those of tetrathiafulvalene. Moreover, the Hückel MO calculation of 2λ⁴δ²-thieno[3,4-*c*]thiophene itself has shown that the HOMO has large coefficients at the 1-, 3-, 4- and 6-positions and that the energy level of the HOMO is higher than that of naphthalene.[9] These facts led us to explore the nucleophilic behaviour of 2λ⁴δ²-thieno[3,4-*c*]thiophenes **1a**–**e** toward electrophiles such as trifluoroactic acid (TFA) and Vilsmeier reagent. In this paper, we report that a proton from TFA undergoes addition to the 2λ⁴δ²-thieno[3,4-*c*]thiophene ring system to give the corresponding thiones by cleavage of the Bu^t–S bond, and Vilsmeier reagent adds to give mono- or di-formyl-substituted 2λ⁴δ²-thieno[3,4-*c*]thiophenes by removal of an alkylthio group. In addition, we describe a novel method for converting the t-butylthio group of 1,3,4,6-tetrakis(t-butylthio)-2λ⁴δ²-thieno-[3,4-*c*]thiophene **1a** into other alkylthio groups. A part of this study has been reported in our preliminary papers.[10]



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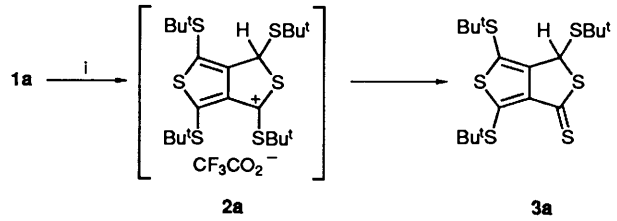
a; $R^1 = R^2 = R^3 = R^4 = Bu^t$
b; $R^1 = R^2 = R^3 = R^4 = Pr^i$
c; $R^1 = R^2 = R^3 = Bu^t$, $R^4 = Et$
d; $R^1 = R^3 = Bu^t$, $R^2 = R^4 = Et$
e; $R^1 = R^4 = Bu^t$, $R^2 = R^3 = Et$

Results and Discussion

Reaction of 2λ⁴δ²-Thieno[3,4-c]thiophenes **1a**–**e** *with TFA.*—Compound **1a** treated with TFA in benzene at 35 °C to give 3,4,6-tris(t-butylthio)thieno[3,4-*c*]thiophene-1(3*H*)-thione **3a** as a reddish purple solid in 90% yield. The structure of compound **3a** was determined by its conversion into the known compound **4**[11] by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone. The reaction was followed by ^{1}H NMR spectroscopy. After TFA had been added to a solution of compound **1a** in $CDCl_3$, the ^{1}H NMR spectrum of the solution was measured immediately. The spectrum of substrate **1a** changed spontaneously to that of 1,3,4,6-tetrakis(t-butylthio)-1*H*-thieno[3,4-*c*]thiophenium trifluoroacetate **2a**, which exhibited four singlets, at δ 1.46, 1.54, 1.74 and 1.84, for non-equivalent t-butylthio groups, and a singlet, at δ 6.02, for a proton attached to the thieno[3,4-*c*]thiophene ring system. The spectrum of the salt **2a** changed gradually to that of compound **3a** with the passage of time. This result indicates that the reaction proceeds by electrophilic addition of a proton to the 1-position of the 2λ⁴δ²-thieno[3,4-*c*]thiophene ring, followed by cleavage of the Bu^t–S bond, as shown in Scheme 1.

The ^{1}H NMR spectrum of a solution of 1,3,4,6-tetrakis(isopropylthio)-2λ⁴δ²-thieno[3,4-*c*]thiophene **1b** and TFA in $CDCl_3$ exhibited four septets, at δ 3.29, 3.40, 3.77 and 3.96, for the



2a **3a**

Scheme 1 *Reagent:* i, TFA

Table 1 Reaction of $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophenes **1a**, **1c** and **1d** with TFA[a]

Compound	Time (*t*/h)	Product (yield, %)[b]
1a	4	**3a** (90)
1c	6.5	**3'c** (93)
1d	6	**3'd** (83)

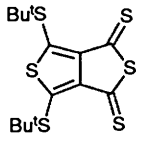
[a] Reactions were carried out in benzene at 35 °C. Molar ratio **1**: TFA 1:3. [b] Isolated yield.

Table 2 Alkylation of compounds **3a** and **3'c** with alkyl iodides[a]

Compound	RI	Product	Yield (%)[b]	λ_{max}/nm[c]
3a	EtI	**1c**	94	508
	MeI	**5**	98	515
	Pr^iI	**6**	97	508
	CH_2=$CHCH_2I$	**7**	80	508
3'c	EtI	**1e**	90	508

[a] Reactions were carried out in DMF at room temp. Molar proportions **3**:NaH:RI 1:2:2. [b] Isolated yields based on compound reagent **3a** or **3'c**. [c] Absorption maximum in visible region in hexane solution.

methine protons of non-equivalent isopropylthio groups, seven doublets, at δ 1.38, 1.39, 1.44, 1.63, 1.64, 1.68 and 1.72, for the methyl protons of non-equivalent isopropylthio groups, and a singlet, at δ 6.14, for a proton attached to the thieno[3,4-*c*]thiophene ring system, thus indicating the formation of 1,3,4,6-tetrakis(isopropylthio)-1*H*-thieno[3,4-*c*]thiophenium trifluoroacetate **2b**. This spectrum did not change with time. Furthermore,



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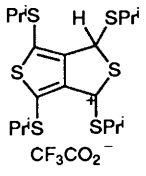
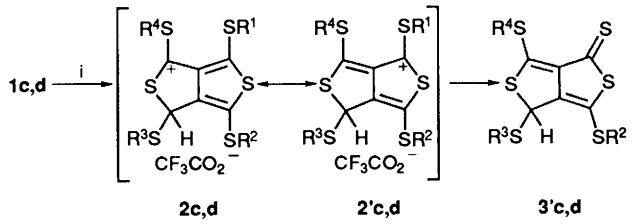


2b

we confirmed that the reaction of compound **1b** with TFA does not give the corresponding thione. This indicates that cleavage of the Pr^i–S bond does not take place. 1,3,4-Tris(t-butylthio)-6-ethylthio-and1,4-bis(t-butylthio)-3,6-bis(ethylthio)-$2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene (**1c** and **1d**) reacted with TFA to give 3,4-bis(t-butylthio)-6-ethylthio- and 4-t-butylthio-3,6-bis(ethylthio)thieno[3,4-*c*]thiophene-1(4*H*)-thione **3'c** and **3'd**, respectively (Scheme 2). The structure of compound **3'c** was



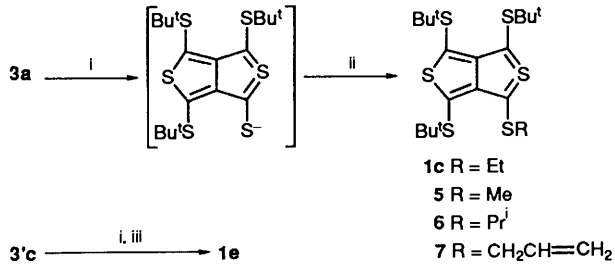
2c,d **2'c,d** **3'c,d**

c; $R^1 = R^2 = R^3 = Bu^t$, R^4 = Et
d; $R^1 = R^3 = Bu^t$, $R^2 = R^4$ = Et

Scheme 2 *Reagent:* i, TFA

determined from the facts that (i) ethylation of compound **3'c** using sodium hydride and then ethyl iodide gave compound **1e** in quantitative yield, as described later, and (ii) the reaction of compound **1c** with TFA in the presence of water gave the 1-one **9**, as described later, without the formation of compound **12**, thus indicating that the protonation of compound **1c** occurs in the 4-position. On the other hand, the position of protonation of compound **1d** by TFA was determined from the fact that reaction of compound **1d** with TFA in the presence of water gave compound **11**, as described later, without the formation of **A**, although there is the possibility that protonation of compound **1d** occurs at either 1- or 3-position. The yields are summarized in Table 1. The position of the thiocarbonyl group of compounds **3'c** and **3'd** was different from that of compound **3a**. This result indicates that the reaction proceeds *via* the intermediary formation of salts **2'c** and **2'd**, in which a positive charge is delocalized, followed by cleavage of the Bu^t–S bond, as shown in Scheme 2. The reaction of 1,6-bis(t-butylthio)-3,4-bis(ethylthio)-$2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene **1e** with TFA did not give the thione derivative at all, although substrate **1e** was protonated at the 1-position, thus indicating that the Bu^t–S bond of this compound is not cleaved. As described above, it became apparent that the protonation takes place at the position of the t-butylthio group in the thiophene ring having the ethylthio substituent.

