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# AROMATIC ANNULATION WITH NAPHTHO[1,8-de]-1,3-DITHIIN CARBOCATIONS

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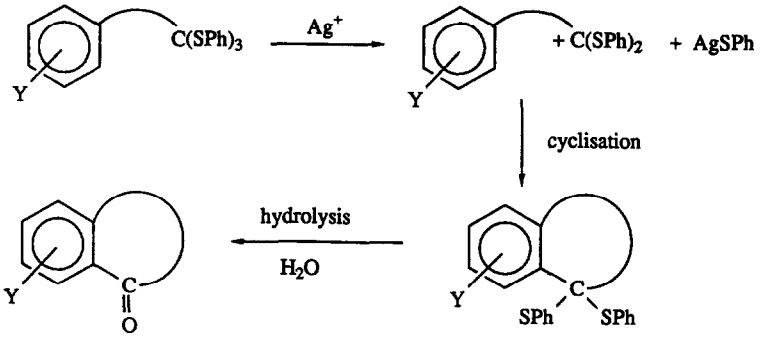
**ABSTRACT** - The title carbocations have been produced by the reaction of silver trifluoromethanesulfonate with mixed orthothioesters. Intramolecular aromatic electrophilic substitution (annulation) of the cationic intermediates proceeds readily and provides an efficient, chemoselective route for appending six-membered rings to nonactivated aromatic systems.

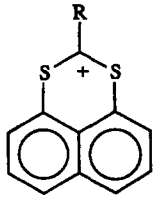
We have previously reported[1] that aromatic annulations involving bisphenylthiocarbocations and activated aromatic systems can be acheived with high efficiency.




Chemospecific cation formation using a suspension of silver trifluoromethanesulfonate (triflate) in dichloromethane was a feature of this sequence, however application to nonactivated aromatic systems gave less favourable results. This paper reports efforts to improve the yields of cyclisation product with less activated systems using modified bisarylthiocarbocations.

Studies[2] of the silver ion-induced formation of thiocarbocations and their subsequent reactions have shown that arylthiocarbocations are generally more effective than their alkyl counterparts. Consideration of suitable

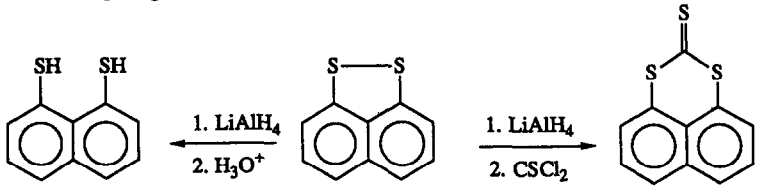
arylthio systems with reduced steric requirements to those of bisphenylthiocarbocations lead to this investigation of the preparation and reactions of the 1,8-naphthalenedithio substituted cations **1**. The formation and proton nuclear magnetic resonance ($^1$H n.m.r.) spectrum of 2-methylnaphtho[1,8-de]-1,3-dithiin cation **1** (R = Me) in 96% sulfuric acid has been reported previously[3] however, to our knowledge, studies of the reactivity of these species has not appeared before.



**1**

## PREPARATION OF CYCLISATION PRECURSORS

Preparation of suitable substrates for cyclisation (**2-10**) required an adequate supply of 1,8-naphthalenedithiol **11** which was available by reduction of naphtho[1,8-cd]-1,2-dithiole **12** (Scheme I). The disulfide **12** is a well known compound[4] and has been produced by various synthetic sequences. The need for appreciable amounts of **11** from readily available starting materials prompted a brief review of the various published methods. Despite several modifications of the literature procedure[5] the preparation of **12** from 8-amino-1-naphthalene sulfonic acid gave only modest return for the effort. In an alternative approach, reaction of 1,8-dichloronaphthalene (**13**) with disodium disulfide gave **12** in 47% yield[6]. A recent report[7] of the direct conversion of **13** to **12** with sodium benzylthiolate also appears attractive. However the difficulty with both of these routes is in obtaining the required reactant **13**. The dichloride **13** is prepared[8], in a capricious reaction from 1,8-diaminonaphthalene (**14**) *via* a very sensitive tetrazonium salt. Conversion of **14** to 1,8-diiodonaphthalene (**15**) is a much more amenable reaction[9], however displacement of the iodine in **15** by sulfur nucleophiles did not proceed well. Ultimately, **15** did provide the most convenient route to **12** by treatment of 1,8-dilithionaphthalene, produced from **15** by metal-halogen exchange, with elemental sulfur.[10] A recent report[11] of the facile preparation of **15** by bisiododecarboxylation of the readily available 1,8-naphthalene dicarboxylic acid makes this approach even more attractive. Naphtho[1,8-de]-1,3-dithiin-2-thione **16** was also required for substrate preparation and this material was obtained by treating the reduction mixture of **12** directly with thiophosgene[6] (Scheme I).

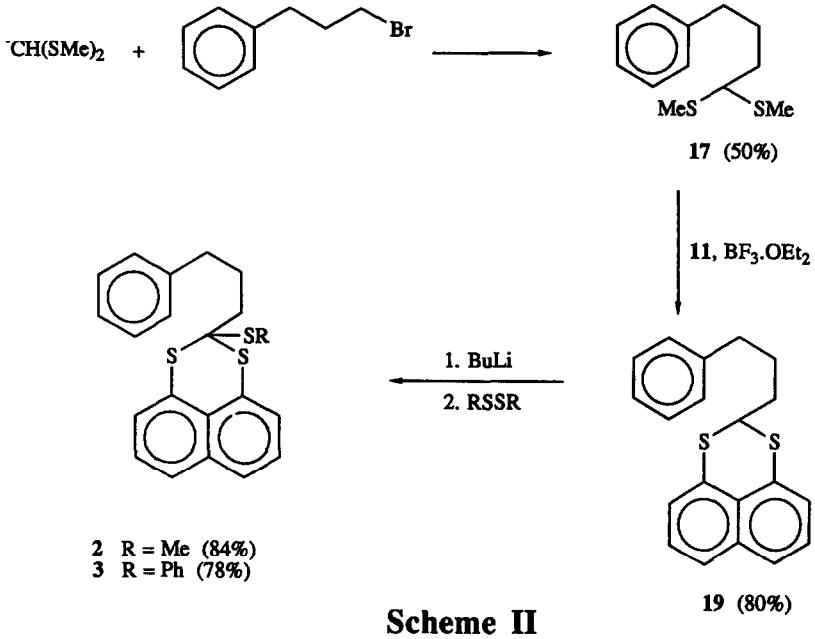



**11** **12** **16**

**Scheme I**

Two general sequences were adopted to produce the required selection of compounds. The major synthetic approach was to utilise the observed proclivity[12] of **11** towards cyclic thioacetal formation by virtue of the *peri* positioned sulfur atoms, and react **11** with acyclic bisalkylthioacetals, α-chlorophenylthio ethers or aldehydes. The third sulfur function was then introduced by deprotonation of the thioacetal followed by sulfenation with an appropriate disulfide. The second route, which involved reaction of the appropriately substituted trithiocarbanions with a primary alkyl iodide, was used in some situations when the requisite carbanion was readily prepared and amenable to alkylation.

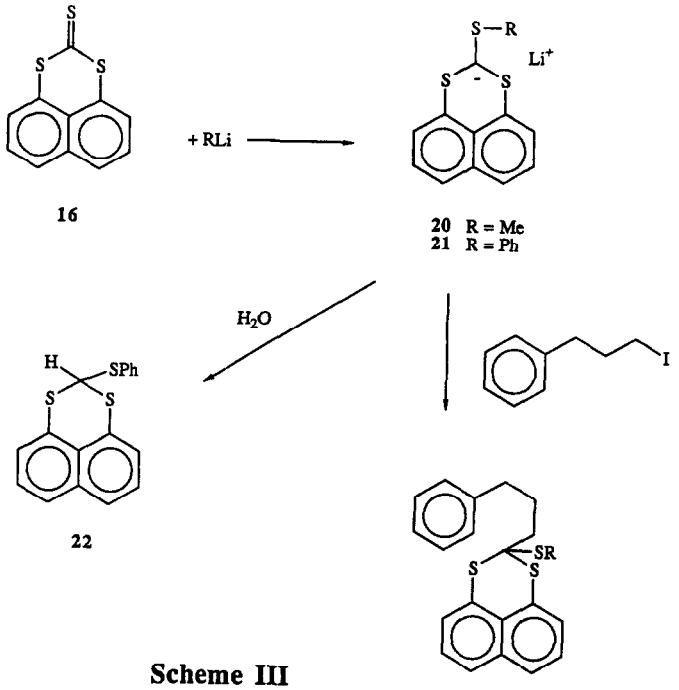
The synthesis of **2** and **3** from 1-bromo-3-phenylpropane is outlined in Scheme II. Displacement of the bromine with bis(methylthio)methyl anion gave the thioacetal **17**. Interestingly, reaction of 2-lithionaphtho[1,8-de]-1,3-dithiin (**18**) with various alkyl halides gave unsatisfactory returns. Thioacetal exchange of **17** with **11** to give **19** proceeded well and the final sulfur functionality could be introduced readily by treatment of **19** with butyllithium followed by the appropriate disulfide.



