Anionic [4 + 2] Cycloaddition with Thiophthalides: an Integrated Approach to the Synthesis of Olivin and Pillaromycinone

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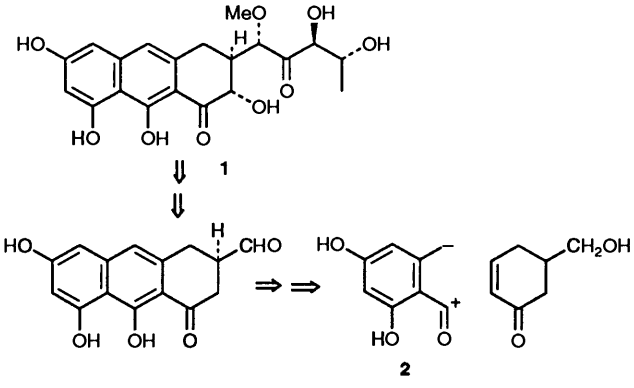
A systematic study of the potential reactivity of the thiophthalides **4** and **18–20** as 1,4-dipolar synthons, has shown that 3-phenylthiothiophthalide **19** is the best annulating agent for the preparation of tricyclic intermediates related to olivin. The reagent **19** underwent anionic [4 + 2] cycloaddition with cyclohex-2-enone **5a** in the presence of lithium *tert*-butoxide to give the anthracenones **24a** and **25** in a combined yield of 90%.

Olivin **1**, the aglycone of the clinically effective antitumour agent olivomycin A[1] has received much attention as a synthetic target because of its intricate tricyclic structure with a side-chain bearing multiple stereogenic centres. Several research groups are actively involved in pursuing the synthesis[2] of natural olivin **1**. In a recent publication, Roush and co-workers first reported the total synthesis[3] of natural olivin **1**. Earlier, reports from Weinreb group and Franck group described the total synthesis of tri-*O*-methylolivin.[4]

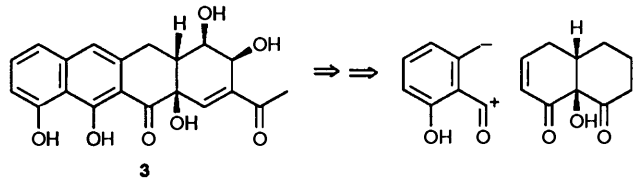
Having worked on a synthetic strategy possessing sufficient flexibility to allow the stereocontrolled synthesis of structural analogues of olivin we have now developed an efficient method for the annulation of aromatic rings with functionalized cyclohexenones using suitable 1,4-dipolar synthons such as **2** (see Scheme 1). Such a strategy also provides ready access to the tetracyclic skeleton of another important aglycone, namely, pillaromycinone **3**[5] (Scheme 2). Although similar retrosynthetic analysis[6] has been made before, execution of the above annulation (Scheme 1) has proven to be far more frustrating than expected. Thus, *ortho*-toluates, phthalides and homophthalic anhydrides which are considered 1,4-dipolar synthon equivalents fail to undergo annulation[7] with cyclohexenones. An alternative photoannulation[8] giving rise to *peri*-oxygenated anthracenone ring systems provides only extremely low yields of the products. Nevertheless, Snider's free-radical approach[9] to such systems holds promise for the efficient preparation of the olivin nucleus. In connection with these studies we have looked into the chemistry of thiophthalides **4** which, in sharp contrast to phthalide chemistry, has remained unexplored.

We had two reasons for choosing thiophthalides as 1,4-dipolar synthon equivalents: first, the sulfur atom in thiophthalide would lead to a more stabilized[10] carbanion at C-3, minimizing self-dimerization[11] and second, it would render carbonyl function of the thiol ester group more susceptible to a nucleophilic attack in the ring-closure step, in comparison to its oxygen counterpart, *i.e.* phthalide. Furthermore, the sulfur atom could be conveniently removed from annulated products under a variety of conditions.

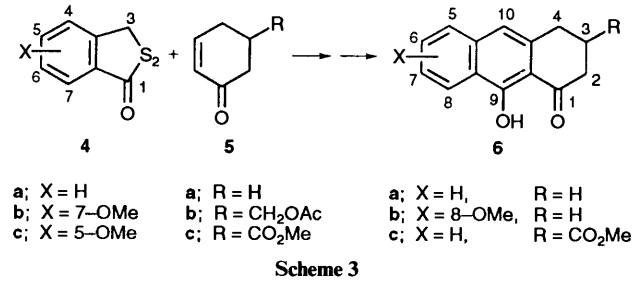
In a recent communication,[12] we demonstrated that thiophthalides **4** could succcessfully be annulated with cyclohexenones to give anthracenones derivatives **6** (Scheme 3). Since this annulation scheme proved inefficient on a larger scale, we functionalized the thiophthalide **4a** at C-3 with bromine, phenylthio and phenylsulfonyl groups. This ensured that the corresponding carbanion at C-3 was softer and thus more suited to the initial Michael addition, and enhanced the reactivity of the thiolactone function in the subsequent Dieckmann cyclization step which is, in all likelihood, the slower of the two steps. These three thiophthalides were then allowed to react