Next, attempts were made to regenerate the $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene system from thiones **3a** and **3'c**. Compounds **3a** and **3'c** were treated with sodium hydride (2 mol equiv.) in *N*,*N*-dimethylformamide (DMF) and then with various alkyl iodides (2 mol equiv.) (Scheme 3). As Table 2 shows, $2\lambda^4\delta^2$-thieno[3,4-

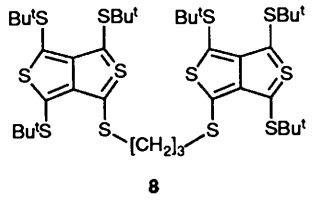


1c R = Et
5 R = Me
6 R = Pr^i
7 R = $CH_2CH{=}CH_2$

Scheme 3 *Reagents and conditions:* i, NaH, DMF, room temp.; ii, RI; iii, EtI

c]thiophenes **1c** and **1e**, and **5**–**7** were obtained in high yield. All products showed the characteristic absorption due to the $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene ring, as shown in Table 2. When 1,3-diiodopropane (0.5 mol equiv.) was used as an alkylating reagent, it was found that the $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene derivative **8** (λ_{max} 510 nm) linked by a trimethylene chain was obtained in 80% yield. These reactions provided a novel method for converting a t-butylthio group of compound **1a** into other alkythio groups.

Furthermore, we carried out the reaction of compounds **1a**–**e** with TFA in the presence of water. The substrates reacted with TFA (3 mol equiv.) and water (10 mol equiv.) in benzene at room temperature to give thieno[3,4-*c*]thiophen-1(3*H*)-ones **9**–**12** as the major product, accompanied by the formation



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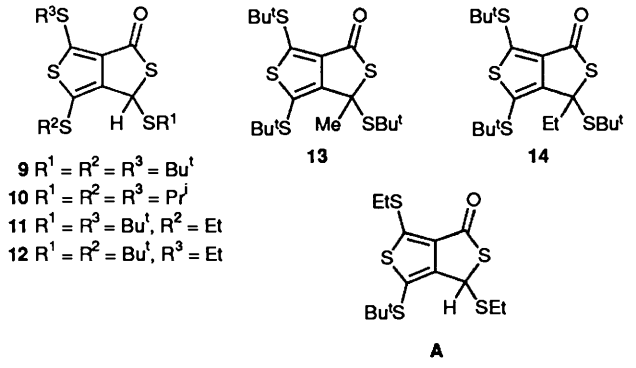
of thiones **3a**, **3'c** and **3'd**, as shown in Table 3. These results indicated that the 1*H*-thieno[3,4-*c*]thiophenium intermediate reacts immediately with water to give thieno[3,4-*c*]thiophen-1(3*H*)-ones. Compound **9** was treated with sodium hydride and then with an alkylating reagent such as iodomethane, methyl



9 $R^1 = R^2 = R^3 = Bu^t$
10 $R^1 = R^2 = R^3 = Pr^i$
11 $R^1 = R^3 = Bu^t$, $R^2 = Et$
12 $R^1 = R^2 = Bu^t$, $R^3 = Et$

13 **14** **A**

Table 3 Reaction of $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophenes **1a–e** with TFA in the presence of water[a]

Compound	Time (*t*/h)	Product (yield, %)[b]
1a	14	**9** (73), **3a** (25)
1b	4	**10** (90)
1c	24	**9** (75), **3'c** (14)
1d	7	**11** (76), **3'd** (13)
1e	24	**12** (94)

[a] Reactions were carried out in benzene at room temp. Molar proportions 1:TFA:water 1:3:10. [b] Isolated yield.

Table 4 Reaction of $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophenes **1a** and **1b** with Vilsmeier reagent[a]

Compound	Vilsmeier reagent (mol equiv.)	Time (*t*/h)	Product (yield, %)[b]
1a	10	3.5	**15a** (40)
1b	1.5	1	**15b** (33), **16b** (14)
1b	5	1	**16b** (51)

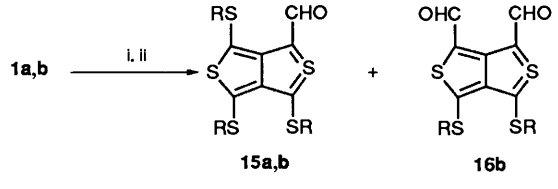
[a] Reactions were carried out in DMF at room temp. [b] Isolated yield. There were many other products which could not be identified.

Table 5 Visible spectra of compounds **1a**, **1b**, **15a**, **15b** and **16b** in acetonitrile solution

	1a	**1b**	**15a**	**15b**	**16b**
λ_{max}/nm	507	506	542	580	590

toluene-*p*-sulphonate or triethyloxonium tetrafluoroborate. 3,4,6-Tris(t-butylthio)-3-methylthieno[3,4-*c*]thiophen-1(3*H*)-one **13** was obtained in 50 and 58% yield, respectively, and the corresponding 3-ethyl derivative **14** in 68% yield. Hence, it was impossible to regenerate the $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene system from compound **9** by this route.

Reaction of $2\lambda^4\delta^2$-*Thieno*[3,4-c]*thiophenes* **1a** *and* **1b** *with Vilsmeier Reagent.*—Vilsmeier reagent was prepared from DMF and phosphorus trichloride oxide. Compound **1a** reacted with Vilsmeier reagent (10 mol equiv.) to give only 1,4,6-tris(t-butylthio)-3-formyl-$2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene **15a**, as shown in Scheme 4. On the other hand, reaction of compound **1b** with Vilsmeier reagent gave 1-formyl-3,4,6-tris(isopropylthio)- and 1,6-diformyl-3,4-bis(isopropylthio)-$2\lambda^4\delta^2$-thieno-[3,4-*c*]thiophene **15b** and **16b**. When 1.5 mol equiv. of the reagent was used, the maximal yield of monoformyl derivative **15b** was achieved. Use of excess of Vilsmeier reagent (5 mol equiv.) resulted in the exclusive formation of the diformyl product **16b** (Table 4). The formation of diformyl compound **16b** indicates that the 6-position of compound **15b** is more nucleophilic than the 3- and 4-position. As Table 5 shows, the monoformyl-substituted derivatives **15a** and **15b** exhibited UV–VIS absorptions at 542 and 580 nm, respectively, shifted to longer wavelength as compared with those of the parent compounds **1a** and **1b**. The absorption of the diformyl-substituted derivative **16b** appeared at longer wavelength as compared with that of the monoformyl-substituted derivative **15b**. These bathochromic shifts seem to be attributable to the formyl groups.



15a,b **16b**

a; R = Bu^t
b; R = Pr^i

Scheme 4 *Reagents and conditions:* i, $POCl_3$, DMF, room temp.; ii, saturated aq. $NaHCO_3$

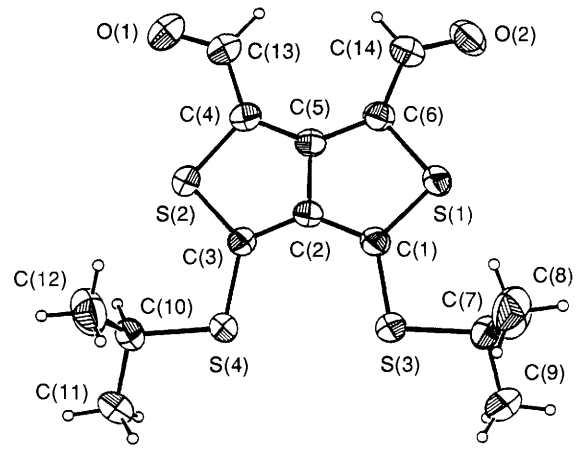


Fig. 1 X-Ray molecular structure of compound **16b**. There are two crystallographically independent molecules (A and B) in the asymmetric unit. An ORTEP drawing of molecule A is shown; the conformations of the two molecules (A and B) are almost identical except for the isopropyl residues. Crystallographic numbering scheme is shown.

