Lewis Acid-promoted Hetero Diels–Alder Reaction of α,β-Unsaturated Thioketones

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α,β-Unsaturated thioketones **1** were regenerated from their precursors, the dithiine-type dimers **3**, and readily underwent the Lewis acid-promoted hetero Diels–Alder reactions with a variety of carbonyl-activated dienophiles such as methyl acrylate **4**, methyl vinyl ketone **6**, acrolein **7**, N,N- dimethylacrylamide **8**, methyl methacrylate **9**, dimethyl fumarate **10**, methyl crotonate **11** and N-p-tolylmaleimide **12**, to give [4 + 2]cycloadducts **5** and **13–19**, respectively. Among the Lewis acids investigated, AlCl₃ and EtAlCl₂, when used in diethyl ether and dichloromethane, respectively, were found to remarkably accelerate the reaction even at lower temperatures (25–35 °C); the reaction is very slow in the absence of the catalyst. A moderate enhancement of the stereoselectivity (*endo/exo*) was observed compared with that of the thermal reactions at 80 °C in benzene. The structure determination of the cycloadducts by ¹H NMR spectroscopic studies are described and the configurations and relative conformations are also discussed.

It is well known that Lewis acids accelerate Diels–Alder reactions between carbodienes and an electron-poor dienophiles by lowering the LUMO energy of the latter by complexation with the Lewis acid.[1,2] On the other hand, an α,β-unsaturated carbonyl compound (1-oxabuta-1,3-diene) usually undergoes an inverse electron demand hetero Diels–Alder (HDA) reaction with an electron-rich dienophile under vigorous thermal conditions.[3] In this case the Lewis acid combines with the carbonyl oxygen to lower its LUMO energy, thus accelerating the reaction.

Previously, we reported that under thermal reaction conditions α,β-unsaturated thioketones (1-thiabuta-1,3-dienes) readily underwent HDA reaction with a variety of dienophiles.[4] The reaction was found to proceed smoothly either with electron-poor or electron-rich dienophiles and the results were explored in terms of the CNDO/2 calculation method.[4] Meantime, several groups also reported the thermal HDA reactions of such a 1-thiabuta-1,3-diene system.[5] However, very little has been known about the Lewis acid-promoted HDA reaction.† In this context, it appeared of interest to investigate the efficiency of Lewis acids in the HDA reaction of these α,β-unsaturated thioketones.

Results and Discussion

Since the monomeric α,β-unsaturated thioketones **1** formed from the corresponding ketones by thionation, readily dimerise
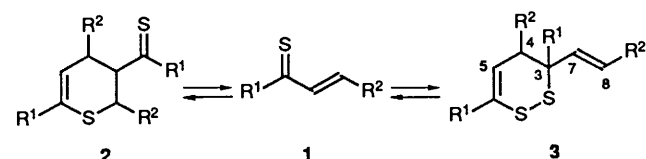
a; R¹ = R² = Ph
b; R¹ = Ph, R² = p -ClC₆H₄
c; R¹ = Ph, R² = p -MeC₆H₄
d; R¹ = R² = p -ClC₆H₄

Scheme 1

† Only one precedent has recently been reported by us (ref. 6).

Table 1 Preparation of thioketone dimers 3

	Ar¹	Ar²	t/h	Yield (%)[a]
3a	Ph	Ph	3	24
3b	Ph	p-ClC₆H₄	3	19
3c	Ph	p-MeC₆H₄	3	13
3d	p-ClC₆H₄	p-ClC₆H₄	4.5	35

[a] As a mixture of 3,4-*cis*- and 3,4-*trans*-isomers.

at ambient temperatures to dimers **2** and **3** which regenerate the monomers at higher temperatures,[7] the uncatalysed thermal reaction requires thermolysis in the presence of appropriate dienophiles.[4] On the contrary, the Lewis acid-catalysed reaction using dimer **2** was unsuccessful when **2** was added to an ethereal solution of a dienophile activated by a Lewis acid such as AlCl₃, EtAlCl₂ or BF₃. The dimer **2** instantaneously decomposed, precluding the cycloaddition, probably due to the collapsing action of the Lewis acid on the thiocarbonyl group in compound **2**. In order to implement the cycloaddition, we examined the reaction of the alternative dimer **3** containing no thiocarbonyl group and met with success. This article describes results in this line, and forms the first full account of Lewis acid-promoted hetero Diels–Alder reaction of a 1-thiabuta-1,3-diene system.†
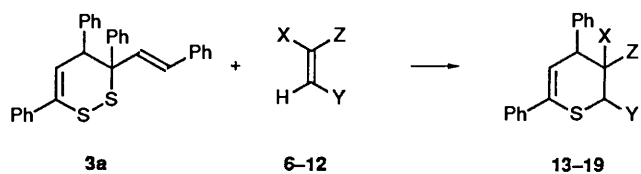
The prerequisite dithiine-type dimers **3a–d** could be obtained under controlled reaction conditions in moderate yields (Table 1).[8] The ¹H NMR spectra of **3a–d** exhibited two sets of signals for the 4-H, 5-H, 7-H and 8-H protons of almost equal intensity, indicating 1:1 mixtures of 3,4-*cis*- and 3,4-*trans*-isomers (see Experimental Section).