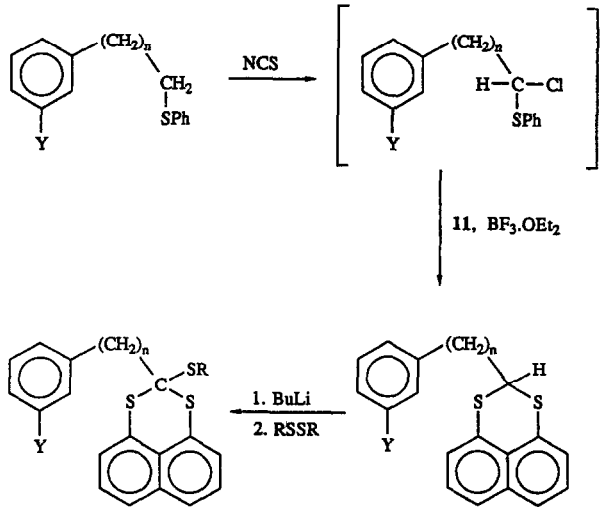

**Scheme II**

An alternative synthesis of **2** was also achieved by alkylating the carbanion **20** with 1-iodo-3-phenylpropane (Scheme III). The requisite anion **20** was produced by the addition of methyllithium to the thiocarbonyl sulfur of the trithiocarbonate **16** under conditions which minimised undesired dimerisation reactions.[13] The comparable reaction with phenyllithium was unsuccessful although the anion **21** was clearly formed as, after hydrolysis, 2-phenylthionaphtho[1,8-de]-1,3-dithiin (**22**) could be isolated in high yield. Reaction of **16** with 2-thienyllithium (Scheme III) was moderately successful and sufficient amounts of the required alkylated product, **4**, could be obtained for study.

Compounds **6-10** were prepared by the general sequence outlined in Scheme IV. The phenyl alkyl thioethers were obtained either by halide displacement with sodium thiophenoxide (for **6**, **7**, **8**) or by the regioselective free radical addition of thiophenol to monosubstituted alkenes[14] (for **9** and **10**). Reaction of the phenyl alkyl thioethers with N-chlorosuccinimide[15] produced unstable α-chlorothioethers which were promptly treated with **11** in the presence of boron trifluoride etherate to provide the stable thioacetals in acceptable yields. Deprotonation followed by sulfenylation as described previously (Scheme II) gave the required compounds.




**Scheme III**




6 n = 2, Y = H, R = Me
7 n = 2, Y = H, R = Ph
8 n = 2, Y = OMe, R = Ph
9 n = 4, Y = H, R = Ph
10 n = 5, Y = H, R = Ph

**Scheme IV**

The preparation of **5** involved the thioacetalisation of the aldehyde, dimethoxyacetal mixture obtained from ozonolysis of 4,4-dimethyl-5-phenyl-1-pentene **23**. Routine deprotonation of the thioacetal **24** followed by sulfenylation completed this synthesis.

## CYCLISATION STUDIES

The cyclisation reactions were carried out by reacting the various substrates with silver triflate in dichloromethane. In contrast to the reactions involving tris(phenylthio)orthoesters[1], the initial thioacetal cyclisation product could be isolated and identified. It was ascertained by separate experiments that hydrolysis of the thioacetals to cyclic ketones did not take place to any significant extent under the reactions conditions nor during product isolation. The formation of a naptho[1,8-de-]-1,3-dithiin carbocation was indicated by the production of a characteristic blue colour in the reaction solutions and utilisation of all the cation was indicated by a solution colour change from blue to yellow. This colouration had been noted previously[3]. A summary of the results are presented in the Table.

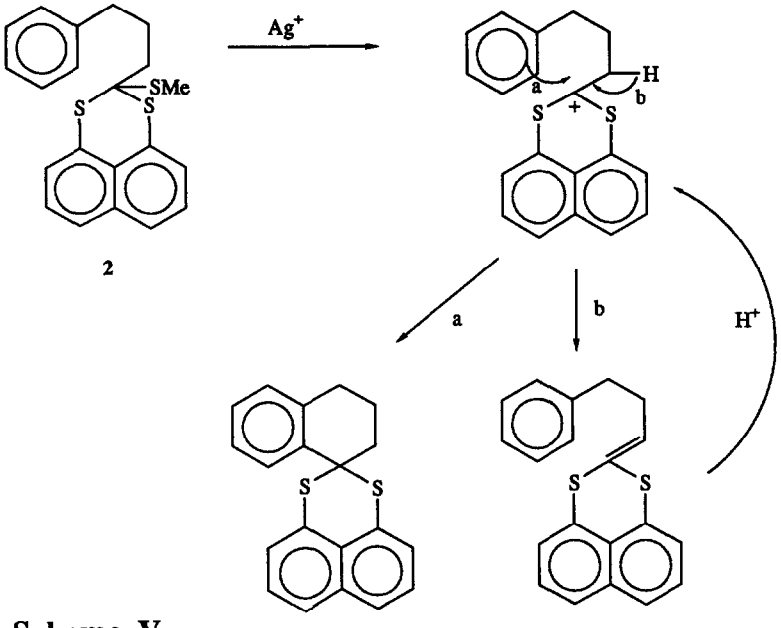
**TABLE**

**Silver Triflate Induced Formation and Reactions of Naphtho[1,8-de]-1,3-dithiin Carbocations in Dichloromethane**

| Entry | Substrate | AgOTf [a]/ equiv | Time[b] for consumption of substrate | Time[b] for reaction | Products | Yield/% |
|---|---|---|---|---|---|---|
| 1 | **2** | 3 | 1 | 1 | **25 + 26** | 31, 31 |
| 2 | **2** | 3 | 1 | 18 | **25** | 65 |
| 3 | **3** | 3 | 1 | 18 | **25** | 80 |
| 4 | **3** | 3,+1 eq HOTf | 1 | 18 | **25** | 56 |
| 5 | **3** | 1.1 | 3 | 48 | **25** | 70 |
| 6 | **3** | 3[c] | 0.17 | 2 | **25** | 81 |
| 7 | **3** | 1.1[c] | 0.25 | 3 | **25** | 91 |
| 8 | **4** | 3 | 0.75 | 18 | **25** | 63 |
| 9 | **5** | 3 | 0.15 | 4 days | **28** | 46 |
| 10 | **6** | 3 | 0.5 | 0.5 | **29** | [e] |
| 11 | **7** | 3 | 1 | 6 days | [d] | - |
| 12 | **7** | 3[c] | 0.17 | 3 days | [d] | - |
| 13 | **8** | 3 | 1 | 28 | **30** | 34 |

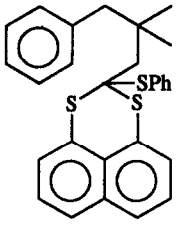
[a] reaction at room temperature unless stated otherwise
[b] in hr unless stated otherwise
[c] refluxing dichloromethane (38°C)
[d] mixture of products
[e] the only product identified by $^1$H n.m.r.

Initial studies on the cyclisation of **2** were carried out at room temperature. Thin layer chromatography (t.l.c.) examination of the reaction solution after 1 hr indicated that all the starting material had been consumed and workup of the blue solution at this stage gave 1:1 mixture of thioacetal **25** and ketenethioacetal **26** (entry 1). The noncyclised product, **26**, presumably results from proton elimination from the intermediate carbocation during the workup (Scheme V). Treatment of this mixture of **25** and **26** in $CD_2Cl_2$ with triflic acid rapidly reformed the carbocation as shown by $^1H$ n.m.r. Further $^1H$ n.m.r. examination of this reaction mixture after 18 hr showed that **25** was now the major component of the reaction mixture. The characteristic blue colour had disappeared by this time. Subsequently, reaction of **2** for 18 hr gave **25** in 65% yield (entry 2).




**Scheme V**

Reaction of **3** with 3 equivalents of silver triflate gave **25** in 80% yield after stirring 18 hr (entry 3). This result compares favourably with the corresponding reaction involving the -SMe leaving group (entry 2). The rates of consumption of **2** and **3** were approximately the same under the same reaction conditions, indicating that the rate determining step was the second step in the reaction and hence should not depend upon the nature of the thio leaving group. Previous work on the cyclisation of 1,3-dithiane-based orthothioesters has also shown little difference between -SMe and -SPh leaving groups[2]. An explanation of the albeit small, but real difference in yield in the cyclisation of **2** and **3** does not appear obvious at this stage. Notwithstanding this uncertainty further refinement of the cyclisation protocol was carried with **3**. Reaction of **3** with silver triflate in the presence of 1 equivalent of triflic acid (entry 4) for 18 hr gave only 56% of the cyclised product **25**. This result indicates that the reaction was probably not proceeding via **26** and, in fact, acid was decreasing the efficiency of the process.