Table 6 Selected bond lengths (Å) with esds for compound **16b**

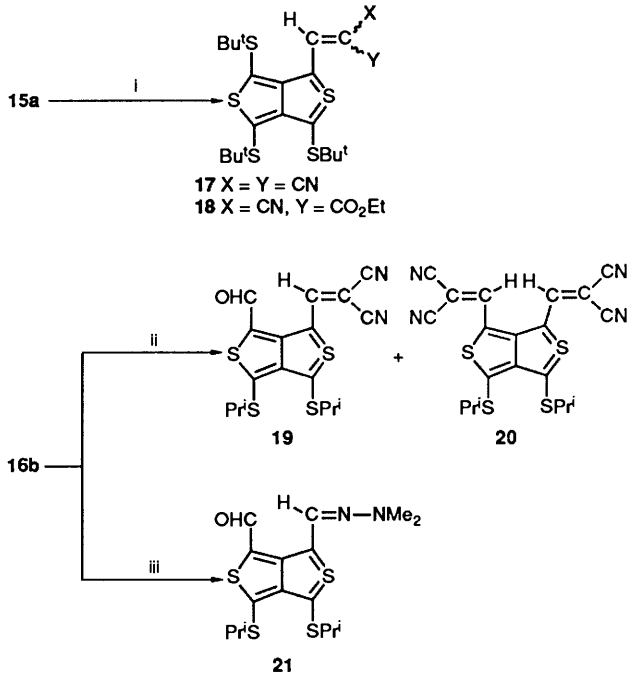
S(1)–C(1)	1.701(1)	C(2)–C(3)	1.409(2)
S(1)–C(6)	1.742(2)	C(2)–C(5)	1.441(2)
S(2)–C(3)	1.697(2)	C(4)–C(5)	1.408(3)
S(2)–C(4)	1.734(1)	C(4)–C(13)	1.422(4)
S(3)–C(1)	1.716(2)	C(5)–C(6)	1.408(3)
S(3)–C(7)	1.822(3)	C(6)–C(14)	1.411(3)
S(4)–C(3)	1.723(1)	C(7)–C(8)	1.518(3)
S(4)–C(10)	1.829(2)	C(7)–C(9)	1.517(4)
O(1)–C(13)	1.222(4)	C(10)–C(11)	1.516(2)
O(2)–C(14)	1.227(3)	C(10)–C(12)	1.514(3)
C(1)–C(2)	1.410(3)		

The position of the two formyl groups of compound **16b** was determined by X-ray diffraction. Fig. 1 shows the molecular structure of compound **16b**. Selected bond lengths are presented in Table 6. The $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene ring system and the two formyl groups were coplanar and the bond distances of the C(6)–C(14) and C(4)–C(13) bonds were shorter than that of the usual carbon–carbon single bond. The lengths of the C(1)–S(1) and C(3)–S(2) bonds were shorter than those of the C(6)–S(1) and C(4)–S(2) bonds. This fact indicates the effective conjugation of the formyl groups. Compound **16b** was stable in air for several weeks, although other $2\lambda^4\delta^2$-thieno[3,4-*c*]thio-

Table 7 Condensation of compounds **15a** and **16b** with malononitrile, ethyl cyanoacetate and UDMH[a]

Compound	Reagent	Mol equiv.	Reaction conditions	Product (yield, %)[b]
15a	$CH_2(CN)_2$	1.2	Reflux, 6 h	**17** (50)[c]
	$CH_2(CN)CO_2Et$	1.2	60 °C, 80 h	**18** (40)[d]
16b	$CH_2(CN)_2$	2.5	Room temp., 66 h	**19** (38), **20** (52)
	H_2NNMe_2[b]	2.5	40 °C, 12 h	**21** (62)

[a] Reactions were carried out in dry ethanol in the presence of piperidine (0.1 mol equiv.). [b] Isolated yield. [c] Compound **15a** was recovered in 50% yield. [d] There were many other products which could not be identified.



Scheme 5 *Reagents:* i, CH_2XY, piperidine; ii, $CH_2(CN)_2$, piperidine; iii, UDMH

Table 8 Visible spectra of compounds **17–21** in acetonitrile solution

	17	**18**	**19**	**20**	**21**
λ_{max}/nm	658	587	647	435	647

phenes have been found to be relatively sensitive to air. This remarkable stability depends on the electromeric effect of the formyl groups.

To develop other thieno[3,4-*c*]thiophene derivatives from the aldehydes **15a** and **16b**, we carried out condensation of compounds **15a** and **16b** with malononitrile, ethyl cyanoacetate and *N*,*N*-dimethylhydrazine (UDMH) (Scheme 5). The monoformyl-substituted $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene **15a** underwent condensation with malononitrile and ethyl cyanoacetate in the presence of piperidine to give compounds **17** and **18**, respectively. The 1,6-diformyl-substituted $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene **16b** reacted with malononitrile in the presence of piperidine to give compounds **19*** and **20**. The yields and the reaction conditions are summarized in Table 7. On the other hand, condensation of compound **16b** with UDMH yielded only the monohydrazone derivative **21*** (66%) by reaction with one of the formyl groups. Further treatment of the product **21** with UDMH under similar conditions resulted in the recovery of substrate **21**. The absorption maxima of compounds **17–19** and **21** appeared at longer wavelength compared with those of the original formyl-substituted derivatives, owing to the extension of the conjugated system, as Table 8 shows. In contrast, compound **20**, having two dicyanovinyl groups, exhibited its absorption maximum at shorter wavelength, compared with those of compounds **16b** and **19**. This hypsochromic shift seems to be caused by the distortion of the conjugated system due to the steric hindrance between the two dicyanovinyl groups. This postulate was supported by the fact that the ^{1}H NMR spectrum of compound **20** showed four doublets and two singlets for non-equivalent isopropylthio groups, and two singlets for non-equivalent vinylic protons.

Conclusions.—The results presented here show that the electrophilic addition of a proton or Vilsmeier reagent to the $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene ring system results in the formation of the corresponding thiones and mono- and di-formyl-substituted $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophenes, respectively. Furthermore, the regeneration of the $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene system from thiones by treatment with sodium hydride and then with an alkyl iodide provided a novel method for the convenient conversion of the t-butylthio group of compound **1a** into other alkylthio groups.

Experimental

M.p.s were determined on a Yanaco MP-S3 melting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 215 spectrometer. UV spectra were obtained on a Shimadzu UV-160 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX270 FT NMR spectrometer for solutions in $CDCl_3$ with tetramethylsilane as internal standard; *J*-values are in Hz. Mass spectra were recorded on a Shimadzu LKB-9000 spectrometer operating at 70 eV by a direct-inlet system. Column chromatography was performed on silica gel (Wakogel C-300). All solvents were dried and purified by the usual methods. DMF was distilled on calcium hydride under reduced pressure. Phosphorus trichloride oxide, ethyl cyanoacetate, and piperidine were distilled under reduced pressure. Methyl toluene-*p*-sulphonate and triethyloxonium tetrafluoroborate were prepared by the methods described in the literature.[11] Compounds **1a**, **1b** and **1d** were prepared according to the method described previously.[6]

Reaction of 1,3,4,6-*Tetrakis*(*t-butylthio*)-$2\lambda^4\delta^2$-*thieno*[3,4-c]-*thiophene* **1a** *with TFA.*—TFA (137 mg, 1.2 mmol) was added under nitrogen to a solution of compound **1a** (197 mg, 0.40 mmol) in benzene (20 cm^3) and the mixture was stirred at 35 °C for 4 h. The solvent was evaporated off under reduced pressure.