Initially, the reactions of thiochalcones **1** (generated from **3**) with methyl acrylate **4** in the presence of several Lewis acids were examined (Scheme 2, Tables 2 and 3). When the dimers **3a–d** were treated with **4** in the presence of AlCl₃ in diethyl
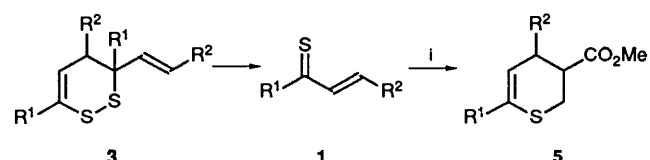
Scheme 2 *Reagent:* i, CH₂=CHCO₂Me **4**

3a   **6–12**   **13–19**

6, 13 X = COMe, Y = Z = H
7, 14 X = CHO, Y = Z = H
8, 15 X = CONMe₂, Y = Z = H
9, 16 X = CO₂Me, Y = H, Z = Me
10, 17 X = Y = CO₂Me, Z = H
11, 18 X = CO₂Me, Y = Me, Z = H
12, 19 X = H, Y–Z = CO–NAr–CO (Ar = p -Tol)

Scheme 3

ether,* the reactions proceeded readily at 25 °C to afford cycloadducts 5a–d in good yields (Table 2, Runs 2–5 and 11–13), whereas the uncatalysed reaction was very slow.† The use of more than an equimolar amount of $AlCl_3$ led to significant acceleration of the reaction (Runs 4 and 5) while a half equimolar amount of the Lewis acid gave, after 3 h, 5a in 95% yield (Run 2). This suggests that a catalytic amount of the Lewis acid is sufficient for completion of the reaction under these conditions. Among the other Lewis acids investigated, $EtAlCl_2$ also showed a remarkable effect on the reaction rate while Pr^iOAlCl_2, BF_3 and $ZnCl_2$ required longer reaction times to give reasonable yields (Runs 6–10). These reactions were investigated further with the same Lewis acids in dichloromethane * with varied molar amounts of the Lewis acids and at temperatures of 35, 25 or 0 °C (Table 3). Compared with the corresponding runs in Table 2, the reaction rates increased in all cases, however the yields decreased in all cases except for the reactions with $EtAlCl_2$ catalyst (Runs 6–11). This is reasonably ascribed to the consideration that the Lewis acids (especially, the stronger Lewis acid, $AlCl_3$) which are solvated less well in CH_2Cl_2 than Et_2O actually accelerate the reaction but simultaneously lead to partial decomposition of the dithiine-type dimer 3 (or thioketone 1 itself), as observed typically in the reaction with the thiopyran-type precursor 2. $EtAlCl_2$ (Runs 6–11) is the best catalyst under the conditions used in this reaction.

It is known that Lewis acids enhance regioselectivity (orientational) and stereoselectivity (endo vs. exo) for Diels–Alder reactions.[9] Since the thermal reaction of compound 1 showed perfect regioselectivity but moderate stereoselectivity (Run 1 in Tables 2 and 3, and ref. 4), the effects of Lewis acids on the selectivities were also determined in this reaction. ¹H NMR spectroscopy (270 and/or 500 MHz) and HPLC of the crude product mixture revealed that it consisted of 3,4-cis-5a (major) and 3,4-trans-5a (minor) without any other cycloadducts. The ratios of cis-5a/trans-5a formed under the varied catalytic or thermal conditions are also summarized in Tables 2 and 3. In comparison with the ratio (72/28) under the typical thermal conditions (in boiling benzene, Table 2, Run 1), all the catalytic reactions showed improvements in stereoselectivity, to give ratios which are comparable with that of the uncatalysed reaction at 35 °C (Table 3, Run 1).

Finally, the reactions of 3a with a variety of carbonyl-activated dienophiles ‡ 6–12 in the presence of $AlCl_3$ or $EtAlCl_2$ were examined and the results are shown in Table 4. Methyl vinyl ketone 6, acrolein 7, N,N-dimethylacrylamide 8, methyl methacrylate 9 and dimethyl fumarate 10 reacted readily at 25 °C to give the corresponding cycloadducts 13–17 in reasonable yields (Runs 1–3, 5–8 and 11–15). Methyl crotonate 11 was less reactive at 25 °C so those reactions were carried out at 35 °C and the use of excess of catalyst moderately increased the yield of 18 (Runs 18 and 19). Employing $AlCl_3$ in Et_2O or $EtAlCl_2$ in CH_2Cl_2 (Runs 5, 8, 11, 14 and 15) had a much greater effect on both the reaction rates and yields than did the other catalysts (Runs 6, 7, 12 and 13) to give cycloadducts 16 and 17, as analogously observed above (Tables 2 and 3). N-p-Tolyl maleimide 12 was so reactive that the reaction proceeded successfully at 25 °C both in the absence or presence of the catalyst (Runs 21 and 22). The observed ratios of the cis- and trans-cycloadducts are also summarized in Table 4.

Thus, the present study demonstrates that by utilizing the common Lewis acids, the α,β-unsaturated thioketones can undergo the facile Diels–Alder reaction under very mild reaction conditions with a variety of carbonyl-activated dienophiles.