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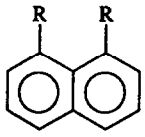
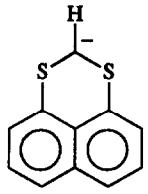



13 R = Cl
14 R = $NH_2$
15 R = I

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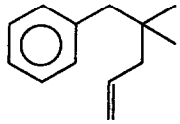

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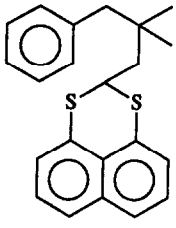


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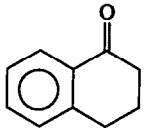


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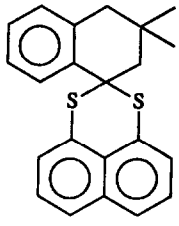


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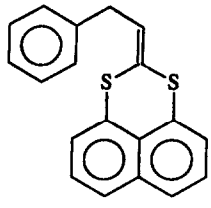


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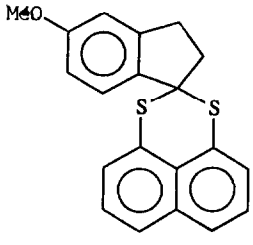


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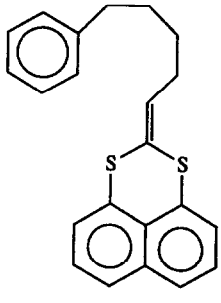



31

Reactions using 3 equivalents of silver triflate were carried out for comparison with previous work[1] using tris(phenylthio)orthoesters. However the stoichiometric demand for production of the thioacetal **25** is for only one equivalent of Lewis acid. Reaction of **3** with 1.1 equivalents of silver triflate at room temperature (entry 5) gave **25** in 70% yield but required stirring for 48 hr to completely consume the blue carbocation. Presumably the lowered amount of Lewis acid available compared with entry 3 reduced the availability of the cation and hence slowed the cyclisation process. These extended reaction times were considered to be detrimental to high efficiency, so in order to increase the rate of reaction experiments were run in refluxing dichloromethane solution. Reaction of **3** with 3 equivalents of silver triflate at reflux temperature (entry 6) resulted in the consumption of **3** after only 10 min and **25** was isolated in 81% yield after 2 hr when the blue cation colour had gone. Similar reaction with 1.1 equivalents of silver triflate (entry 7) gave **25** in 91% yield after 3 hr and represented the highest yield achieved for this reaction. For comparison the related tris(phenylthio)orthoester cyclisation[1] gave 1-tetralone (**27**) in only 54% yield after 15 hr.

Efforts to increase the reactivity of the system by rapid complete production of the isolated cation from **3** using the more reactive[16] thiophilic Lewis acid dimethylmethylthiosulfonium tetrafluoroborate (DMTSF) produced only complex mixtures which did not contain **25**, **26** or **27**. The familiar blue solution was obtained but the colour was retained even after stirring for 48 hr. The effect of copper(I) as the thiophilic Lewis acid for this reaction was also examined using tetrakis(acetonitrile)copper(I) tetrafluoroborate in dichloromethane. All of the starting material **3** was consumed after 5 hr at room temperature but ketene thioacetal **26** was the major product even after 18 hr reaction. A preference for elimination over cyclisation using copper(I) salts in conjunction with acetonitrile has been noted previously[17].

The 2-thienylthio group has been used as a possible bidentate ligand for copper(I) ions[18]. Substrate **4** was selected in order to examine if the possible bidentate binding ability of the 2-thienylthio moiety would assist $Ag^+$ in rapidly producing the required cationic intermediate. Reaction of **4** with 3 equivalents of silver triflate (entry 8) gave **25** in 63% yield after 18 hr. The formation of the thiocarbocation was complete in 45 min signalling some enhanced leaving ability over simple SR groups, however the lower yield of **23** in this reaction compared with -SPh as leaving group (entry 3) indicated no advantage using the more complex thio substituent.

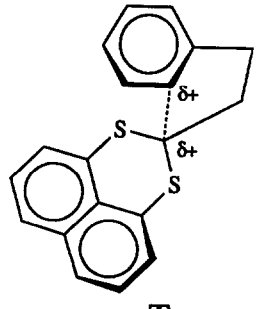
The influence of suitably positioned *gem*-dimethyl groups in increasing cyclisation efficiencies by favouring certain acyclic conformations has been well documented[19]. This effect was examined with **5**. Complete loss of **5** was observed after stirring for 30 min at room temperature with 3 equivalents of silver triflate (entry 9) and **28** was isolated in 46% yield after stirring 4 days. Although the cyclisation did occur, the reaction was significantly slower than for **3** and, as noted previously, the yield is significantly reduced - presumably by side reactions - during these extended reaction periods. This result indicated that conformational effects did indeed play a significant part in this reaction but a wider consideration of all the conformational factors was required. This feature was made more apparent in experiments designed to produce five, seven

and eight membered rings.

The utility of the naphtho[1,8-de]-1,3-dithiin carbocation in producing five membered rings was examined with **6** and **7**. Reaction of **6** with 3 equivalents of silver triflate (entry 10) gave only ketene thioacetal **29** after stirring 30 min at room temperature. The $^1$H n.m.r. spectrum confirmed the proposed structure of **29**, in particular a 2-proton doublet at δ 3.77 assigned to the benzylic protons and a 1-proton triplet at δ 6.53 assigned to olefinic proton were deemed significant. The effect of a thiophenyl leaving group was examined with the substrate **7**. Reaction of **7** with 3 equivalents of silver triflate at room temperature was complete after 1 hr however the blue solution colour finally faded after 6 days. A complex mixture of unidentified compounds was obtained. As previously noticed with **2** (entry 1), workup of the blue solution led to the isolation of the corresponding elimination product **29**. Reaction of **7** with 3 equivalents of silver triflate in refluxing dichloromethane was examined (entry 12) and the starting material was found to have completely reacted after 10 min. Again a complex mixture of products was obtained after the blue colour had gone (3 days). It therefore appeared that the carbocation was indeed being formed in the reaction medium but for some reason the intramolecular reaction did not ensue and, after an extended period, the carbocation decomposed to give a mixture of products. Sufficient electronic impetus for cyclisation was provided by activating the aromatic ring with a methoxy group *viz* **8**. Reaction of **8**, with 3 equivalents of silver triflate at room temperature slowly produced the cyclised product **30** in 34% yield (entry 13). This yield was lower than that obtained[1] from the related tris(phenylthio)orthoester (59%).

An explanation for this reactivity difference between the thiocarbocations towards five membered ring formation can be advanced based on the examination of the molecular models of the transition state for cyclisation. The model derived from **8** appears to require significantly more energy to adopt the appropriate conformation for orbital overlap with the aromatic pi-system compared with the related bis(phenylthio)cation. The transition state conformation has less flexibility as a spiro carbon skeleton **T** is required.

Similar results were obtained from attempts to make medium sized rings with **9** and **10**. The cations could be readily created but cyclisation was inhibited and the only recognisable products after extended reaction times was the ketene thioacetals e.g. **31** derived by proton elimination.




**T**

## CONCLUSION

The naphtho[1,8-de]-1,3-dithiin carbocation thus proved to be readily prepared and an excellent reaction intermediate for intramolecular aromatic cyclisation to create six membered rings. These compounds, based on 1,8-disubstituted naphthalene, were clearly more efficient than acyclic aryl orthothioesters in this regard. However, application to five, seven and eight membered ring formation were less successful for reasons which may be related to the conformational rigidity of the fused heterocyclic cation. Futher studies with more flexible aryl dithiols are presently being undertaken to clarify this point.

## EXPERIMENTAL

General experimental conditions have been described previously.[1]

Radial chromatography was performed using a "Chromatotron" model 7924 (Harrison Research, Palo Ato, USA) preparative centrifugal thin layer chromatograph on 1, 2 and 4 mm silica gel layers, prepared according to the manufacturers' instructions. Solvents were delivered by gravity feed. All crude samples were pretreated by passing through a short silica gel column (~ 5g) in ether or dichloromethane prior to application to the Chromatotron plate. Eluting bands were observed under ultraviolet light.

*Naphtho[1,8-cd]-1,2-dithiole[6] 12*

(a) [6]A mixture of sodium metal (0.575 g, 25 mmol) and sulfur (0.800 g; 25 mmol) in hexamethylphosphoramide (50 ml) was stirred for 1 hr at 110°C. To the resultant blue solution was added 1,8-dichloronaphthalene[8] **13** (1.97 g; 10 mmol) and the stirring was continued at 150°C under argon for 24 hr. After cooling to room temperature a solution of saturated sodium chloride (100 ml) was added and the product was extracted with ether (3 x 50 ml). The combined organic extract was washed with distilled water (3 x 30 ml), dried ($MgSO_4$) and solvents were evaporated to give a crude product (1.3 g) which recrystallised from hexane to give naphtho[1,8-cd]-1,2-dithiole **12** (0.893 g; 47%); m.p. 120°C (Lit[6] 123°C).

(b) [10]A solution of BuLi in hexane (62.5 ml; 100 mmol) was added over 15 min to a solution of 1,8-diiodonaphthalene[9] **15** (13.99 g, 50 mmol) in tetrahydrofuran (200 ml) at -78°C under nitrogen. After stirring 1.6 hr elemental sulfur (3.2 g, 100 mmol) was added and stirred 45 min by which time all the sulfur had dissolved. The mixture was quenched by addition of saturated ammonium chloride (50 ml) and warmed to room temperature. Air was passed through this mixture for 2 hr, then it was diluted with dichloromethane (300 ml) and the organic layer was separated washed with water (100 ml) saturated sodium chloride (100 ml) and dried ($MgSO_4$). Evaporation of solvents gave a crude product (10 g), which was purified by chromatography on a silica gel column (300 g) with hexane to give **12** (4.0 g, 42%).