* The π-electrons in the $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene ring system of compound **16b** are delocalized, since the ^{1}H NMR spectrum of this compound indicates that both the formyl and both the isopropylthio groups are equivalent. Therefore, malonitrile and *N*,*N*-dimethylhydrazine react indistinguishably with either of the two formyl groups of this compound. The structural formula of the $2\lambda^4\delta^2$-thieno[3,4-*c*]-thiophene ring system of compounds **19** and **21** described here represents one of the canonical structures.

The residue was chromatographed on silica gel with dichloromethane–hexane (1:2) as eluent to give 3,4,6-*tris*(*t*-*butylthio*)*thieno*[3,4-c]*thiophene*-1(3H)-*thione* **3a** as a reddish purple solid (157 mg, 90%), m.p. 129.5–130.0 °C (decomp.) (from MeOH–EtOH) (Found: C, 49.3; H, 6.8. $C_{18}H_{28}S_6$ requires C, 49.5; H, 6.5%); ν_{max}(KBr)/cm^{-1} 2950, 2925 and 2860 (C–H), 1515, 1455, 1415, 1365, 1205, 1160, 1055, 960, 775 and 720; λ_{max}(hexane)/nm 286 (log ε/dm^3 mol^{-1} cm^{-1} 4.27), 300sh (4.16), 366 (3.94) and 400sh (3.81); δ_H 1.42 (9 H, s, 3-SBu^t), 1.45 (9 H, s, 4-SBu^t), 1.57 (9 H, s, 6-SBu^t) and 5.67 (1 H, s, 3-H); δ_C 30.63, 31.11, 31.28, 45.34, 49.21, 50.01, 51.27, 125.58, 143.61, 146.29, 153.70 and 213.58 (C=S); *m*/*z* 436 (M^+).

Reaction of 1,3,4,6-*Tetrakis*(*isopropylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophene* **1b** *with TFA*.—TFA (103 mg, 0.90 mmol) was added under nitrogen to a solution of compound **1b** (131 mg, 0.30 mmol) in benzene (15 cm^3) and the mixture was stirred at 35 °C for 6 h. The thione derivative was not detected by TLC. The solvent was evaporated off under reduced pressure to give a reddish brown oil, which changed gradually to compound **10** by reaction with moisture.

Reaction of 1,3,4-*Tris*(*t*-*butylthio*)-6-(*ethylthio*)-2λ^{4}δ^2-*thieno*-[3,4-c]*thiophene* **1c** *with TFA*.—TFA (103 mg, 0.90 mmol) was added under nitrogen to a solution of compound **1c** (139 mg, 0.30 mmol) in benzene (15 cm^3) and the mixture was stirred at 35 °C for 6.5 h. The solvent was evaporated off under reduced pressure and the residue was chromatographed on silica gel with dichloromethane–hexane (1:1) as eluent to give 3,4-*bis*(*t*-*butylthio*)-6-(*ethylthio*)*thieno*[3,4-c]*thiophene*-1(4H)-*thione* **3'c** as an orange solid (114 mg, 93%), m.p. 130–131 °C (from MeOH) (Found: C, 47.0; H, 5.95. $C_{16}H_{24}S_6$ requires C, 47.0; H, 5.9%); ν_{max}(KBr)/cm^{-1} 2950, 2925 and 2855 (C–H), 1505, 1470, 1455, 1430, 1375, 1360, 1265, 1215, 1160, 1050, 975 and 910; λ_{max}-(hexane)/nm 283 (log ε/dm^3 mol^{-1} cm^{-1} 4.31), 302sh (4.30), 362 (3.97) and 399 (3.98); δ_H 1.40 (9 H, s, 4-SBu^t), 1.45 (9 H, s, 3-SBu^t), 1.48 (3 H, t, *J* 7.3, 6-SCH$_2$*Me*), 3.06 (2 H, q, *J* 7.3, 6-SC*H*$_2$Me) and 5.73 (1 H, s, 4-H); δ_C 13.35, 29.31, 31.08, 31.18, 45.29, 49.17, 52.63, 123.14, 144.18, 149.18, 154.01 and 212.57 (C=S); *m*/*z* 408 (M^+).

Reaction of 1,4-*Bis*(*t*-*butylthio*)-3,6-*bis*(*ethylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophene* **1d** *with TFA*.—The reaction of compound **1d** (131 mg, 0.30 mmol) with TFA (103 mg, 0.90 mmol) was carried out in a similar manner to the case of compound **1c** to give 4-*t*-*butylthio*-3,6-*bis*(*ethylthio*)*thieno*[3,4-c]*thiophene*-1(4H)-*thione* **3d** as an orange solid (95 mg, 83%), m.p. 99.5–100.5 °C (from MeOH) (Found: C, 43.9; H, 5.4. $C_{14}H_{20}S_6$ requires C, 44.2; H, 5.3%); ν_{max}(KBr)/cm^{-1} 2950, 2925 and 2860 (C–H), 1515, 1430, 1375, 1265, 1220, 1170, 1050 and 965; λ_{max}(hexane)/nm 283 (log ε/dm^3 mol^{-1} cm^{-1} 4.35), 300sh (4.23), 359 (3.91) and 398 (3.97); δ_H 1.21 (3 H, t, *J* 7.3, 3-SCH$_2$*Me*), 1.42 (9 H, s, 4-SBu^t), 1.49 (3 H, t, *J* 7.3, 6-SCH$_2$*Me*), 2.51 (1 H, dq, *J* 12.3 and 7.3, 3-SC*H*HMe), 2.72 (1 H, dq, *J* 12.3 and 7.3, 3-SCH*H*Me), 3.06 (1 H, q, *J* 7.3, 6-C*H*HMe), 3.07 (1 H, q, *J* 7.3, 6-CH*H*Me) and 5.76 (1 H, s, 4-H); δ_C 13.35, 13.76, 24.27, 29.40, 31.08, 49.64, 54.09, 122.67, 144.49, 149.44, 154.23 and 212.57 (C=S); *m*/*z* 380 (M^+).

Reaction of 1,6-*Bis*(*t*-*butylthio*)-3,4-*bis*(*ethylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophene* **1e** *with TFA*.—The reaction of compound **1e** (131 mg, 0.30 mmol) with TFA under conditions similar to the case of compound **1b** gave a reddish brown oil, which changed gradually to compound **12** by reaction with moisture.

Detection of 1,3,4,6-*Tetrakis*(*t*-*butylthio*)-1H-*thieno*[3,4-c]-*thiophenium Trifluoroacetate* **2a**.—TFA (0.10 cm^3) was added to a solution of compound **1a** (10 mg) in $CDCl_3$ (0.90 cm^3) containing tetramethylsilane as internal standard in a sample tube at room temperature, and then the ^{1}H NMR spectrum was recorded immediately. The ^{1}H NMR spectrum showed peaks for the salt **2a** at δ 1.46 (9 H, s, 1-SBu^t), 1.54 (9 H, s, 6-SBu^t), 1.74 (9 H, s, 4-SBu^t), 1.84 (9 H, s, 3-SBu^t) and 6.02 (1 H, s, 1-H). This spectrum changed to that of compound **3a** on keeping the sample tube at 40 °C for 7 h.

Detection of 1,3,4,6-*Tetrakis*(*isopropylthio*)-1H-*thieno*[3,4-c]-*thiophenium Trifluoroacetate* **2b**.—In a similar manner to the case of compound **1a**, the ^{1}H NMR spectrum of a solution of compound **1b** and TFA in $CDCl_3$ was measured. The spectrum showed peaks for the salt **2b** at δ 1.39 (6 H, d, *J* 6.7, SCH*Me*$_2$), 1.38, 1.44, 1.63, 1.64, 1.68 and 1.72 (each 3 H, d, *J* 6.7, SCH*Me*Me), 3.29, 3.40, 3.77 and 3.96 (each 1 H, dq, *J* 6.7 and 6.7, SC*H*Me$_2$) and 6.14 (1 H, s, 1-H). This spectrum did not change after the solution had been stored at room temperature for 24 h.