Structure Determination.—The structural and stereochemical (relative configurations and conformations) assignments of all the cycloadducts were performed mainly by ¹H NMR spectroscopic studies. The ¹H NMR spectral data of 3,4-cis- and 3,4-trans-diastereoisomers of compounds 5a and 13–20 are listed in Table 5. For each compound significant signals of the thiopyran ring protons (2-H, 3-H, 4-H and 5-H) can be assigned based on their chemical shifts and coupling patterns of network starting from the readily identified 5-H. In compound cis-5a, for example, the olefinic proton (5-H) resonated at δ 6.16 as doublet with J 6.2 Hz. This coupling constant value was observed besides in 4-H (δ 4.21, dd) which coupled further with 3-H by J 5.8 Hz. Consequently, a signal of 3-H (δ 3.24) splits as ddd with J 5.8, 12.5 and 1.1 Hz by coupling further with two geminal 2-Hs. The 2α-H and 2β-H showed typical geminal coupling constant J 11.7 Hz, and resonated at δ 3.20 and 2.93, respectively. Inspection of the magnitudes of the observed coupling constants gives evidence for the relative configurations (cis and trans) and preferred conformations of the dihydrothiopyran ring system by assuming that for each compound of a 3,4-cis and 3,4-trans series, the thiopyran ring takes either one of two possible half-chair conformations A and B (Fig. 1) or both in the equilibrium in analogy to cyclohexene derivatives.

For a cis series of compounds 5a, 13 and 15, a large coupling constant (J 12.5, 12.2 and 11.7 Hz) between 2α-H and 3-H indicates a trans-diaxial relationship between these protons: namely the substituent, X, occupies an equatorial position (IA or, if the compounds are trans, IIB). A small coupling constant (J 1.1, <1 and 2.5 Hz) between 2β-H (equatorial) and 3-H also supports this constitution. The axial 3-H shows a medium magnitude of coupling constant (J 5.8, 4.3 and 5.1 Hz) with 4-H, suggesting a synclinal arrangement between them. All these observations are consistent with a IA-conformation only.

For compound 20 (cis), which was obtained by mCPBA (m-chloroperbenzoic acid) oxidation of cis-13, a considerably large coupling constant (J 13.5 Hz) between 2α-H and 3-H suggests

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* Diethyl ether and dichloromethane were found to be the best solvents on these reactions and other solvents such as tetrahydrofuran, diglyme, 1,4-dioxane, diisopropyl ether, toluene and anisole gave unsatisfactory results.

† Either the dimer 2 or 3 is able to react readily with 4 under thermal conditions at higher temperatures, e.g. in boiling benzene (Run 1),[4] whereas in the absence of a Lewis acid, they hardly react below ca. 25 °C even after one day.

‡ With non-carbonyl-activated dienophiles such as styrene and acrylonitrile and with electron-rich dienophiles, vinyl ethers, no cycloaddition products were detected in the presence of $AlCl_3$ in diethyl ether at temperatures 25–35 °C. These results contrast with those from the thermal reactions to give cycloadducts with both electrophilic and nucleophilic dienophiles.

Table 2 Effect of Lewis acid in Et_2O at 25 °C on the reactivity of thioketones 1 toward methyl acrylate 4 and on ratio of *cis*- and *trans*-cycloadducts 5

Run	Thioketone dimer	Lewis acid (equiv.)	t/h[b]	Cycloadduct	Yield[c] (%)	Ratio *cis*/*trans*
1	3a	none[e]	0.5	5a	96	72/28
2	3a	$AlCl_3$ (0.5)	3	5a	95	77/23
3	3a	$AlCl_3$ (1.0)	1	5a	94	80/20
4	3a	$AlCl_3$ (2.0)	0.5	5a	95	79/21
5	3a	$AlCl_3$ (3.0)	0.5	5a	97	80/20
6	3a	$EtAlCl_2$ (0.5)	5	5a	90	79/21
7	3a	$EtAlCl_2$ (1.0)	5	5a	82	76/24
8	3a	Pr^iOAlCl_2 (1.0)	12	5a	71	76/24
9	3a	BF_3 (1.0)	11	5a	90	83/17
10	3a	$ZnCl_2$ (1.0)	30	5a	79	82/18
11	3b	$AlCl_3$ (1.0)	2	5b	94	—[d]
12	3c	$AlCl_3$ (1.0)	1	5c	88	—[d]
13	3d	$AlCl_3$ (1.0)	6	5d	75	—[d]

[a] Reactions were carried out in a molar ratio of 1(3):4:Lewis acid = 1.0(0.5):3.0:0–3.0. [b] Monitored by TLC to determine the end points. [c] *cis*- and *trans*-5 mixture. [d] Not determined. [e] At 80 °C in benzene.

Table 3 Effect of Lewis acid in CH_2Cl_2 on reactivity of thioketones 1a toward methyl acrylate 4 and on ratio of *cis*-and *trans*-cycloadducts 5a

Run	Lewis acid (equiv.)	$T/°C$	t/h[b]	Yield[c] (%)	Ratio *cis*/*trans*
1	none	35	4[d]	68	78/22
2	$AlCl_3$ (0.5)	25	0.2	77	78/22
3	$AlCl_3$ (1.0)	25	0.2	73	78/22
4	$AlCl_3$ (1.0)	35	0.2	57	78/22
5	$AlCl_3$ (2.0)	25	0.2	56	77/23
6	$EtAlCl_2$ (0.1)	25	0.2	93	77/23
7	$EtAlCl_2$ (0.5)	25	0.2	90	79/21
8	$EtAlCl_2$ (1.0)	25	0.2	91	79/21
9	$EtAlCl_2$ (2.0)	25	0.2	92	77/23
10	$EtAlCl_2$ (3.0)	25	0.2	89	78/22
11	$EtAlCl_2$ (2.0)	35	0.2	89	78/22
12	$EtAlCl_2$ (1.0)	0	6	60	78/22
13	Pr^iOAlCl_2 (1.0)	25	0.3	75	76/24
14	$ZnCl_2$ (1.0)[e]	25	3	55	85/15
15	$ZnCl_2$ (1.0)[e]	35	3	57	82/18
16	$ZnCl_2$ (2.0)[e]	35	2	55	82/18