*1,8-Naphthalenedithiol 11*

To a solution of naphtho[1,8-cd]-1,2-dithiole **12** (0.190 g; 1 mmol) in dry ether (10 ml), was added lithium aluminium hydride (0.038 g; 1 mmol). The mixture was refluxed for 30 min, during which time the colour of the solution changed from orange red to colourless. After cooling to room temperature excess lithium aluminium hydride was destroyed with aqueous 10% hydrochloric acid (20 ml) and the product was extracted with ether (2 x 10 ml). The ethereal solution was dried ($MgSO_4$) then evaporated to give a crude product (0.190 g) which recrystallised from tetrahydrofuran/hexane to give 1,8-naphthalenedithiol **11** (0.185 g, 96%) as white shiny plates m.p.120-121°C (Lit[6] 122°C).

*Naphtho[1,8-de]-1,3-dithiin-2-thione 16*

To a solution of naphtho[1,8-cd]-1,2-dithiole **12** (0.190 g; 1 mmol) in dry ether (10 ml) was added lithium aluminium hydride (0.038 g; 1 mmol). The mixture was refluxed for 10 min then thiophosgene (0.15 ml; 2 mmol) was added and the refluxing was continued for 10 min. The reaction mixture was stirred at room temperature overnight, then poured into a solution of 10% ammonium chloride (30 ml) and extracted with dichloromethane (2 x 10 ml). The combined extract was washed with 10% hydrochloric acid (15 ml) then

filtered through a 15 cm silica gel column with dichloromethane. Evaporation of the solvents gave a crude crystalline product (0.150 g), which recrystallized from benzene/hexane to give **16** (0.108 g; 49%); m.p. 196°C (Lit[6] 201-202°C); I.r. (KBr) $\nu_{max}$ 1040 $cm^{-1}$ (C=S).

*1,1-Bis(methylthio)-4-phenylbutane 17*

A solution of BuLi in hexane (3.4 ml; 5 mmol) was added to a stirred solution of bis(methylthio)methane (0.5 ml; 5 mmol) in dry tetrahydrofuran (20 ml) at -78°C under nitrogen. After stirring 45 min, a solution of 1-bromo-3-phenylpropane (0.995 g; 5 mmol) in tetrahydrofuran (5 ml) was added. The mixture was then stirred for further 4 hr at -78°C. Work up as usual gave a crude product (1.20 g) which was separated on a Chromatotron. Elution with 1:9 dichloromethane/hexane gave pure **17** (0.570 g; 50%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.73-1.92 (m, 4H, $-CH_2-$), 2.06 (s, 6H, $-S-CH_3$), 2.63 (t, J = 7.25 Hz, 2H, $-CH_2-Ph$), 3.64 (t, J = 6.94 Hz, 1H, $-C\underline{H}(SCH_3)_2$), 7.15-7.31 (m, 5H, aromatic). (Found: C, 63.2; H, 8.4. $C_{12}H_{18}S_2$ requires C, 63.7; H, 8.0%).

*2-(3-Phenylpropyl)-naphtho[1,8-de]-1,3-dithiin 19*

A solution of 1,1-bis(methylthio)-4-phenylbutane **17** (0.226 g; 1 mmol) in dry dichloromethane (3 ml) was added to a stirred solution of 1,8-naphthalenedithiol (0.192 g; 1 mmol) and 2 drops of $BF_3.OEt_2$ in dry dichloromethane (10 ml) at room temperature under nitrogen. After stirring overnight at room temperature under nitrogen the reaction mixture was poured into cold water (100 ml) extracted with dichloromethane (3 x 10 ml). The combined extracts were washed with 10% sodium hydroxide then water and dried ($MgSO_4$). Evaporation of the solvents gave a crude product (0.383 g) which was filtered through a short silica gel column in dichloromethane and separated on a Chromatotron. Elution with 3:17 dichloromethane/hexane gave pure **19** (0.283 g; 88%); m.p. 124-125°C; $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.94-2.07 (m, 4H, $-CH_2-CH_2-$), 2.67 (t, J = 7.20 Hz, 2H, $-CH_2-Ph$), 4.32 (t, J= 6.81 Hz, 1H, $-CH(-S-)_2$), 7.17-7.43 (m, 9H, aromatic), 7.65 (d, J = 8.05 Hz, 2H, aromatic). (Found: C, 74.3; H, 5.3; S, 19.9. $C_{20}H_{18}S_2$ requires C, 74.5; H, 5.6; S, 19.9%).

*2-Methylthio-2-(3-phenylpropyl)-naphtho[1,8-de]-1,3-dithiin 2*

(a) A solution of BuLi in dry hexane (1.7 ml; 2.5 mmol) was added to a stirred solution of 2-(3-phenylpropyl)-naphtho[1,8-de]-1,3-dithiin **19** (0.807 g; 2.5 mmol) in dry tetrahydrofuran (30 ml) at -78°C under nitrogen. After stirring 45 min, deuteration of an aliquot followed by $^1$H n.m.r. examination showed anion formation was complete so a solution of dimethyl disulfide (0.282 g; 3 mmol) in dry tetrahydrofuran (3 ml) was added. The yellow mixture rapidly became colourless. The mixture was stirred for 4 hr at -78°C under nitrogen. Work up as usual gave a crude product (0.932 g), which was separated on a Chromatotron. Elution with 1:9 dichloromethane/hexane gave pure **2** (0.771 g; 84%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 2.10 (s, 3H, $-SCH_3$), 2.05-2.15 (m, 2H, $-CH_2-$), 2.21-2.24 (m, 2H, $-CH_2-$) 2.69 (t, J = 7.50 Hz, 2H $-CH_2-Ph$), 7.10-7.40 (m, 9H, aromatic) 7.65-7.69 (m, 2H, aromatic). Despite several attempts, satisfactory analytical data could not be obtained for this compound.

(b) [13]A solution of naphtho[1,8-de]-1,3-dithiin-2-thione **16** (0.458 g; 2 mmol) in tetrahydrofuran (30 ml) was added slowly to a stirred solution of methyllithium (6 ml; 6 mmol) in tetrahydrofuran (5 ml) at -78°C under nitrogen. After stirring 30 min a solution of 1-iodo-3-phenylpropane (0.492 g; 2 mmol) in tetrahydrofuran (3 ml) was added and stirring was continued for a further 1 hr. The reaction mixture was worked up as usual to give a crude product (0.7 g) which was chromatographed on a column of silica gel. Elution with 3:7 dichloromethane/hexane gave **2** (0.60 g; 82%).

*2-(3 Phenylpropyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin 3*

A solution of BuLi in dry hexane (0.7 ml; 0.88 mmol) was added to a stirred solution of 2-(3-phenylpropyl)-naphtho[1,8-de]-1,3-dithiin **19** (0.283 g; 0.88 mmol) in dry tetrahydrofuran (10 ml) at -78°C under nitrogen. After stirring 45 min a solution of diphenyl disulfide (0.191 g; 0.88 mmol) in dry tetrahydrofuran (3 ml) was added. The mixture was stirred for further 5 hr at -78°C under nitrogen and work up as usual gave a crude product (0.407 g). Recrystallization from ethanol gave pure **3**, (0.293 g; 78%); m.p. 122-123°C; $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 2.13-2.31 (m, 4H, $-CH_2-CH_2-$), 2.68 (t, J = 7.02 Hz, 2H, $-CH_2-Ph$), 7.19-7.40 (m, 14H, aromatic), 7.69-7.72 (m, 2H, aromatic). (Found: C, 72.8; H, 4.9; S, 22.6. $C_{26}H_{22}S_3$ requires C, 72.6; H, 5.1; S, 22.3%).

*2-(3-Phenylpropyl)-2-(2-thienylthio)-naphtho[1,8-de]-1,3-dithiin 4*

A solution of BuLi in dry hexane (3.3 ml; 5 mmol) was added to a stirred solution of thiophene (0.41 ml; 5.1 mmol) in dry tetrahydrofuran (10 ml) at -78°C under nitrogen. The mixture was stirred for 30 min at -78°C, 30 min at -20°C and then recooled to -78°C. A solution of **16** (0.234 g; 1 mmol) in dry tetrahydrofuran (10 ml) was added slowly over 1 hr. After stirring 1 hr at -78°C a solution of 1-iodo-3-phenylpropane (0.246 g; 1 mmol) in tetrahydrofuran (3 ml) was added and the mixture was stirred for a further 20 min. Work up as usual gave a crude product (0.449 g), which was chromatographed on silica gel. Elution with 1:9 dichloromethane/hexane gave pure **4** (0.161 g; 37%); m.p. 99-100°C; $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 2.21-2.33 (m, 4H, $-CH_2-CH_2-$), 2.72 (t, 2H, $-CH_2-Ph$), 6.83-7.73 (m, 14H, aromatic). (Found: C, 66.3; H, 4.6; S, 29.4. $C_{24}H_{20}S_4$ requires C, 66.1; H, 4.6; S, 29.4%).