Alkylation of Compounds **3a** *and* **3'c** *with Alkyl Iodides*.—A solution of compound **3a** or compound **3'c** (0.20 mmol) in DMF (1 cm^3) was added under nitrogen to a suspension of sodium hydride (9.6 mg, 0.40 mmol) in DMF (5 cm^3) at room temperature. The mixture was stirred for 0.5 h and then an alkyl iodide (0.40 mmol) was added. After being stirred for 0.5 h, the mixture was poured into water, extracted with dichloromethane, and the extract was dried over anhydrous sodium sulphate. The solvent was evaporated off under reduced pressure to give 2λ^{4}δ^2-thieno[3,4-*c*]thiophenes **1c**, **1e** and **5**–**7**.

1,3,4-*Tris*(*t*-*butylthio*)-6-(*ethylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophene* **1c** (87 mg, 94%) was prepared from compound **3a** by reaction with iodoethane, and had m.p. 121–122 °C (from MeOH) (Found: C, 51.5; H, 7.1. $C_{20}H_{32}S_6$ requires C, 51.7; H, 7.0%); ν_{max}(KBr)/cm^{-1} 2960, 2925, 2900 and 2860 (C–H), 1475, 1455, 1365, 1260, 1240, 1220 and 1165; λ_{max}(hexane)/nm 257 (log ε/dm^3 mol^{-1} cm^{-1} 4.27), 303 (4.02) and 508 (4.10); δ_H 1.32 (9 H, s, SBu^t), 1.34 (9 H, s, SBu^t), 1.34 (3 H, t, *J* 7.3, SCH$_2$*Me*), 1.37 (9 H, s, SBu^t) and 3.02 (2 H, q, *J* 7.3, SC*H*$_2$Me); δ_C 14.00, 30.66, 30.76, 31.20, 32.23, 49.92, 50.12, 111.78, 117.20, 117.24, 121.58, 150.65 and 152.90; *m*/*z* 464 (M^+).

1,6-*Bis*(*t*-*butylthio*)-3,4-*bis*(*ethylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]-*thiophene* **1e** (78 mg, 90%) was prepared from compound **3c** by reaction with iodoethane, and had m.p. 119–120 °C (from MeOH) (Found: C, 49.7; H, 6.6. $C_{18}H_{28}S_6$ requires C, 49.5; H, 6.5%); ν_{max}(KBr)/cm^{-1} 2955, 2850 and 2860 (C–H), 1455, 1365, 1255, 1235 and 1160; λ_{max}(hexane)/nm 257 (log ε/dm^3 mol^{-1} cm^{-1} 4.29), 302 (4.00) and 507 (4.11); δ_H 1.32 (6 H, t, *J* 7.3, 2 × SCH$_2$*Me*), 1.33 (18 H, s, 2 × SBu^t) and 3.00 (4 H, q, *J* 7.3, 2 × SCH$_2$*Me*); δ_C 14.14, 30.72, 33.75, 50.02, 113.34, 119.93, 149.66 and 153.08; *m*/*z* 436 (M^+).

1,4,6-*Tris*(*t*-*butylthio*)-3-(*methylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophene* **5** (88 mg, 98%) was prepared from compound **3a** by reaction with iodomethane, and had m.p. 105–106 °C (from MeOH) (Found: C, 50.4; H, 6.7. $C_{19}H_{30}S_6$ requires C, 50.6; H, 6.7%); ν_{max}(KBr)/cm^{-1} 2955, 2900 and 2860 (C–H), 1475, 1455, 1360, 1320, 1240, 1160, 1005 and 735; λ_{max}(hexane)/nm 256 (log ε/dm^3 mol^{-1} cm^{-1} 4.27), 303 (3.96) and 515 (4.06); δ_H 1.32, 1.34 and 1.37 (each 9 H, s, SBu^t) and 2.61 (3 H, s, SMe); δ_C 20.61, 30.64, 30.76, 49.94, 50.16, 109.60, 116.81, 117.32, 125.08, 149.74 and 152.92; *m*/*z* 450 (M^+).

1,4,6-*Tris*(*t*-*butylthio*)-3-(*isopropylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]-*thiophene* **6** (93 mg, 97%) was prepared from compound **3a** by reaction with 2-iodopropane, and had m.p. 154–155 °C (decomp.) (from MeOH) (Found: C, 52.5; H, 7.3. $C_{21}H_{34}S_6$ requires C, 52.7; H, 7.2%); ν_{max}(KBr)/cm^{-1} 2950, 2920 and 2860 (C–H), 1475, 1455, 1365, 1230, 1220 and 1165; λ_{max}(hexane)/nm 256 (log ε/dm^3 mol^{-1} cm^{-1} 4.28), 302 (4.05) and 508 (4.17); δ_H 1.31 (6 H, d, *J* 6.5, SCH*Me*$_2$), 1.33, 1.34 and 1.37 (each 9 H, s,

SBu^t) and 3.46 (1 H, sep, *J* 6.5, SC*H*Me$_2$); δ_C 22.59, 30.68, 30.72, 30.76, 42.28, 49.92, 49.98, 50.14, 114.02, 117.18, 117.56, 119.70, 151.54 and 152.94; *m/z* 478 (M^+).

1-*Allylthio*-3,4,6-*tris*(*t-butylthio*)-2$\lambda^4\delta^2$-*thieno*[3,4-c]*thiophene* **7** (76 mg, 80%) was prepared from compound **3a** by reaction with 3-iodopropene, and had m.p. 103.5–104 °C (from MeOH) (Found: C, 52.8; H, 6.8. $C_{21}H_{32}S_6$ requires C, 52.9; H, 6.8%); ν_{max}(KBr)/cm^{-1} 2950, 2900 and 2860 (C–H), 1475, 1455, 1370, 1225, 1160, 1000 and 925; λ_{max}(hexane)/nm 257 (log ε/dm^3 mol^{-1} cm^{-1} 4.26), 306 (4.04) and 508 (4.17); δ_H 1.31, 1.33 and 1.37 (each 9 H, s, SBu^t), 3.57 (2 H, d, *J* 7.3, SC*H*$_2$CH=CH$_2$), 4.88–5.02 (2 H, m, SCH$_2$CH=C*H*$_2$) and 5.81–5.96 (1 H, m, SCH$_2$-C*H*=CH$_2$); δ_C 30.70, 30.76, 41.63, 50.00, 50.18, 50.26, 113.84, 116.99, 117.76, 118.47, 119.18, 132.90, 151.14 and 152.90; *m/z* 476 (M^+).

1′,3,3′,4,6,6′-*Hexakis*(*t-butylthio*)-1,4′-*trimethylenedithiobi*-2$\lambda^4\delta^2$-*thieno*[3,4-c]*thiophene* **8** (73 mg, 80%) was prepared from compound **3a** by reaction with 1,3-diiodopropane (0.10 mmol), and had m.p. 109–110 °C (from MeOH) (Found: C, 51.0; H, 6.65. $C_{39}H_{60}S_{12}$ requires C, 51.3; H, 6.6%); ν_{max}(KBr)/cm^{-1} 2960, 2925, 2900 and 2860 (C–H), 1475, 1460, 1365, 1240, 1225 and 1160; λ_{max}(hexane)/nm 256 (log ε/dm^3 mol^{-1} cm^{-1} 4.52), 302 (4.27) and 510 (4.26); δ_H 1.32, 1.34 and 1.35 (each 18 H, s, SBu^t), 2.02 (2 H, quint., *J* 7.3, CH$_2$C*H*$_2$CH$_2$) and 3.16 (4 H, t, *J* 7.3, C*H*$_2$CH$_2$C*H*$_2$); δ_C 27.73, 30.68, 30.74, 30.78, 37.25, 50.00, 50.04, 50.18, 112.97, 117.14, 117.60, 120.23, 150.89 and 152.92; *m/z* 509 (M^+ − 403).