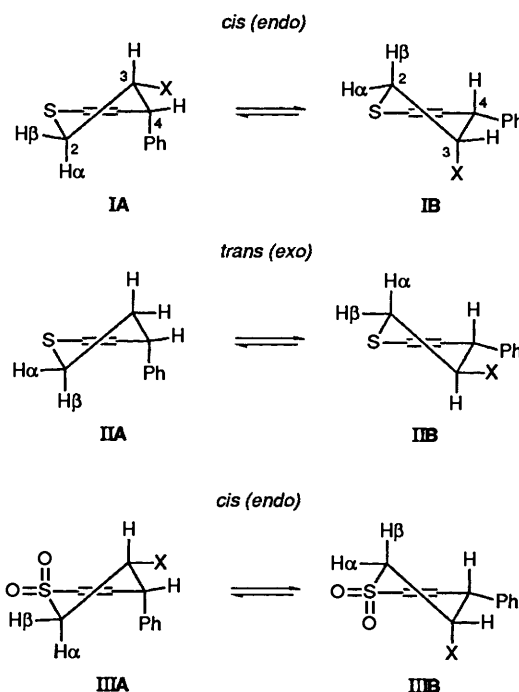[a–c] See the corresponding footnote in Table 2. [d] The reaction was incomplete. [e] Under suspension.

more axially oriented positions in **IIIA**, compared to those in **IA**. This is in accordance with consideration that **IIIB** is unlikely because it involves a repulsive 1,3-diaxial interaction between the one oxygen of the sulfone and the substituent X.

For compound *trans*-**15**, the large coupling constants (*J* 11.0 and 10.6 Hz) between 2α-H and 3-H, and 3-H and 4-H, undoubtedly show *trans*-diaxial relationships between them, respectively, being fully consistent with **IIB** occupation.

On the other hand, the relatively small coupling constants (*J* 9.1–9.5 Hz and 8.1–8.4 Hz) of 2α,3 and 3,4 for *trans*-diaxial relationships in compounds *trans*-**5a** and *trans*-**13** suggest the predominant conformation **IIB** with a small contribution of **IIA** in equilibration. The **IIA**-contribution may be ascribed to the gauche interaction between the substituents X and Ph present in **IIB**.

For compounds *cis*- and *trans*-**16** and **17**, and *cis*-**18** and **19**, the configurations and preferred conformations are consistent with those **IV–IX** illustrated in Fig. 2, based on the similar studies above.

As a consequence, a series of 3,4-*cis* (*endo*) and *trans* (*exo*) compounds can readily be discriminated by comparing $J_{3,4}$ and $J_{4,5}$ values of 4.3–5.8 Hz and 6.2–6.6 Hz, respectively, for the former and of 8.1–10.6 Hz and 2.5–4.6 Hz for the latter.

Fig. 1 Configurations and conformations for 5, 13–15 and 20

Experimental

Preparation of Thioketone Dimers **3a–d**. *General Procedure.*[7,8]—A solution of ketone (28–30 mmol) and Lawesson's reagent (10 g) in THF (50 cm³) was heated under reflux

Table 4[a] Effect of Lewis acid in Et_2O or CH_2Cl_2 on reactivity of thioketone **1a** toward a variety of carbonyl-activated dienophiles **6–12**

Run	Dienophile	Lewis acid (equiv.)	$T/°C$	t/h[b]	Cycloadduct	Yield[c] (%)	Ratio cis/trans
1	6	$AlCl_3$ (1.0)	25	0.5	13	81	89/11
2	7	$AlCl_3$ (1.0)	25	0.5	14	55	52/48
3	8	$AlCl_3$ (1.0)	25	2	15	76	56/44
4	9	none[e]	25	24[g]	16	24	51/49
5	9	$AlCl_3$ (1.0)	25	3	16	87	47/53
6	9	$AlCl_3$ (1.0)[c]	25	2	16	70	54/46
7	9	$EtAlCl_2$ (2.0)	25	4	16	76	47/53
8	9	$EtAlCl_2$ (2.0)[e]	25	0.5	16	81	52/48
9	10	none[f]	80	0.3	17	98	77/23
10	10	none[e]	25	24[g]	17	83	81/19
11	10	$AlCl_3$ (2.0)	25	8	17	82	76/24
12	10	$AlCl_3$ (1.0)[e]	25	0.3	17	56	74/26
13	10	$EtAlCl_2$ (2.0)	25	7	17	84	80/20
14	10	$EtAlCl_2$ (1.0)[e]	25	0.3	17	94	72/28
15	10	$EtAlCl_2$ (2.0)[e]	25	0.2	17	96	70/30
16	11	none[e]	35	24[g]	18	10	95/5
17	11	$AlCl_3$ (1.0)	35	7	18	30	—[d]
18	11	$AlCl_3$ (2.0)	35	6	18	49	—[d]
19	11	$AlCl_3$ (3.0)	35	5	18	55	—[d]
20	11	$EtAlCl_2$ (2.0)[e]	35	1	18	74	96/4
21	12	none	25	3	19	90	>99/1
22	12	$AlCl_3$ (1.0)	25	3	19	82	—[d]

[a–d] See the corresponding footnote in Table 2. [e] In CH_2Cl_2. [f] In boiling benzene. [g] The reaction was incomplete.