*3-Phenyl-1-phenylthiopropane*

A solution of thiophenol (2.6 ml; 0.025 mol) in dry dimethyl formamide (10 ml) was added dropwise to a stirred suspension of sodium hydride (50% oil dispersion) (1.2 g; 0.025 mol) in dry dimethyl formamide (10 ml) at room temperature under nitrogen. A solution of 1-bromo-3-phenylpropane (4.98 g; 0.025 mol) in dimethyl formamide (10 ml) was added after all the sodium hydride had reacted (1 hr). After stirring for a further 1 hr, a saturated solution of aqueous ammonium chloride (50 ml) was added and the product was extracted with ether (2 x 50 ml). The combined extracts were washed with water, 5% sodium hydroxide, water then dried ($MgSO_4$). Evaporation of solvents in vacuuo gave a crude product (5.1 g) which was separated on a silica gel column with 3:17 dichloromethane/hexane to give pure 3-phenyl-1-phenylthiopropane (4.649 g; 82%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.96 (quintet, J = 7.37 Hz, 2H, $-CH_2-$), 2.75 (t, J = 8.01 Hz, 2H, $-CH_2-Ph$), 2.91 (t, J = 7.26 Hz, 2H, $-CH_2-S-$), 7.15-7.31 (m, 10H, aromatic). (Found: C, 79.2; H, 7.3; S, 14.0. $C_{15}H_{16}S$ requires C, 78.9; H, 7.0; S, 14.0%).

*2-(2-Phenylethyl)-naphtho[1,8-de]-1,3-dithiin*

A suspension of N-chlorosuccinimide (0.160 g; 1.1 mmol) in a solution of 3-phenyl-1-phenylthiopropane (0.228 g; 1 mmol) and carbon tetrachloride (10 ml) was stirred at room temperature under argon for 1 hr. The reaction mixture was then filtered under nitrogen into a solution of 1,8-naphthalenedithiol **11** (0.192 g; 1 mmol) and $BF_3.Et_2O$ (0.12 ml; 1 mmol) in dichloromethane (10 ml) held under argon at room temperature. The reaction mixture was stirred overnight at room temperature under argon then poured into ice cold water (30 ml) and extracted with ether (2 x 75 ml). The combined organic extracts were washed with 10% sodium hydroxide and dried ($MgSO_4$). Evaporation of the solvents gave a crude product (0.322 g), which was separated on a silica gel column with 1:4 dichloromethane/hexane to give pure product (0.220 g; 71%). A sample, recrystallized from ethanol, had m.p. 70°C; $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 2.31 (q, J = 7.59 Hz, 2H, $-CH_2-\underline{CH_2}-CH$), 2.94 (t, J = 7.50 Hz, 2H, $-\underline{CH_2}-Ph$), 4.21 (t, J = 7.31 Hz, 1H, $-CH(-S-)_2$), 7.18-7.68 (m, 11H, aromatic). (Found: C, 73.7; H, 5.1; S, 21.1. $C_{19}H_{16}S_2$ requires C, 74.0; H, 5.2; S, 20.8%).

*2-Methylthio-2-(2-phenylethyl)-naphtho[1,8-de-]-1,3-dithiin 6*

A solution of BuLi in dry hexane (0.2 ml; 0.2 mmol) was added to a stirred solution of 2-(2 phenylethyl)-naphtho[1,8-de]-1,3-dithiin (0.077 g; 0.25 mmol) in dry tetrahydrofuran (10 ml) at -78°C under nitrogen. After stirring 30 min at -78°C, deuteration of an aliquot of the resulting yellow solution followed by $^1$H n.m.r. examination showed anion formation was complete, so a solution of dimethyl disulfide (0.02 ml; 0.25 mol) in dry tetrahydrofuran (3 ml) was added. After stirring for a further 1 hr at -78°C work up as usual gave a crude product (0.08 g), which was separated on a Chromatotron with 3:22 dichloromethane/hexane to give pure **6** (0.054 g, 67%); m.p. 82°C; $^1$H n.m.r. ($CDCl_3$, 60 MHz) δ 2.23 (S, 3H, $-SCH_3$), 2.30-2.70 (m, 2H, $-CH_2-$) 2.80-3.20 (m, 2H, $-CH_2-$), 7.10-7.90 (m, 11H, aromatic). (Found: C, 67.4; H, 5.1; S, 26.7. $C_{20}H_{18}S_3$ requires C, 67.8; H, 5.1; S, 27.1%).

*2-(2-Phenylethyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin 7*

A solution of BuLi in dry hexane (0.2 ml; 0.25 mmol) was added to a stirred solution of 2-(2-phenylethyl)-naphtho[1,8-de]-1,3-dithiin (0.077 g; 0.25 mmol) in dry tetrahydrofuran (10 ml) at -78°C under nitrogen. After stirring 30 min, a solution of diphenyl disulfide (0.03 g; 0.25 mmol) in dry tetrahydrofuran (3 ml) was added and the reaction mixture was stirred a further 1 hr at -78°C. Work up as usual gave a crude product (0.15 g), which was separated on a silica gel column. Elution with 3:17 dichloromethane/hexane gave pure **7** (0.042 g; 40%), which was recrystallized from ethanol; m.p. 106°C; $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 2.41-2.47 (m, 2H, $-CH_2-Ph$), 3.15-3.20 (m, 2H, $CH_2-C(-S-)_3$), 7.16-7.49 (m, 14H, aromatic), 7.70-7.74 (d, d, J = 6.90, 2.38 Hz, 2H, aromatic). (Found: C, 72.0; H, 4.6; S, 22.8. $C_{25}H_{20}S_3$ requires C, 72.1; H, 4.8; S, 23.1%).

*3-(m-Methoxyphenyl)-1-phenylthiopropane*
A solution of thiophenol (0.412 ml; 5 mmol) in dimethylformamide (5 ml) was slowly added to a suspension of sodium hydride (50% oil dispersion) (0.25 g; 5 mmol) in dimethylformamide (5 ml). After all the sodium hydride had reacted (1 hr), a solution of 1-bromo-3-(m-methoxyphenyl)propane[1] (1.225 g; 5 mmol) in dimethylformamide (5 ml) was added, and the mixture was stirred for a further 90 min at room temperature under nitrogen. A saturated solution of ammonium chloride (20 ml) was then added, and the product was extracted with ether (2 x 15 ml). The combined extracts were washed with water, 10% sodium hydroxide, water, and dried ($MgSO_4$). Evaporation of the solvents gave crude product (1.29 g), which was separated on a Chromatotron with 3:17 dichloromethane/hexane to give the pure product (0.682 g, 60%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.94 (quintet, J = 7.49 Hz, 2H, -$CH_2$-), 2.71 (t, J = 7.60 Hz, 2H, -$CH_2$-Ph), 2.89 (t, J = 6.81 Hz, 2H, -$CH_2$-), 3.75 (s, 3H, -$OCH_3$), 6.74 (t, J = 7.60 Hz, 3H, aromatic), 7.11-7.31 (m, 6H, aromatic). (Found: C, 74.6; H, 7.0; S, 12.6. $C_{16}H_{18}OS$ requires C, 74.4; H, 7.0; S, 12.4%).

*2-(2-m-Methoxyphenylethyl)-naphtho[1,8-de]-1,3-dithiin*
A suspension of N-chlorosuccinimide (0.160 g; 1.1 mmol) in a solution of 3-(m-methoxyphenyl)-1-phenylthiopropane (0.258 g; 1 mmol) and carbon tetrachloride (10 ml) was stirred at room temperature under argon for 1.5 hr. The reaction mixture was directly filtered under argon into a stirred solution of 1,8-naphthalenedithiol **11** (0.192 g; 1 mmol) and $BF_3.OEt_2$ (0.12 ml; 1 mmol) in dichloromethane (10 ml). After stirring overnight at room temperature the reaction mixture was poured into cold water, extracted with dichloromethane (2 x 10 ml), washed with 10% sodium hydroxide, then water and dried ($MgSO_4$). Evaporation of the solvents gave a crude product (0.391 g), which was separated on a Chromatotron with 1:19 ether/hexane to give pure product (0.209 g, 62%); $^1$H n.m.r. ($CDCl_3$, 60 MHz) δ 2.13-2.46 (m, 2H, -$CH_2$-), 2.97 (t, J = 8.00 Hz, 2H, -$CH_2$-Ph), 3.83 (s, 3H, -$OCH_3$), 4.27 (t, J = 8.00 Hz, 1H, -CH(-S-)$_2$), 6.76-7.83 (m, 10H, aromatic). (Found: C, 71.1; H, 5.3; S, 18.9. $C_{20}H_{18}OS_2$ requires C, 71.0; H, 5.3; S, 18.9%).