Reaction of 2$\lambda^4\delta^2$-*Thieno*[3,4-c]*thiophenes* **1a–e** *with TFA in the Presence of Water*.—TFA (103 mg, 0.90 mmol) and water (16 mg, 9.0 mmol) was added to a solution of a substrate **1a–e** (0.30 mmol) in benzene (15 cm^3) at room temperature and the mixture was stirred for 4–24 h. The reaction was followed by monitoring of the consumption of reactant **1a–e** by TLC. After the reaction, the mixture was dried by passage through a column packed with anhydrous sodium sulphate, and the eluate was evaporated. The residue was chromatographed on silica gel with dichloromethane–hexane (1 : 2) as eluent to give thieno[3,4-*c*]thiophen-1(3*H*)-ones **9–12**.

3,4,6-*Tris*(*t-butylthio*)*thieno*[3,4-c]*thiophen*-1(3H)-*one* **9** (92 mg, 73%) was prepared from compound **1a**, together with the by-product **3a** (33 mg, 25%). *Compound* **9** was obtained as a solid, m.p. 123.5–124.0 °C (from MeOH) (Found: C, 51.2; H, 6.9. $C_{18}H_{28}OS_5$ requires C, 51.4; H, 6.7%); ν_{max}(KBr)/cm^{-1} 2950, 2900 and 2860 (C–H), 1690 (C=O), 1505, 1470, 1460, 1420, 1370, 1165, 1130, 1100, 970, 785, 765, 740 and 690; λ_{max}(hexane)/nm 249 (log ε/dm^3 mol^{-1} cm^{-1} 4.15) and 305 (3.82); δ_H 1.41 (9 H, s, 3-SBu^t), 1.43 (9 H, s, 4-SBu^t), 1.47 (9 H, s, 6-SBu^t) and 5.62 (1 H, s, 3-H); δ_C 30.76, 31.02, 31.20, 45.32, 46.57, 49.13, 50.31, 130.84, 137.00, 142.30, 153.00 and 185.66 (C=O); *m/z* 420 (M^+). The Compound **9** (92 mg, 73%) also was prepared from compound **1c**.

3,4,6-*Tris*(*isopropylthio*)*thieno*[3,4-c]*thiophen*-1(3H)-*one* **10** (102 mg, 90%) was prepared from compound **1b**, and was obtained as an *oil* (Found: C, 50.0; H, 5.9. $C_{15}H_{22}OS_5$ requires C, 47.6; H, 5.9%); ν_{max}(neat)/cm^{-1} 2950, 2920 and 2860 (C–H), 1690 (C=O), 1515, 1440, 1385, 1370, 1245, 1155, 1050 and 990; λ_{max}(hexane)/nm 250 (log ε/dm^3 mol^{-1} cm^{-1} 4.21) and 345 (3.88); δ_H 1.24 (3 H, d, *J* 6.7, 4-SCH*Me*Me), 1.34 (3 H, d, *J* 6.7, 3-SCH*Me*Me), 1.35 (3 H, d, *J* 6.7, 4-SCHMe*Me*), 1.37 (3 H, d, *J* 6.7, 3-SCHMe*Me*), 1.41 (3 H, d, *J* 6.7, 6-SCH*Me*Me), 1.42 (3 H, d, *J* 6.7, 6-SCHMeMe), 3.20 (1 H, sep, *J* 6.7, 3-SC*H*Me$_2$), 3.35 (1 H, sep, *J* 6.7, 4-SC*H*Me$_2$), 3.55 (1 H, qq, *J* 6.7 and 6.7, 6-SC*H*Me$_2$) and 5.70 (1 H, s, 3-H); δ_C 22.67, 22.97, 23.08, 23.60, 23.70, 36.68, 40.89, 42.26, 48.26, 127.40, 138.16, 141.80, 151.80 and 185.62; *m/z* 378 (M^+).

3,6-*Bis*(*t-butylthio*)-4-(*ethylthio*)*thieno*[3,4-c]*thiophen*-1(3H)-*one* **11** (90 mg, 76%) was prepared from compound **1d**, together with the by-product **3d** (15 mg, 13%). *Compound* **11** was an oil (Found: C, 48.6; H, 6.1. $C_{16}H_{24}OS_5$ requires C, 48.9; H, 6.2%); ν_{max}(neat)/cm^{-1} 2925 and 2860 (C–H), 1700 (C=O), 1515, 1435, 1370, 1270, 1220, 1155, 1010, 960, 965, 800, 760 and 740; λ_{max}(hexane)/nm 248 (log ε/dm^3 mol^{-1} cm^{-1} 4.18) and 300 (3.76); δ_H 1.38 (3 H, t, *J* 7.3, 4-SCH$_2$*Me*), 1.40 (9 H, s, 3-SBu^t), 1.47 (9 H, s, 6-SBu^t), 2.96 (1 H, q, *J* 7.3, C*H*HMe), 2.99 (1 H, q, *J* 7.3, CH*H*Me) and 5.66 (1 H, s, 3-H); δ_C 14.67, 30.76, 31.10, 45.55, 49.34, 50.41, 133.79, 134.18, 143.01, 148.71 and 185.85 (C=O); *m/z* 392 (M^+).

3,4-*Bis*(*t-butylthio*)-6-(*ethythio*)*thieno*[3,4-c]*thiophen*-1(3H)-*one* **12** (111 mg, 94%) was prepared from compound **1e**, and was obtained as a solid, m.p. 108–109 °C (from MeOH) (Found: C, 49.1; H, 6.2. $C_{16}H_{24}OS_5$ requires C, 48.95; H, 6.2%); ν_{max}(KBr)/cm^{-1} 2940 (C–H), 1660 (C=O), 1440, 1365, 1255, 1140, 1050 and 970; λ_{max}(hexane)/nm 250 (log ε/dm^3 mol^{-1} cm^{-1} 4.26) and 342 (3.97); δ_H 1.39 (9 H, s, 3-SBu^t), 1.43 (3 H, t, *J* 7.3, 6-SCH$_2$*Me*), 1.46 (9 H, s, 4-SBu^t), 3.08 (2 H, q, *J* 7.3, 6-SCH$_2$*Me*) and 5.65 (1 H, s, 3-H); δ_C 13.84, 29.60, 31.08, 31.16, 45.31, 47.92, 49.05, 125.22, 136.84, 144.38, 153.12 and 185.97 (C=O); *m/z* 392 (M^+).

Alkylation of Compound **9** *with Iodomethane and with Methyl Toluene*-p-*sulphonate*.—A solution of compound **9** (84 mg, 0.20 mmol) in DMF (1 cm^3) was added under nitrogen to a suspension of sodium hydride (9.6 mg, 0.40 mmol) in DMF (5 cm^3) at room temperature. The mixture was stirred for 0.5 h and then iodomethane (56 mg, 0.40 mmol) was added. After being stirred for 0.5 h, the mixture was poured into water, extracted with dichloromethane, and the extract was dried over anhydrous sodium sulphate before being evaporated under reduced pressure, and the residue was chromatographed on silica gel with dichloromethane–hexane (1 : 2) as eluent to give 3,4,6-*tris*(*t-butylthio*)-3-*methylthieno*[3,4-c]*thiophen*-1(3H)-*one* **13** as a solid (43 mg, 50%), m.p. 144–145.5 °C (from MeOH) (Found: C, 52.3; H, 7.1. $C_{19}H_{30}OS_5$ requires C, 52.5; H, 7.0%); ν_{max}(KBr)/cm^{-1} 2950 and 2860 (C–H), 1690 (C=O), 1510, 1460, 1420, 1395, 1370, 1165, 1100, 1075, 975, 780 and 755; λ_{max}(hexane)/nm 259 (log ε/dm^3 mol^{-1} cm^{-1} 4.11) and 321 (3.86); δ_H 1.27 (9 H, s, 3-SBu^t), 1.43 (9 H, s, 4-SBu^t), 1.48 (9 H, s, 6-SBu^t) and 2.26 (3 H, s, Me); δ_C 30.78, 30.84, 31.53, 31.65, 48.73, 49.01, 50.26, 60.86, 130.94, 135.09, 142.91, 156.47 and 185.32 (C=O); *m/z* 434 (M^+).