Table 5[a] ¹H NMR spectral data of compounds **5a, 13–19** and **20**

Compd.	$J_{H,H}/Hz$					$δ_H$					Others[b] Me and ArH
	2α,2β	2α,3	2β,3	3,4	4,5	2α	2β	3	4	5	
cis-5a	11.7	12.5	1.1	5.8	6.2	3.20	2.93	3.24	4.21	6.16	3.60(s) 7.17–7.56(m)[e]
trans-5a	12.8	9.1	2.9	8.1	3.7	3.29	3.10	3.02	4.06	6.06	3.61(s) 7.17–7.56(m)[e]
cis-13	10.6	12.2	<1	4.3	6.6	3.25	2.84	3.19	4.19	6.18	2.12(s) 7.12–7.56(m)
trans-13	12.8	9.5	2.6	8.4	3.3	3.21	3.01	3.09	3.98	6.06	1.96(s) 7.22–7.55(m)
cis-14	c	c	c	4.6	5.8	c	c	c	4.33	6.22	7.21–7.56(m) 9.80 (d, J 0.9)
cis-15	13.5	11.7	2.5	5.1	6.2	3.29	2.78	3.41	4.01	6.16	2.92, 3.27(s) 7.04–7.58(m)
trans-15	12.8	11.0	2.2	10.6	2.5	3.50	2.88	3.18	4.02	6.12	2.44, 2.79(s) 7.23–7.57(m)
cis-16	13.5	—	1.6[d]		6.6	3.50	2.69	—	3.71	6.10	1.56, 3.46(s) 7.17–7.56(m)[e]
trans-16	12.9	—	—	—	4.6	3.32	2.92	—	4.20	6.12	1.10, 3.71(s) 7.17–7.56(m)[e]
cis-17	—	11.6	—	4.6	6.6	4.24	—	3.46	4.23	6.22	3.59, 3.74(s) 7.14–7.54(m)[e]
trans-17	—	10.6	—	10.6	3.0	4.54	—	3.18	3.87	6.05	3.43, 3.75(s) 7.14–7.54(m)[e]
cis-18	—	11.2	—	4.9	6.3	3.54	—	2.95	4.09	6.16	1.35, 3.54(s) 7.12–7.86(m)
cis-19	—	—	8.9	4.6	5.3	—	4.40	3.96	4.02	6.89	2.31(s) 6.89, 7.15(d) 7.25–7.72(m)
cis-20	14.2	13.5	2.5	5.1	5.8	3.59	3.37	3.97	4.41	6.40	2.23(s) 7.18–7.64(m)

[a] For the geminal protons 2-H's α refers to position *trans* to 3-H, β *cis* to 3-H (3-Me for **16**). [b] s: singlet, d: doublet, m: multiplet. [c] Not clearly resolved due to ambiguity of couplings by overlaps. [d] $^4J_{2β,4}$ of a W-lattice long range coupling. [e] Unseparable data of a couple of *cis*- and *trans*-adducts.

for 2–3 h. Removal of the solvent and column chromatography of the blue–green coloured residue on Florisil gel using benzene–hexane (1:1) as the eluent gave slightly coloured **3** contaminated with **2**. Recrystallization (×2) of crude **3** from diethyl ether and benzene–hexane (0–50%) afforded pure **3** (1:1 mixture of diastereoisomers) as colourless crystals in 13–35% yield (Table 1).

3,4,6-*Triphenyl*-3-[(E)-2-*phenylvinyl*]-3,4-*dihydro*-1,2-*dithiine* **3a**. Colourless needles, m.p. 121–122 °C (decomp.) (Found: C, 80.1; H, 5.3. $C_{30}H_{24}S_2$ requires C, 80.3; H, 5.4%); $δ_H$ 3.98 (d, J 5.6, 0.5 H, 4-H),4.45 (d, J 4.8, 0.5 H, 4-H), 5.93 (d, J 16.0, 0.5 H), 6.22 (d, J 16.0, 0.5 H), 6.33 (d, J 5.6, 0.5 H, 5-H), 6.36 (d, J 4.8, 0.5 H, 5-H), 6.45 (d, J 16.0, 0.5 H), 6.62 (d, d, J 16.0, 0.5 H) and 6.89–7.57 (m, 20 H, ArH); m/z (FD) 448 (M⁺), 416, 325 and 224 (M⁺/2).
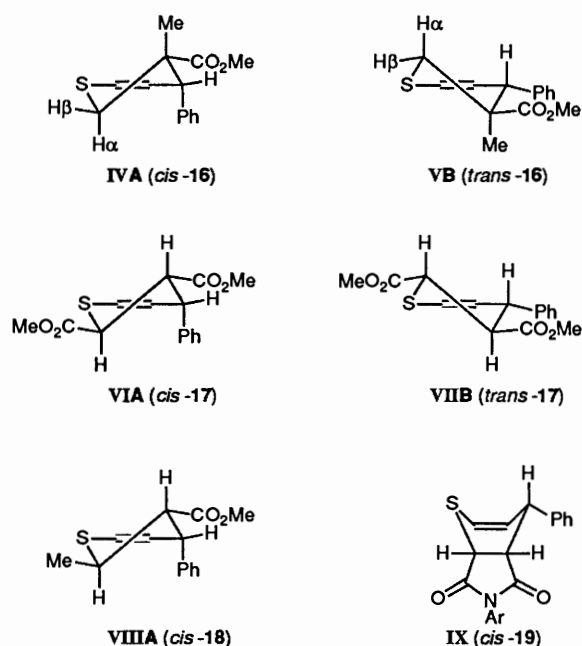
Fig. 2 Configurations and preferred conformations for **16**, **17**, **18** and **19**