Scheme 1



Scheme 2



a; X = H
b; X = 7–OMe
c; X = 5–OMe

a; R = H
b; R = CH_2OAc
c; R = CO_2Me

a; X = H, R = H
b; X = 8–OMe, R = H
c; X = H, R = CO_2Me

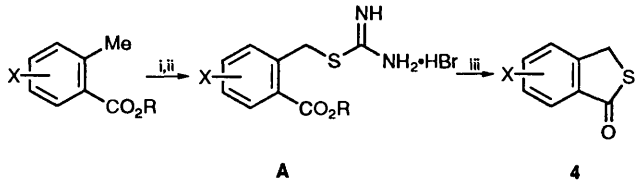
Scheme 3

with selected cyclohexenones under basic conditions. Finally, it was found that 3-phenylthiothiophthalide **19** is the most suitable 1,4-dipolar synthon equivalent for annulation of cyclic enones.

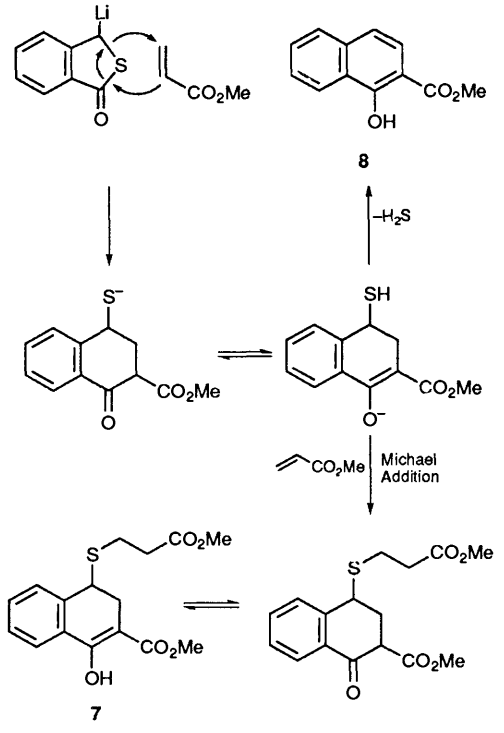
Here, we present full detail of these studies.

Results and Discussion

Preparation of Thiophthalides **4**.—Little has been published on the chemistry of thiophthalides and no systematic study of



Scheme 4 *Reagents and conditions:* i, *N*-bromosuccinimide, CCl_4, heat; ii, thiourea, acetone, heat; iii, saturated aq. $NaHCO_3$, heat



Scheme 5

either their preparation or their reactions has appeared. Since *ortho*-toluates are readily accessible, we briefly examined their conversion[13] into thiophthalides. A variety of substituted thiophthalides used in this study were prepared by this general route (see Scheme 4). The most striking feature of this route is the direct decomposition of the thiouronium salts A to thiophthalides **4** when gently heated with saturated aqueous $NaHCO_3$.

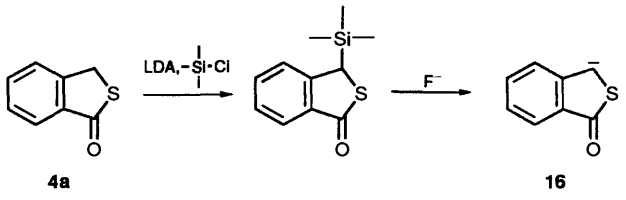
Annulation with 3-Unsubstituted Thiophthalides **4**.—The parent thiophthalide **4a** was treated with a freshly prepared solution of lithium diisopropylamide (LDA) at −60 °C followed by addition of methyl acrylate (2 equiv.), in analogy with phthalide[14] chemistry. Work-up of the reaction mixture at room temperature led to an intractable mixture of products. The same reaction, when performed in the presence of lithium *tert*-butoxide at −60 °C provided the annulated compound **7** as an oil (26%), the ^1H NMR spectrum of which clearly indicated that the product exists exclusively in the enolic form **7**. The identity of this product was further authenticated by its Raney-nickel degradation to 2-methoxycarbonyl-α-tetralone which, in turn, was prepared by an independent route.[15] A small amount (2%) of methyl 1-hydroxy-2-naphthoate **8** was obtained as a co-product of **7** from the reaction of **4a** and methyl acrylate. Thus, it is likely that the formation of **7** and **8** follows a cascade of reactions involving Michael addition of the conjugate base of thiophthalide **4a** to methyl acrylate followed by Dieckmann cyclization at the thiolactone function (see Scheme 5).