When methyl toluene-*p*-sulphonate (74 mg, 0.40 mmol) was used as alkylating reagent, compound **13** was obtained in 58% yield.

Alkylation of Compound **9** *with Triethyloxonium Tetrafluoroborate*.—Compound **9** (84 mg, 0.20 mmol) was treated with sodium hydride (9.6 mg, 0.40 mmol) by the procedure described above. Triethyloxonium tetrafluoroborate (75 mg, 0.40 mmol) was added directly to the reaction mixture. After being stirred for 0.5 h, the mixture was worked up by a procedure similar to that of the methylations, to give 3,4,6-*tris*(*t-butylthio*)-3-*ethylthieno*[3,4-c]*thiophen*-1(3H)-*one* **14** (61 mg, 68%), with recovery of reactant **9** (17 mg, 20%). Compound **14** was a solid, m.p. 121–122 °C (from MeOH) (Found: C, 53.2; H, 7.4. $C_{20}H_{32}OS_5$ requires C, 53.5; H, 7.2%); ν_{max}(KBr)/cm^{-1} 2960 and 2925 (C–H), 1690 (C=O), 1505, 1455, 1420, 1365, 1165, 1145, 1090, 1010, 975, 950, 900, 835, 770 and 745; λ_{max}(hexane)/nm 257 (log ε/dm^3 mol^{-1} cm^{-1} 4.17) and 324 (3.75); δ_H 1.00 (3 H, t, *J* 7.3, CH$_2$*Me*), 1.28 (9 H, s, 3-SBu^t), 1.41 (9 H, s, 4-SBu^t), 1.49 (9 H, s, 6-SBu^t), 2.41 (1 H, dq, *J* 7.3 and 14.6, C*H*HMe) and 2.69 (1 H, tq, *J* 7.3 and 7.3, CH*H*Me); δ_C 9.47, 30.82, 31.67, 31.95, 33.65, 48.75, 49.21, 50.29, 66.54, 131.18, 134.48, 143.82, 154.71 and 185.82 (C=O); *m/z* 448 (M^+).

Reaction of Compound **1a** *with Vilsmeier Reagent*.—Phos-

phorus trichloride oxide (307 mg, 2.0 mmol) was added under nitrogen to DMF (5 cm^3) at 0 °C and the mixture was warmed to room temperature during 1.5 h. A solution of compound **1a** (100 mg, 0.20 mmol) in dichloromethane (15 cm^3) was added. After being stirred for 3.5 h, the mixture was poured into saturated aq. sodium hydrogen carbonate to undergo hydrolysis, then was extracted with dichloromethane, and the extract was dried over anhydrous sodium sulphate. The solvent was evaporated off and the residue was chromatographed on silica gel with dichloromethane as eluent to yield 3,4,6-*tris*(*t-butylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophene*-1-*carbaldehyde* **15a** as a reddish purple solid (35 mg, 40%), m.p. 174–177 °C (decomp.) (from MeOH) (Found: C, 52.5; H, 6.5. $C_{19}H_{28}OS_5$ requires C, 52.7; H, 6.5%); ν_{max}(KBr)/cm^{-1} 2910 (C–H), 1595 (C=O), 1450, 1400, 1365, 1330 and 1140; λ_{max}(MeCN)/nm 310 (log ε/dm^3 mol^{-1} cm^{-1} 4.07), 344 (3.55) and 542 (4.06); δ_H 1.38 (18 H, s, 2 × SBu^t), 1.57 (9 H, s, SBu^t) and 10.8 (1 H, s, CHO); δ_C 30.53, 30.74, 30.80, 50.90, 51.10, 51.32, 115.93, 122.30, 125.82, 139.31, 151.19, 151.28 and 178.90 (C=O); *m/z* 432 (M^+).

Reaction of Compound **1b** *with Vilsmeier Reagent.*—Phosphorus trichloride oxide (104 mg, 0.68 mmol) was added dropwise under nitrogen to stirred DMF (5 cm^3) at 0 °C. A solution of compound **1b** (200 mg, 0.46 mmol) in dichloromethane (5 cm^3) was added slowly. The mixture was stirred for 1 h at room temperature, poured into saturated aq. sodium hydrogen carbonate, and extracted with dichloromethane. The extract was dried over anhydrous sodium sulphate, concentrated and chromatographed on silica gel with dichloromethane as eluent to yield 3,4,6-*tris*(*isopropylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophene*-1-*carbaldehyde* **15b** (59 mg, 33%) as a purple solid, and 3,4-*bis*(*isopropylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophene*-1,6-*dicarbaldehyde* **16b** (22 mg, 14%) as a purple solid. Compound **15b** had m.p. 75–77 °C (decomp.) (from MeOH) (Found: C, 49.0; H, 5.8. $C_{16}H_{22}OS_5$ requires C, 49.2; H, 5.7%); ν_{max}(KBr)/cm^{-1} 2950, 2900 and 2855 (C–H), 1610 (C=O), 1445, 1410, 1345, 1295, 1280, 1250, 1160, 1105, 1090 and 1050; λ_{max}(MeCN)/nm 309 (log ε/dm^3 mol^{-1} cm^{-1} 4.14), 378 (3.62) and 580 (4.00); δ_H 1.29, 1.35 and 1.46 (each 6 H, d, *J* 6.7, SCH*Me*$_2$), 3.26, 3.37 and 3.69 (each 1 H, sep, *J* 6.7, SC*H*Me$_2$) and 10.5 (1 H, s, CHO); δ_C 22.73, 23.04, 42.11, 42.40, 44.12, 114.20, 118.53, 127.16, 146.42, 147.80, 150.42 and 177.42 (C=O); *m/z* 390 (M^+).

Compound **16b** had m.p. 151–152 °C (from MeOH) (Found: C, 48.7; H, 4.5. $C_{14}H_{16}O_2S_4$ requires C, 48.8; H, 4.7%); ν_{max}(KBr)/cm^{-1} 2900 (C–H), 1580 (C=O), 1515, 1430, 1355, 1240, 1200, 1130, 1110, 1085 and 1030; λ_{max}(MeCN)/nm 307 (log ε/dm^3 mol^{-1} cm^{-1} 4.31), 375 (3.95), 395 (3.84) and 590 (4.15); δ_H 1.59 (12 H, d, *J* 6.7, 2 × SCH*Me*$_2$), 3.70 (2 H, sep, *J* 6.7, 2 × SC*H*Me$_2$) and 10.2 (2 H, s, 2 × CHO); δ_C 22.60, 43.34, 120.16, 144.36, 150.44 and 178.52 (C=O); *m/z* 344 (M^+).

Crystal Data for Compound **16b**.—$C_{14}H_{16}O_2S_4$, *M* = 344.54. Triclinic, *a* = 11.670(2), *b* = 15.493(2), *c* = 11.594(2) Å, α = 115.52(1), β = 116.08(1), γ = 63.63(1), *V* = 1606.5 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 73 Å), space group $P\bar{1}$, *Z* = 4, D_x = 1.42 g cm^{-3}. Crystal dimensions 0.4 × 0.2 × 0.2 mm, (Mo-Kα) = 5.7 cm^{-1}.

Data Collection and Processing.—CAD4 diffractometer, ω/2θ mode with ω scan width = 0.90 + 0.35 tanθ, graphite-monochromated Mo-Kα radiation; 7339 reflections measured (1.5 < θ < 27.5°, *h*, *k*, +1), absorption correction (max., min. transmission factors = 0.999, 0.901), 4737 unique reflections with $I > 3\sigma(I)$.