4-(4-*Chlorophenyl*)-3-[(E)-2-(4-*chlorophenyl*)*vinyl*]-3,6-*diphenyl*-3,4-*dihydro*-1,2-*dithiine* **3b**. Colourless crystals, m.p. 133–134 °C (decomp.) (Found: C, 69.7; H, 4.3. $C_{30}H_{22}Cl_2S_2$ requires C, 69.6; H, 4.3%); δ_H 4.01 (d, *J* 6.0, 0.5 H, 4-H), 4.49 (d, *J* 5.4, 0.5 H, 4-H), 5.89 (d, *J* 16.2, 0.5 H), 6.26 (*J* 16.2, 0.5 H), 6.36 (d, *J* 6.0, 0.5 H, 5-H), 6.38 (d, *J* 5.4, 0.5 H, 5-H), 6.44 (*J* 16.2, 0.5 H), 6.70 (d, *J* 16.2, 0.5 H) and 6.80–7.64 (m, 18 H, ArH); *m/z* (EI) 257 (^{35}Cl) (M$^+$/2 − H, 91%), 223 (M$^+$/2 − Cl, 100), 189 (21) and 121 (21).

3,6-*Diphenyl*-4-(4-*tolyl*)-3-[(E)-2-(4-*tolyl*)*vinyl*]-3,4-*dihydro*-1,2-*dithiine* **3c**. Colourless crystals, m.p. 115–116 °C (decomp.); δ_H 2.19 (s, 1.5 H, Me), 2.28 (s, 1.5 H, Me), 2.29 (s, 1.5 H, Me), 2.32 (s, 1.5 H, Me), 4.01 (d, *J* 5.8, 0.5 H, 4-H), 4.47 (d, *J* 5.2, 0.5 H, 4-H), 5.94 (d, *J* 16.1, 0.5 H), 6.29 (d, *J* 16.1, 0.5 H), 6.41 (d, *J* 5.8, 0.5 H, 5-H), 6.43 (d, *J* 5.2, 0.5 H, 5-H), 6.60 (d, *J* 16.1, 0.5 H), 6.71 (d, *J* 16.1, 0.5 H) and 6.67–7.94 (m, 18 H, ArH); *m/z* (EI) 237 (M$^+$/2 − H, 56%) and 223 (M$^+$/2 − Me, 100).

3,4,6-*Tris*(4-*chlorophenyl*)-3-[(E)-2-(4-*chlorophenyl*)*vinyl*]-3,4-*dihydro*-1,2-*dithiine* **3d**. Colourless crystals, m.p. 106–107 °C (decomp.) (Found: C, 61.4; H, 3.6. $C_{30}H_{20}C_{14}S_2$ requires C, 61.4; H, 3.4%); δ_H 3.97 (d, *J* 5.9, 0.5 H, 4-H), 4.38 (d, *J* 5.7, 0.5 H, 4-H), 5.97 (d, *J* 16.2, 0.5 H), 6.15 (d, *J* 16.2, 0.5 H), 6.32 (d, *J* 5.9, 0.5 H, 5-H), 6.32 (d, *J* 5.7, 0.5 H, 5-H), 6.39 (d, *J* 16.2, 0.5 H), 6.65 (d, *J* 16.2, 0.5 H) and 6.68–7.86 (m, 16 H, ArH); *m/z* (EI) 291 (M$^+$/2 − H, 72%) and 257 (M$^+$/2 − Cl, 100).

Typical Procedure for the Reaction of Thioketone 1 (*from Dimer* 3) *with a Dienophile in the Presence of a Lewis Acid.*—To a solution of aluminium chloride (0.5 mmol) in anhydrous diethyl ether (25 cm^3) was added methyl acrylate **4** (1.5 mmol) at 25 °C (Table 2, Run 3). In the reactions in dichloromethane (Tables 3 and 4), a Lewis acid was added to a dienophile solution to prepare a clean solution of the complex. After the solution had been stirred for some time, a thioketone dimer **3a** (0.5 mmol as a monomer) was added in one portion to the solution. The reaction mixture was stirred at the same temperature for 1 h until compound **3a** had been consumed (monitored by TLC). Having been quenched with saturated aqueous ammonium chloride, the organic layer was separated, washed with water, dried (MgSO$_4$) and evaporated. The remaining crude **5a** (^{1}H NMR spectroscopy) was subjected to column chromatography on silica gel [benzene–hexane (1:1)] to give a

mixture of *cis*- and *trans*-**5a** (94%) (ratio determined by ^{1}H NMR spectroscopy). Recrystallization (several times) from dichloromethane–hexane gave pure *cis*-**5a** as colourless rhombs. The ^{1}H NMR spectral data of *cis*- and *trans*-**5** are summarized in Table 5. Conspicuous differences in the ^{13}C NMR spectra between *cis*- and *trans*-**5** were not observed. The reactions of **1a** with the other dienophiles **6–12** to afford the adducts **13–19**, respectively, were carried out similarly. In cases of the adducts **13** and **15**, *cis*- and *trans*-isomers could be separated by column chromatography [silica gel, ethyl acetate–hexane (1:40–4)].