*2-(2-m-Methoxyphenylethyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin* ***8***
A solution of BuLi (0.5 ml; 0.7 mmol) in dry hexane was added to a solution of 2-(2-m-methoxyphenylethyl)-naphtho[1,8-de]-1,3-dithiin (0.209 g; 0.618 mmol) in dry tetrahydrofuran (15 ml) at -78°C under nitrogen. After stirring for 1 hr, deuteration of an aliquot of the resulting yellow solution followed by $^1$H n.m.r. examination showed anion formation was complete, so a solution of diphenyl disulfide (0.136 g; 0.624 mmol) in tetrahydrofuran (3 ml) was added and the stirring was continued for a further 6 hr at -78°C, work up as usual gave a crude product (0.23 g), which was separated on a Chromatotron with 3:17 dichloromethane/hexane to give pure **8** (0.174 g, 63%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 2.41-2.46 (m, 2H, -$CH_2$-), 3.12-3.17 (m, 2H, -$CH_2$-), 3.75 (s, 3H, -$OCH_3$), 6.70-7.71 (m, 15H, aromatic). (Found: C, 69.9; H, 4.8; S, 21.5. $C_{26}H_{22}OS_3$ requires C, 70.0; H, 4.9; S, 21.5%).

*5-Phenyl-1-pentene*
A solution of allyl magnesium chloride, prepared from allyl chloride (3.3 ml; 40 mmol) and magnesium (0.96 g; 40 mmol) in tetrahydrofuran (40 ml), was added to a stirred solution of 1-iodo-2-phenylethane (3.6 g; 15 mmol) and dilithium tetrachlorocuprate[20] (1 ml, ≈ 1 mmol) in dry tetrahydrofuran (10 ml) at 0°C. After stirring 2 hr at 0°C and overnight at room temperature, a solution of ammonium chloride (100 ml) was added. Extraction with ether (3 x 20 ml) followed by drying ($MgSO_4$) and evaporation of solvents gave a crude product (1.9 g) which was separated on a silica gel column with hexane to give pure product (1.133 g; 50%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.70 (quintet, J = 7.60 Hz, 2H, -$CH_2$-), 2.08 (q, J = 7.18 Hz, 2H, -$CH_2$-), 2.60 (t, J = 7.76 Hz, 2H, -$CH_2$-Ph), 4.94-5.04 (m, 2H, =$CH_2$), 5.75-5.89 (m, 1H, =CH-), 7.15-7.28 (m, 5H, aromatic). (Found: C, 90.3; H, 9.9. $C_{11}H_{14}$ requires C, 90.4; H, 9.6%).

*5-Phenyl-1-phenylthiopentane*
5-Phenyl-1-pentene (0.584 g; 4 mmol), thiophenol (4 ml) and azoisobutyronitrile (0.02 g) were heated and stirred for 5 hr at 90°C under argon. After cooling to room temperature, 10% sodium hydroxide (30 ml) was added. The product was extracted with ether (2 x 20 ml) and dried ($MgSO_4$). Evaporation of the solvents gave a crude product (0.958 g), which was separated on a Chromatotron with 1:9 dichloromethane/hexane to give pure thioether (0.728 g, 71%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.39-1.50 (m, 2H, -$CH_2$-), 1.56-1.72 (m, 4H, -$CH_2$-), 2.58 (t, J = 7.66 Hz, 2H, -$CH_2$- Ph), 2.88 (t, J = 7.23 Hz, 2H, -$CH_2$-S), 7.13-7.50 (m, 10H, aromatic). (Found: C, 80.0; H, 7.8; S, 12.8. $C_{17}H_{20}S$ requires C, 79.7; H, 7.8; S, 12.5%).

*2-(4-Phenylbutyl)-naphtho[1,8-de]-1,3-dithiin*
A suspension of N-chlorosuccinimide (0.320 g; 2.2 mmol) in a solution of 5-phenyl-1-phenylthiopentane (0.512 g; 2 mmol) and carbon tetrachloride (20 ml) was stirred for 2 hr at room temperature. The mixture was then filtered into a solution of 1,8-naphthalenedithiol **11** (0.384 g; 2 mmol) and $BF_3.OEt_2$ (0.24 ml; 2 mmol) in dichloromethane (20 ml) at room temperature under nitrogen. After stirring overnight, 10% sodium hydroxide (30 ml) was added and the product was extracted with dichloromethane (2 x 10 ml). Evaporation of solvents gave a crude product (0.75 g), which was separated on a Chromatotron with 1:9 dichloromethane/hexane to give pure thioacetal (0.3 g, 45%); m.p. 56°C; $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.65-1.70 (m, 4H, -$CH_2$-), 2.01-2.11 (m, 2H, -$CH_2$-), 2.63 (t, 2H, -$CH_2$-Ph), 4.29 (t, J = 6.00 Hz, 1H, -CH(-S-)$_2$), 7.15-7.44 (m, 9H, aromatic), 7.64-7.67 (m, 2H, aromatic). (Found: C, 75.2; H, 6.2; S, 19.2. $C_{21}H_{20}S_2$ requires C, 75.0; H, 6.0; S, 19.2%).

*2-(4-Phenylbutyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin* **9**
A solution of BuLi in dry hexane (0.60 ml; 0.72 mmol) was added to a solution of 2-(4-phenylbutyl)-naphtho[1,8-de]-1,3-dithiin (0.216 g; 0.64 mmol) in dry tetrahydrofuran (15 ml) at -78°C under nitrogen. After stirring 1 hr, deuteration of an aliquot of the resulting yellow solution followed by $^1$H n.m.r. examination showed anion formation was complete, so a solution of diphenyl disulfide (0.155 g; 0.53 mmol) in dry tetrahydrofuran (3 ml) was added and the stirring was continued for a further 5 hr at -78°C under nitrogen. Work up as usual gave a crude product (0.287 g), which was separated on a Chromatotron with 1:9 dichloromethane/hexane to give pure **9** (0.2 g, 70%); m.p. 83°C; $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.61-1.71 (m, 2H, -$CH_2$-), 1.85-1.95 (m, 2H, -$CH_2$-), 2.12-2.17 (m, 2H, -$CH_2$-), 2.64 (t, J = 7.69 Hz, 2H, -$CH_2$-Ph), 7.16-7.40 (m, 14H, aromatic), 7.67-7.71 (m, 2H, aromatic). (Found: C, 72.8; H, 5.2; S, 21.2. $C_{27}H_{24}S_3$ requires C, 73.0; H, 5.4; S, 21.6%).

*6-Phenyl-1-hexene*
A solution of allyl magnesium chloride (prepared from allyl chloride (3.3 ml; 40 mmol) and magnesium (0.96 g; 40 mmol) in tetrahydrofuran (40 ml)) was added to a stirred solution of 1-bromo-3-phenylpropane (1.975 ml; 13 mmol) and dilithium tetrachlorocuprate[20] (1 ml ≈ 1 mmol) in tetrahydrofuran (10 ml) at 0°C. After stirring 2 hr at 0°C the reaction mixture was allowed to warm to room temperature overnight. A solution of ammonium chloride was added and the product was extracted with ether (2 x 30 ml) and dried ($MgSO_4$). Evaporation of the solvents gave a crude product (1.815 g), which was separated on a Chromatotron. Elution with hexane gave pure alkene (1.228 g, 59%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.41-1.49 (m, 2H, -$CH_2$-), 1.58-1.67 (m, 2H, -$CH_2$-), 2.04-2.16 (m, 2H, -$CH_2$-), 2.61 (t, J = 7.68 Hz, 2H, -$CH_2$-Ph), 4.92-5.00 (m, 2H, =$CH_2$), 5.72-5.86 (m, 1H, -CH=), 7.15-1.30 (m, 5H, aromatic). (Found: C, 89.8; H, 10.1. $C_{12}H_{16}$ requires C, 90.0; H, 10.0%).

*6-Phenyl-1-phenylthiohexane*
A solution of 6-phenyl-1-hexene (0.8 g; 5 mmol), azoisobutyronitrile (0.02 g) and thiophenol (5 ml) was stirred and held under argon at 90°C for 5 hr. After cooling to room temperature, 10% sodium hydroxide (30 ml) was added and the product was extracted with ether (3 x 15 ml) and dried ($MgSO_4$). Evaporation of the solvent gave a crude product (1.10 g), which was separated on a Chromatotron with 1:9 dichloromethane/hexane to give pure phenylthioether (0.982 g, 73%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.28-1.67 (m, 4H, -$CH_2$-$CH_2$-), 1.45-1.58 (m, 4H, -$CH_2$-$CH_2$-), 2.58 (t, J = 7.91 Hz, 2H, -$CH_2$-Ph), 2.89 (t, J = 7.00, 2H, -$CH_2$-S-), 7.11-7.32 (m, 10H, aromatic). (Found: C, 80.3; H, 8.3; S, 11.8. $C_{18}H_{22}S$ requires C, 80.0; H, 8.2; S, 11.9%).

*2-(5-Phenylpentyl)-naphtho[1,8-de]-1,3-dithiin*
A suspension of N-chlorosuccinimide (0.160 g; 1.1 mmol) in a solution of 6-phenyl-1-phenylthiohexane (0.270 g; 1 mmol) in carbon tetrachloride (10 ml) was stirred for 1 hr at room temperature under argon. The reaction mixture was then poured into a solution of 1,8-naphthalenedithiol **11** (0.192 g; 1 mmol) and $BF_3.OEt_2$ (0.12 ml; 1 mmol) in dichloromethane (10 ml) and stirred overnight. The resulting solution was poured into cold water, extracted with dichloromethane (2 x 10 ml) and the combined extracts were washed with 10% sodium hydroxide (20 ml) and dried ($MgSO_4$). Evaporation of the solvents gave a crude product (0.438 g), which was separated on a Chromatotron with 1:9 dichloromethane/hexane to give pure thioacetal (0.267 g, 76%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.33-1.44 (m, 2H, -$CH_2$-), 1.59-1.71 (m, 4H, -$CH_2$-$CH_2$-), 1.97-2.04 (m, 2H, -$CH_2$-), 2.61 (t, J = 7.71 Hz, 2H, -$CH_2$-Ph), 4.29 (t, J = 7.38, 1H, -CH(-S-)$_2$), 7.15-7.67 (m, 11H, aromatic). (Found: C, 75.4; H, 6.3; S, 18.3. $C_{22}H_{22}S_2$ requires C, 75.4, H, 6.3; S, 18.3%).