Structure Analysis and Refinement.—The structure was solved by direct methods using MULTAN. Full-matrix least-squares refinement led to the final *R* (R_w)-value of 0.027 (0.036) with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic. The weighting scheme is $w = 4I/[\sigma^2(I) + (0.05I)^2]$. Calculations were carried out on a micro VAX II using the SDP package. Tables of atomic co-ordinates, bond lengths and angles, and anisotropic thermal parameters, deposited on publication of the paper cited as reference 10, are available on request from the Cambridge Crystallographic Data Centre.*

{3,4,6-*Tris*(*t-butylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophene*-1-*yl*}-*methylenemalononitrile* **17**.—A mixture of compound **15a** (50 mg, 0.12 mmol), malononitrile (9.2 mg, 0.14 mmol), and piperidine (1.0 mg, 0.012 mmol) in dry ethanol (5 cm^3) was refluxed under nitrogen for 6 h. The solvent was evaporated off and the residue was washed with methanol to give *compound* **17** as a purple solid (29 mg, 50%), m.p. 215–216 °C (from MeOH) (Found: C, 54.7; H, 6.1. $C_{22}H_{28}N_2S_5$ requires C, 55.0; H, 5.9%); ν_{max}(KBr)/cm^{-1} 2950 (C–H), 2210 (C≡N), 1540 (C=C), 1390, 1365, 1320, 1300, 1200 and 1155; λ_{max}(MeCN)/nm 322 (log ε/dm^3 mol^{-1} cm^{-1} 4.10), 409 (3.83), 428 (3.92) and 658 (4.23); δ_H 1.38, 1.40 and 1.70 (each 9 H, s, SBu^t) and 9.17 (1 H, s, CH=); *m/z* 480 (M^+).

Ethyl 2-*Cyano*-3-{3,4,6-*tris*(*t-butylthio*)-2λ^{4}δ^2-*thieno*[3,4,*c*]-*thiophen*-1-*yl*}*acrylate* **18**.—A mixture of compound **15a** (50 mg, 0.12 mmol), ethyl cyanoacetate (17 mg, 0.14 mmol) and piperidine (1.0 mg, 0.012 mmol) in dry ethanol (5 cm^3) was stirred under nitrogen at 60 °C for 80 h. The solvent was evaporated off and the residue was chromatographed on silica gel with dichloromethane as eluent to give unchanged reactant **15a** (25 mg, 50% recovery) and *compound* **18** as a purple solid (25 mg, 40%), m.p. 160–162 °C (from MeOH) (Found: C, 54.8; H, 6.5; N, 2.8. $C_{24}H_{33}NO_2S_5$ requires C, 54.6; H, 6.3; N, 2.7%); ν_{max}(KBr)/cm^{-1} 2950, 2915 and 2850 (C–H), 2200 (C≡N), 1710 (C=O), 1550 (C=C), 1365, 1240, 1150, 1105, 1055, 755 and 700; λ_{max}(MeCN)/nm 315 (log ε/dm^3 mol^{-1} cm^{-1} 4.14), 427 (3.75) and 587 (4.28); δ_H 1.38 (3 H, t, *J* 7.3, CH_2*Me*), 1.39, 1.40 and 1.63 (each 9 H, s, SBu^t), 4.34 (2 H, q, *J* 7.3, SCH_2Me) and 9.86 (1 H, s, CH=); *m/z* 527 (M^+).

{6-*Formyl*-3,4-*bis*(*isopropylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophen*-1-*yl*}*methylenemalononitrile* **19** and {3,4-*Bis*(*isopropylthio*)-2λ^{4}δ^2-*thieno*[3,4-c]*thiophene*-1,6-*diyl*}*dimethylenebimalononitrile* **20**.—A solution of piperidine (2.5 mg, 0.029 mmol) in degassed ethanol (5 cm^3) was added under nitrogen to a mixture of compound **16b** (100 mg, 0.29 mmol) and malononitrile (48 mg, 0.73 mmol) in degassed ethanol (25 cm^3). The mixture was stirred at 30 °C for 66 h and the solvent was evaporated off under reduced pressure. The residue was chromatographed on silica gel with dichloromethane as eluent to give *compound* **19** (43 mg, 38%) as a green solid, and *compound* **20** (66 mg, 52%) as a yellow solid.

For *compound* **19**: m.p. 194.5–195.5 °C (from MeOH) (Found: C, 52.1; H, 4.0; N, 7.1. $C_{17}H_{16}N_2OS_4$ requires C, 52.0; H, 4.1; N, 7.1%); ν_{max}(KBr)/cm^{-1} 2925 (C–H), 2215 (C≡N), 1630 (C=O), 1535 (C=C), 1495, 1395, 1370, 1335, 1235, 1150, 1110, 1065, 1040, 950, 865 and 765; λ_{max}(MeCN)/nm 244 (log ε/dm^3 mol^{-1} cm^{-1} 4.30), 322 (4.60), 401 (3.80), 460 (4.33) and 647 (4.31); δ_H 1.62 and 1.63 (each 6 H, d, *J* 6.7, SCH*Me*$_2$), 3.74 and 3.81 (each 1 H, sep, *J* 6.7, SC*H*Me$_2$), 9.43 (1 H, s) and 9.54 (1 H, s); *m/z* 392 (M^+).

For compound **20**: m.p. 201–202 °C (from MeOH) (Found: C, 54.8; H, 3.5; N, 12.5. $C_{20}H_{16}N_4S_4$ requires C, 54.5; H, 3.7; N, 12.7%); ν_{max}(KBr)/cm^{-1} 2215 (C≡N), 1555 (C=C), 1510, 1490, 1410, 1355, 1335, 1275, 1230, 1205, 1155, 1130, 1110, 1055, 1010, 980, 920, 875, 850, 790, 740 and 690; λ_{max}(MeCN)/nm 266 (log ε/dm^3 mol^{-1} cm^{-1} 4.20), 324 (4.24) and 435 (4.51); δ_H 1.25, 1.36,

* *Supplementary data*: see 'Instructions for Authors,' section 5.6.3, *J. Chem. Soc., Perkin Trans. 1*, 1991, issue 1.

1.51 and 1.55 (each 3 H, d, *J* 6.7, SCH*Me*Me), 3.14 and 3.71 (each 1 H, t, *J* 6.4, SC*H*Me_2) and 7.86 and 8.00 (each 1 H, s, CH=); *m/z* 440 (M^+).

3,4-*Bis*(*isopropylthio*)-2$\lambda^4\delta^2$-*thieno*[3,4-c]*thiophene*-1,6-*dicarbaldehyde* 1-*Dimethylhydrazone* **21**.—A solution of UDMH (35 mg, 0.58 mmol) in degassed ethanol (5 cm^3) was added under nitrogen to a solution of compound **16b** (80 mg, 0.23 mmol) in degassed ethanol (25 cm^3). After being stirred at 40 °C for 12 h, the mixture was evaporated under reduced pressure. The residue was chromatographed on silica gel with dichloromethane–ethyl acetate (9:1) as eluent to give *compound* **21** (56 mg, 62%) as a green oil (Found: C; 49.7; H, 5.9; N, 7.3. $C_{16}H_{22}N_2OS_4$ requires C, 49.7; H, 5.7; N, 7.2%); ν_{max}(neat)/cm^{-1} 2880, 2860 and 2830 (C–H), 1615 (C=O), 1540 (C=C), 1505, 1460, 1440, 1415, 1375, 1350, 1240, 1210, 1140, 1110, 1070, 1050, 1030, 995, 885, 820, 780 and 750; λ_{max}(MeCN)/nm 289 (log ε/dm^3 mol^{-1} cm^{-1} 4.41), 396 (3.95) and 648 (3.97); δ_H 1.32 and 1.54 (eachs 6 H, d, *J* 6.7, SCH*Me*$_2$), 3.04 (6 H, s, NMe_2), 3.31 and 6.7 (each 1 H, sep, *J* 6.7, SC*H*Me_2), 8.38 (1 H, s) and 9.63 (1 H, s); *m/z* 386 (M^+).

Acknowledgements

This work was supported by Grant-in Aid for Scientific Research on Priority Areas No. 02230226 from the Ministry of Education, Science and Culture, Japanese Government.

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Paper 0/04534I
Received 24*th October* 1990
Accepted 10*th December* 1990