Methyl 4,6-*diphenyl*-3,4-*dihydrothiopyran*-3(2H)-*carboxylate* **5a**. *cis*-**5a**: Colourless rhombs, m.p. 106–107 °C (Found: C, 73.45; H, 5.8. $C_{19}H_{18}O_2S$ requires C, 73.5; H, 5.8%); ν_{max}(KBr disk)/cm^{-1} 1733 (CO); δ_C 22.75 (t), 42.23 (d), 44.35 (d), 51.52 (q), 121.10 (d), 140.09 (s) and 172.63 (s, CO); *m/z* 310 (M$^+$, 34%), 250 (M$^+$ − CO$_2$Me − H, 59), 223 (**1a**$^+$ − H, 100), 121 (16), 91 (23) and 77 (8).

Methyl 4-(4-*chlorophenyl*)-6-*phenyl*-3,4-*dihydrothiopyran*-3(2H)-*carboxylate* **5b**. *cis*-**5b**: Colourless rhombs, m.p. 147–148 °C (ethyl acetate–hexane) (Found: C, 66.15; H, 4.9. $C_{19}H_{17}ClO_2S$ requires C, 66.2; H, 5.0%); ν_{max}(KBr)/cm^{-1} 1732 (CO); δ_H 2.94 (dd, *J* 2.0 and 12.2, 2α-H), 3.12 (dd, *J* 12.0 and 12.2, 2β-H), 3.22 (ddd, *J* 2.0, 5.6 and 12.2, 3-H), 3.60 (s, Me), 4.18 (dd, *J* 5.6 and 6.3, 4-H), 6.09 (d, *J* 6.3, 5-H) and 7.10–7.55 (m, 9 H, ArH); δ_C 22.68 (t), 41.58 (d), 44.17 (d), 51.72 (q), 119.53 (d) and 172.47 (s); *m/z* 344 (M$^+$, 40%), 284 (M$^+$ − CO$_2$Me − H, 76), 257 (**1b**$^+$ − H, 74) and 223 (**1b**$^+$ − Cl, 100).

Methyl 6-*phenyl*-4-(4-*tolyl*)-3,4-*dihydrothiopyran*-3(2H)-*carboxylate* **5c**. *cis*-**5c**: Colourless needles, m.p. 102–103 °C (hexane) (Found: C, 74.0; H, 6.0. $C_{20}H_{20}O_2S$ requires C, 74.0; H, 6.2%); ν_{max}(KBr)/cm^{-1} 1732 (CO); δ_H 2.31 (s, Me), 2.92 (dd, *J* 2.0 and 9.2, 2α-H), 3.18 (dd, *J* 9.2 and 12.2, 2β-H), 3.23 (ddd, *J* 2.0, 4.0 and 12.2, 3-H), 3.62 (s, OMe), 4.18 (dd, *J* 4.0 and 6.3, 4-H), 6.14 (d, *J* 6.3, 5-H) and 7.04–7.56 (m, 9 H, ArH); δ_C 21.06 (q), 22.75 (t), 41.89 (d), 44.38 (d), 51.61 (q), 120.38 (d) and 172.88 (s); *m/z* 324 (M$^+$, 36%), 264 (M$^+$ − CO$_2$Me − H, 47), 237 (**1c**$^+$ − H, 34) and 223 (**1c**$^+$ − Me, 100).

Methyl 4,6-*bis*(4-*chlorophenyl*)-3,4-*dihydrothiopyran*-3(2H)-*carboxylate* **5d**. *cis*-**5d**: Colourless rhombs, m.p. 140–142 °C (ethyl acetate–hexane) (Found: C, 60.0; H, 4.1. $C_{19}H_{16}Cl_2O_2S$ requires C, 60.2; H, 4.25%); ν_{max}(KBr)/cm^{-1} 1732 (CO); δ_H 2.95 (dd, *J* 2.0 and 12.2, 2α-H), 3.12 (dd, *J* 11.9 and 12.2, 2β-H), 3.22 (ddd, *J* 2.0, 5.6 and 11.9, 3-H), 3.61 (s, OMe), 4.18 (dd, *J* 5.6 and 6.3, 4-H), 6.27 (d, *J* 6.3, 5-H) and 7.09–7.57 (m, 8 H, ArH); δ_C 22.71 (t), 41.56 (d), 44.10 (d), 51.79 (q), 120.03 (d) and 172.34 (s); *m/z* 378 (M$^+$, 38%), 318 (M$^+$ − CO$_2$Me − H, 69), 291 (**1d**$^+$ − H, 60) and 257 (**1d**$^+$ − H − Cl, 100).

3-*Acetyl*-4,6-*diphenyl*-3,4-*dihydro*-2H-*thiopyran* **13**. *cis*-**13**: Colourless rhombs, m.p. 110–111 °C (ethyl acetate–hexane) (Found: C, 77.6; H, 6.05. $C_{19}H_{18}OS$ requires C, 77.5; H, 6.2%); ν_{max}(KBr)/cm^{-1} 1698 (CO); δ_C 23.13 (t), 29.29 (q), 42.41 (d), 51.50 (d), 120.41 (d), 139.73 (s) and 208.48 (s); *m/z* 294 (M$^+$, 27%), 251 (M$^+$ − COMe, 11), 223 (**1a**$^+$ − H, 100) and 121 (29).

trans-**13**: colourless glassy oil; ν_{max}(neat/NaCl)/cm^{-1} 1712; *m/z* 294 (M$^+$, 100%), 251 (43), 223 (95) and 121 (45).

4,6-*Diphenyl*-3,4-*dihydrothiopyran*-3(2H)-*carbaldehyde* **14**. *cis*-**14**: Colourless crystals, m.p. 91.1–91.6 °C (ethyl acetate–hexane) (Found: C, 77.2; H, 5.6. $C_{18}H_{16}OS$ requires C, 77.1; H, 5.75%); ν_{max}(KBr)/cm^{-1} 1724 (CO); δ_C 22.95 (t), 41.02 (d), 49.81 (d), 119.64 (d) and 201.26 (d, CHO); *m/z* 280 (M$^+$, 54%), 252 (M$^+$ − CO, 21), 223 (**1a**$^+$ − H, 100) and 121 (29).