*2-(5 Phenylpentyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin 10*
A solution of BuLi in dry hexane (0.7 ml; 0.8 mmol) was added to a solution of 2-(5 phenylpentyl)-naphtho[1,8-de]-1,3-dithiin (0.267 g; 0.76 mmol) in dry tetrahydrofuran (15 ml) at -78°C under nitrogen. After stirring 45 min deuteration of an aliquot of the resulting yellow solution followed by $^1$H n.m.r. examination showed anion formation was complete so a solution of diphenyl disulfide (0.218 g; 1 mmol) in dry tetrahydrofuran (3 ml) was added. The mixture was stirred for a further 5 hr at -78°C under nitrogen. Work up as usual gave a crude product (0.506 g), which was separated on a Chromatotron with 1:9 dichloromethane/hexane to give pure **10** (0.25 g, 72%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.30-1.42 (m, 2H, $-CH_2-$), 1.61-1.71 (m, 2H, $-CH_2-$), 1.83-1.95 (m, 2H, $-CH_2-$), 2.09-2.15 (m, 2H, $-CH_2-C(-S-)_3$), 2.61 (t, J = 7.62 Hz, 2H, $-CH_2-Ph$), 7.14-7.41 (m, 14H, aromatic), 7.68 (d, d, J = 6.78, 2.66 Hz, 2H, aromatic) (Found: C, 73.3; H, 5.7; S, 21.2. $C_{28}H_{26}S_3$ requires C, 73.3; H, 5.7; S, 21.0%).

*3,3-Dimethyl-4-phenylbutanal*
4,4-Dimethyl-5-phenyl-1-pentene **23** (2.2 g; 12.64 mmol), prepared by adding phenylmagnesium bromide to 2,2-dimethyl-4-pentenal[21] followed by deoxygenation with trifluoroacetic acid/triethylsilane[22], in dry methanol (20 ml) was cooled to -78°C. Ozonized oxygen gas was passed through this solution until a permanent blue green tinge was observed (15 min). Oxygen was then passed through the mixture to remove excess ozone (10 min). Dimethyl sulfide (2 ml) was added and the solution was allowed to warm to room temperature under argon. Excess dimethyl sulfide was then removed by heating on a water bath to 50°C. The residue was diluted with water, extracted with ether (2 x 20 ml) and dried ($MgSO_4$). Evaporation of the solvents gave a mixture containing the required aldehyde and related dimethoxy acetal (1.910 g); $^1$H n.m.r. ($CDCl_3$, 60 MHz) δ 0.97 (s, 6H, $-CH_3$), 1.47 (d, J = 6.00 Hz, 2H, $-CH_2-CH(-O-)_2$), 2.62 (s, 2H, $-CH_2-Ph$), 3.33 (s, 6H, -OMe), 4.60 (t, J = 6.00 Hz, 1H, $-CH(-O-)_2$), 7.27 (m, 5H, aromatic), 9.67 (t, J = 6.00 Hz, 1H, -CHO). This crude mixture was used without further purification.

*2-(2,2-Dimethyl-3-phenylpropyl)-naphtho[1,8-de]-1,3-dithiin 24*
2-3 Drops of $BF_3.OEt_2$ were added to a stirred solution of 2,2-dimethyl-4-phenylbutanal and its dimethoxy acetal (0.222 g; ~1 mmol) and 1,8-naphthalenedithiol **11** (0.192 g; 1 mmol) in dry dichloromethane (10 ml) under nitrogen at room temperature. After stirring overnight, cold water (10 ml) was added and the product was extracted with dichloromethane (2 x 10 ml). The combined extracts were washed with 10% sodium hydroxide and dried ($MgSO_4$). Evaporation of the solvents gave a crude product (0.368 g), which was separated on a Chromatotron. Elution with 1:9 dichloromethane/hexane gave the thioacetal **24** (0.219 g, 63%); $^1$H n.m.r. ($CDCl_3$, 60 MHz) δ 0.90 (s, 6H, $-CH_3$), 1.86 (d, J = 6.00 Hz, 2H, $-CH_2-$), 2.56 (s, 2H, $-CH_2-Ph$), 4.40 (t, J = 6.00 Hz, 1H, $-CH(-S-)_2$), 6.86-7.73 (m, 11H, aromatic). (Found: C, 75.5; H, 6.0; S, 18.2. $C_{22}H_{22}S_2$ requires C, 75.4; H, 6.3; S, 18.3%).

*2-(2,2-Dimethyl-3-phenylpropyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin 5*
A solution of BuLi in hexane (1 ml; 1.5 mmol) was added to a stirred solution of 2-(2,2-dimethyl-3-phenylpropyl)-naphtho[1,8-de]-1,3-dithiin **24** (0.219 g; 0.63 mmol) in dry tetrahydrofuran (15 ml) at -78°C under nitrogen. After stirring for 1 hr, deuteration of an aliquot of the resulting yellow solution followed by $^1$H n.m.r. examination showed anion formation was complete so a solution of diphenyl disulfide (0.136 g; 0.63 mmol) in dry tetrahydrofuran (3 ml) was added. Stirring was continued for a further 3 hr at -78°C. Work up as usual gave a crude product (0.254 g) which was separated on a Chromatotron. Elution with 1:4 dichloromethane/hexane gave **5** (0.130 g; 45%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.20 (s, 6H, $-CH_3$), 2.42 (s, 2H, $-CH_2-$) 2.71 (s, 2H, $-CH_2-Ph$), 7.05-7.75 (m, 16H, aromatic). (Found: C, 61.0; H, 5.7; S, 20.9. $C_{27}H_{26}S_3$ requires C, 61.1; H, 5.7; S, 21.0%).

*CYCLISATION REACTIONS*
*(a) 2-Methylthio-2-(3-phenylpropyl)-naphtho[1,8-de]-1,3-dithiin 2*
(i) A solution of **2** (0.096 g; 0.26 mmol) in dichloromethane (15 ml) was stirred with a suspension of silver triflate (0.192 g; 0.75 mmol) for 1 hr at room temperature under nitrogen. At this time, t.l.c. indicated that all the starting material had reacted and the suspension consisted of a yellow precipitate and a bright blue solution. Column work up by application of the total reaction mixture to silica gel (10 g) and elution with dichloromethane gave an oily product (0.056 g), which showed one spot on t.l.c. (1:9, dichloromethane/hexane). $^1$H n.m.r. showed a 1:1 mixture of **25** and **26**. The presence of **26** was inferred from a $^1$H n.m.r. triplet δ 6.33 (J = 8.00 Hz). A sample of the above mixture (0.030 g) was dissolved in deuterated dichloromethane (0.5 ml) in a n.m.r. tube and triflic acid (8 μl ≈ 1 eq) was added. The initially

colourless solution rapidly changed to blue and the reaction mixture was examined by $^1$H n.m.r.. The olefinic triplet at δ 6.33 disappeared immediately on addition of the triflic acid and, after 18 hr, $^1$H n.m.r. showed only the spectrum of the cyclised product **25**. The solution was pale yellow colour by this time. The solution was washed with water (2 ml) and dried ($MgSO_4$). Evaporation of the solvent gave 1-tetralone-1,8-naphthalene dithioacetal **25** (0.020 g, 67%); m.p. 134°C; $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 1.87-1.95 (m, 2H, $-CH_2-$), 2.28-2.32 (m, 2H, $-CH_2-$), 2.88 (t, J = 6.16 Hz, 2H, $-CH_2$-Ph), 7.17-7.44 (m, 8H, aromatic), 7.65 (d, J = 6.22, 1.56 Hz, 2H, aromatic), 7.80-7.84 (m, 1H, aromatic). (Found: C, 75.2; H, 4.9; S, 19.5. $C_{20}H_{16}S_2$ requires C, 75.0; H, 5.0; S, 20.0%).

(ii) To a suspension of silver triflate (0.20 g; 0.78 mmol) in dichloromethane (10 ml) under nitrogen at room temperature was added a solution of **2** (0.094 g; 0.26 mmol) in dichloromethane (2 ml). The suspension was stirred for 1 hr at room temperature by which time t.l.c. indicated all of the starting material had reacted. The yellow suspension in a blue solution was stirred for a further 17 hr. Column work up of the resultant yellow suspension and colourless solution as in (a) (i) gave a crude product (0.067 g) which was purified by chromatography on a Chromatotron with 1:9 dichloromethane/hexane to give **25** (0.053 g, 65%).

*(b) 2-(3-Phenylpropyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin 3*

(i) A solution of **3** (0.054 g; 0.125 mmol) in dichloromethane (2 ml) was added to a stirred suspension of silver triflate (0.096 g; 0.375 mmol) in dichloromethane (8 ml) under nitrogen at room temperature. The suspension was stirred for 1 hr at room temperature, by which time t.l.c. of the bright blue solution indicated all of the starting material had reacted. Stirring was continued for a further 17 hr, by which time the blue colour had changed to yellow. Column work up as in (a) (i) gave an oily crude product (0.038 g), which was purified by chromatography on a Chromatotron with 1:9 dichloromethane/hexane to give pure **25** (0.032 g; 80%).

(ii) A mixture of **3** (0.108 g; 0.25 mmol) and silver triflate (0.192 g; 0.75 mmol) in dichloromethane (15 ml) was stirred 2 hr at room temperature under nitrogen. Triflic acid (22 μl; 0.25 mmol) was then added and stirring at room temperature was continued for 18 hr, by which time blue colour had been replaced by yellow. Column work up gave a crude product (0.065 g), which was recrystallised from ethanol to give pure **25** (0.045 g, 56%).

(iii) A solution of **3** (0.054g; 0.125 mmol) in dichloromethane (2 ml) was added to a stirred suspension of silver triflate (0.036 g; 0.138 mmol) in dichloromethane (7 ml) under nitrogen at room temperature. Stirring was continued for a 48 hr. Column work up gave an oily crude product (0.042 g) which was purified as in (b) (i) to give pure **25** (0.028 g, 70%).

(iv) A solution of **3** (0.108 g; 0.25 mmol) in dichloromethane (5 ml) was added over a 10 min to a stirred refluxing suspension of silver triflate (0.192 g; 0.75 mmol) in dichloromethane (10 ml) under nitrogen. After refluxing 5 min, t.l.c. indicated all of the starting material had reacted. The refluxing was continued until the blue colour had been replaced by yellow (2 hr). Column work up gave an oily crude product (0.090 g), which was purified by chromatography on a Chromatotron as in (b) (i) to give pure **25** (0.065 g, 81%).

(v) A solution of **3** (0.108 g; 0.25 mmol) in dichloromethane (5 ml) was added to a stirred refluxing suspension of silver triflate (0.070 g; 0.275 mmol) in dichloromethane (10 ml). Stirring and refluxing was continued until the blue colour had disappeared (3 hr). Column work up of the brownish yellow mixture gave an oily crude product (0.089 g), which was purified on a Chromatotron as in (b) (i) to give pure **25** (0.073 g, 91%).

*(c) 2-(3-Phenylpropyl)-2-thienylthionaphtho[1,8-de]-1,3-dithiin 4*

A mixture of **4** (0.074 g; 0.17 mmol) and silver triflate (0.131g; 0.51 mmol) in dichloromethane (10 ml) was stirred for 18 hr at room temperature under nitrogen. Column work up of the resultant yellow mixture gave a product (0.038 g), which was purified by chromatography on a Chromatotron as in (b) (i) to give pure **25** (0.034 g; 63%)

*(d) 2-(2,2-Dimethyl-3-phenylpropyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin 5*
To a stirred suspension of silver triflate (0.109 g; 0.423 mmol) in dichloromethane (5 ml) at room temperature under nitrogen was added a solution of **5** (0.065 g; 0.141 mmol) in dichloromethane (2 ml). T.l.c. indicated that all the starting material had reacted after 30 min. The resultant blue mixture was stirred until all blue colour had disappeared (4 days). Column work up of the reaction mixture gave a crude product (0.033 g), which was purified by chromatography on a Chromatotron with 1:4 dichloro-methane/hexane to give 3,3-dimethyl-1-tetralone-1,8-naphthalenedithioacetal **28** (0.023 g, 46%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 0.97 (s, 6H, $(CH_3)_2$), 2.29 (s, 2H, $-CH_2-$), 2.68 (s, 2H, $-CH_2$-Ph), 7.14-7.83 (m, 10H, aromatic). (Found: C, 75.6; H, 6.0; S, 18.1. $C_{22}H_{20}S_2$ requires C, 75.9; H, 5.8; S, 18.4%).

*(e) 2-Methylthio-2-(2-phenylethyl)-naphtho-[1,8-de]-1,3-dithiin 6*
To a solution of **6** (0.064 g; 0.18 mmol) in dichloromethane (10 ml) at room temperature under nitrogen was added silver triflate (0.13 g; 0.54 mmol). The solution changed from colourless to bright blue. After stirring 30 min, t.l.c. indicated all of the starting material had reacted. Column work up of the blue reaction mixture gave a crude product (0.048 g). The $^1$H n.m.r. and t.l.c. of this material indicated one major product **29** had been produced; $^1$H n.m.r. ($CDCl_3$, 60 MHz) δ 3.77 (d, J = 8.00 Hz, 2H, $-CH_2$-Ph), 6.53 (t, J = 8.00 Hz, 1H, $=CH(S-)_2$), 7.17-7.83 (m, 11H, aromatic). Unsatisfactory analytical data was obtained for this compound.

*(f) 2-(2-Phenylethyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin 7*
(i) To a suspension of silver triflate (0.078 g; 0.3 mmol) in dichloromethane (8 ml) at room temperature was added a solution of **7** (0.042 g; 0.1 mmol) in dichloromethane (2 ml). After stirring 1 hr t.l.c. indicated all of the starting material had reacted and a blue solution colour was observed. Stirring was continued for 6 days, by which time the blue colour had disappeared. Column work up of the resultant yellow mixture gave a product mixture (0.019 g), consisting of several compounds (t.l.c.).

(ii) A solution of **7** (0.052 g; 0.125 mmol) in dichloromethane (2 ml) was added to a stirred refluxing suspension of silver triflate (0.096 g; 0.375 mmol) in dry dichloromethane (5 ml) under nitrogen. The resultant blue solution was refluxed until the blue colour disappeared (3 days). Column work up of the brownish yellow reaction mixture gave a crude product (0.020 g), consisting several compounds (t.l.c.).

*(g) 2-(2-m-Methoxyphenylethyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin 8*
To a stirred suspension of silver triflate (0.132 g; 0.519 mmol) in dichloromethane (8 ml) at room temperature under nitrogen was added a solution of **8** (0.078 g; 0.173 mmol) in dichloromethane (2 ml). The colourless solution changed to orange then blue (30 sec) then finally pink-purple (15 min). This mixture was stirred for 28 hr. Column work up of the reaction mixture gave a crude product (0.053 g). Purification by chromatography on a Chromatotron with 1:9 dichloromethane/hexane gave 5-methoxy-1-indanone-1,8-naphthalenedithioacetal **30** (0.020 g; 34%); $^1$H n.m.r. ($CDCl_3$, 300 MHz) δ 2.65 (t, J = 6.95 Hz, 2H, $-CH_2$-Ph), 3.07 (t, J = 6.95 Hz, 2H, $-CH_2-$), 3.82 (s, 3H, $-OCH_3$), 6.97-6.83 (m, 2H, aromatic), 7.26-7.45 (m, 5H, aromatic), 7.74 (d, J = 7.80 Hz, 2H, aromatic). (Found: C, 71.7; H, 5.1; S, 19.0. $C_{20}H_{16}OS_2$ requires C, 71.4, H, 4.8; S, 19.1%).

*(h) 2-(4-Phenylbutyl)-2-phenylthionaphtho[1,8-de]-1,3-dithiin 9*
A solution of **9** (0.0965 g; 0.217 mmol) in dichloromethane (3 ml) was added to a stirred suspension of silver triflate (0.0613 g; 0.238 mmol) in dichloromethane (9 ml) at room temperature under nitrogen. A blue reaction mixture was rapidly obtained and stirring was continued for 3 days. The reaction mixture was still blue at this stage and column work up gave a crude product (0.053 g) whose t.l.c. indicated one major product; $^1$H n.m.r. ($CDCl_3$, 60 MHz) δ 1.55-2.83 (m, 6H, $-CH_2-CH_2-CH_2-$), 6.33 (t, J = 8.00 Hz, 1H, =CH-), 7.00-7.67 (m, 11H, aromatic).

*(i) 2-(5-Phenylpentyl)-2-phenylthionaphtho[1,8-de]-1,3 dithiin 10*
A solution of **10** (0.101 g; 0.22 mmol) in dichloromethane (2 ml) was added to a stirred suspension of silver triflate (0.062 g; 0.242 mmol) in dichloromethane (10 ml) under nitrogen at room temperature. After stirring 1 hr, t.l.c. of the blue mixture indicated that all of the starting material had reacted. Stirring was continued until blue colour disappeared (18 hr). Column work up of the resultant yellow reaction mixture gave a product (0.074 g) which was purified by chromatography on a Chromatotron with 1:9 dichloromethane/hexane to give the major product (0.037 g) tentatively identified as the ketene thioacetal elimination product, **31**; $^1$H n.m.r.

($CDCl_3$, 60 MHz) δ 1.40-1.90 (m, 4H, $-CH_2-CH_2$), 2.23-2.73 (m, 4H, $-CH_2-CH_2-$), 6.33 (t, J = 8.00 Hz, 1H, =CH-), 7.07-7.67 (m, 11H, aromatic). Satisfactory analytical data could not be obtained for this compound.

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