N,N-*Dimethyl*-4,6-*diphenyl*-3,4-*dihydrothiopyran*-3(2H)-*carboxamide* **15**. *cis*-**15**: Colourless rhombs, m.p. 141–142 °C (Found: C, 74.0; H, 6.4. $C_{20}H_{21}NOS$ requires C, 74.3; H, 6.5%); ν_{max}(KBr)/cm^{-1} 1638 (CO); *m/z* 323 (M$^+$, 64%), 290 (M − SH, 6), 276 (20), 250 (M$^+$ − CONMe$_2$ − H, 20) 223 (**1a**$^+$ − H, 100) and 121 (17).

trans-15: Colourless glassy oil; ν_{max}(neat/NaCl)/cm^{-1} 1660 (CO); m/z 323 (M$^+$, 100%), 290 (7), 276 (14), 250 (62), 223 (35) and 121 (18).

Methyl 3-methyl-4,6-diphenyl-3,4-dihydrothiopyran-3(2H)-carboxylate **16**. *cis*-**16**: Colourless rhombs, m.p. 142–143 °C (dichloromethane–hexane) (Found: C, 74.0; H, 6.1. C$_{20}$H$_{20}$O$_2$S requires C, 74.0; H, 6.2%); ν_{max}(KBr)/cm^{-1} 1728 (CO) and 1108; δ_C 22.77 (t), 29.09 (q), 43.68 (d), 48.86 (s), 51.59 (q), 118.85 (d), 141.17 (s) and 175.34 (CO); m/z 324 (M$^+$, 13%), 223 (1a$^+$ − H, 100) and 121 (7).

Dimethyl 4,6-diphenyl-3,4-dihydrothiopyran-2,3(2H)-dicarboxylate **17**. *cis*-**17**: Colourless needles, m.p. 136–137 °C (ethyl acetate–hexane) (Found: C, 68.65; H, 5.2. C$_{21}$H$_{20}$O$_4$S requires C, 68.5; H, 5.5%); ν_{max}(KBr)/cm^{-1} 1744; δ_C 39.68 (d), 42.70 (d), 46.00 (d), 51.81 (q), 52.87 (q), 120.03 (d), 139.35 (s), 170.83 (CO) and 171.95 (CO); m/z 368 (M$^+$, 12%), 308 (M$^+$ − CO$_2$Me − H, 9), 249 (M$^+$ − 2CO$_2$Me − H, 100) and 223 (1a$^+$ − H, 44).

Methyl 2-methyl-4,6-diphenyl-3,4-dihydrothiopyran-3(2H)-carboxylate **18**. *cis*-**18**: Colourless rhombs, m.p. 80–81 °C (dichloromethane–hexane) (Found: C, 74.3; H, 6.1. C$_{20}$H$_{20}$O$_2$S requires C, 74.0; H, 6.2%); ν_{max}(KBr)/cm^{-1} 1732 (CO), 1618 and 1170; δ_C 19.53 (q), 31.86 (d), 44.74 (d), 51.28 (q), 51.61 (d), 119.57 (d), 140.29 (s) and 172.14 (CO); m/z 324 (M$^+$, 5%), 264 (M$^+$ − CO$_2$Me − H, 7), 249 (14), 223 (1a$^+$ − H, 36) and 28 (100).

5,7-Diphenyl-N-p-tolyl-7,7a-dihydrothiopyrano[2,3-c]-pyrrole-1,3(2H)-dione **19**. *cis*-**19**: Colourless rhombs, m.p. 223–224 °C (dichloromethane–hexane) (Found: C, 75.9; H, 5.0. C$_{26}$H$_{21}$NO$_2$S requires C, 75.9; H, 5.1%); ν_{max}(KBr)/cm^{-1} 1713 (CO); δ_C 19.16 (q), 43.92 (d), 44.24 (d), 49.54 (d), 124.71 (d), 137.18 (s), 172.72 (CO) and 172.87 (CO); m/z 411 (M$^+$, 21%), 378 (M$^+$ − SH, 18), 249 (15), 223 (100) and 191 (18).

Oxidation of cis-13 *with* m-*Chloroperbenzoic Acid* (m*CPBA*) *to give the Sulfone* **20**.- -To a solution of the adduct *cis*-13 (412 mg, 1.4 mmol) in dichloromethane (20 cm^3) was added m*CPBA* (1.2 g, 5.6 mmol) at 0 °C. The reaction mixture warmed up to room temperature with stirring for 3 h and then washed with aqueous sodium carbonate and water, and dried (MgSO$_4$). Removal of the solvent and recrystallization of the residue from dichloromethane–hexane gave the sulfone **20** (443 mg, 97%).

3-Acetyl-4,6-diphenyl-3,4-dihydro-2H-thiopyran S,S-dioxide **20**: m.p. 201–202 °C; ν_{max}(KBr)/cm^{-1} 1708 (CO) and 1296 (SO$_2$); δ_C 28.60 (q), 42.94 (d), 48.32 (t), 49.90 (d), 134.32 (d) and 205.53 (s); m/z 326 (M$^+$, 6%), 283 (M$^+$ − COMe, 2), 262 (M$^+$ − SO$_2$, 14) and 218 (100).

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