The anion of the thiophthalide **4a** when treated with acrylonitrile gave the tetralone **9** as a pale yellow solid (43%), the gross structure of which was established on the basis of ^1H NMR evidence; the *trans* geometry of the substituents on the cyclohexanone ring, however, was only tentatively established on the basis of the coupling constants of 2-H and 4-H [double doublets at δ 4.60 (*J* 3.0 Hz, *J* = 3.2 Hz) and 4.56 (*J* 4.0 Hz, *J* = 13.0 Hz)]. Since the signal at 4.56 ppm has a single large coupling constant (pseudo diaxial ^1H–^1H coupling)[9] whilst the other does not, it was inferred that the substituents, SCH_2CH_2CN and CN, are *trans* to each other; a *cis* disposition would have given large coupling constants for both 2-H and 4-H.

Since our primary concern was to test the feasibility of annulation of a thiophthalide with cyclohex-2-enones, the thiophthalide **4a** was treated with cyclohex-2-enone **5a** in the presence of lithium *tert*-butoxide at −60 °C. The reaction provided an inseparable mixture of products (three enolic hydrogen signals at δ 16.60, 16.20 and 14.16), which upon Raney nickel treatment gave **6a**[8] as the sole product (signal at δ 14.20). Thus, the signals at δ 16.60 and 16.20 were assigned to the enolic protons of the isomeric anthracenones **10** and **11**. In fact, such high δ values for enolic hydrogen are characteristic of decalin systems containing the β-diketone function.[16] Further structural characterization was obtained from ^1H NMR and ^{13}C NMR analysis of isomer **10**. The thiols **10** and **11** slowly decompose to the corresponding aromatized product **6a** on prolonged storage or during chromatography over silica gel; this prevented preparation of analytical samples.

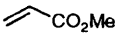
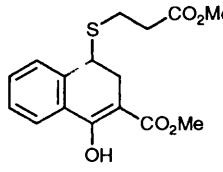
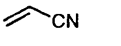
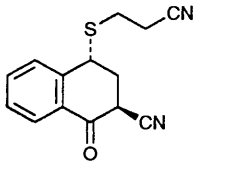
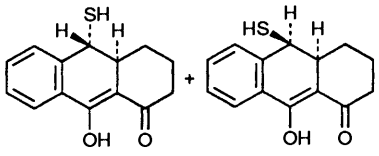
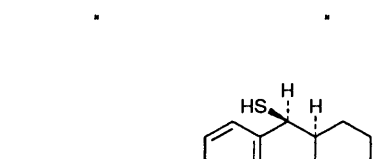
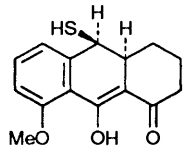
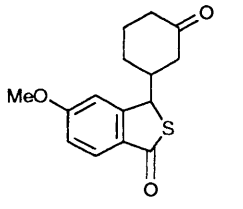
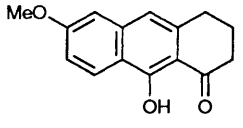
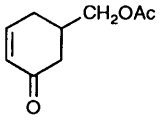
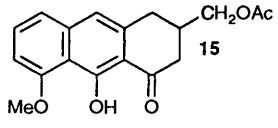
Next, we turned our attention to annulation with methoxy substituted thiophthalides **4b** and **4c** in order to assess the influence of aromatic ring substituents on the efficiency of this annulation. The reaction of **4b** with cyclohex-2-enone **5a** yielded the desired annulated product **12** (31%). The product was aromatized to **6b**[17] by Raney nickel treatment. Although the yield was slightly higher in the case of **4b** than **4a**, the effect of a methoxy group was noticeable with the thiophthalide **4c** which, under similar reaction conditions, underwent only Michael addition to give the product **13**. It is thus evident that the 5-methoxy substituent exerts a strong electron-releasing resonance effect onto the carbonyl group of the thiolactone to reduce its electrophilicity and thus prevent the Dieckmann cyclization. However, the cyclization could be effected at reflux temperature to give product **14** albeit in poor yield (14%). It also shows that the success of this annulation, in part, depends on the reactivity of thiolactone function. In a further step towards olivin, 5-acetoxymethylcyclohex-2-enone **5b** was treated with 7-methoxythiophthalide **4b** under the specified conditions to give the desired product **15** (23%).

Having generalized the annulation methodology, we directed our efforts to improving the yields of these reactions. First, we considered the generation of thiophthalide anion **16** (Scheme 6) in the presence of mild base, conditions under which the polymerization of cyclohex-2-enones, a known problem, would be minimized. One of the ways to achieve this would be fluoride ion-induced desilylation of 3-silyl substituted thiophthalide (see Scheme 6). However, all our attempts to silylate the thiophthalide **4a** by the standard protocol[18] failed to give the



Scheme 6

Table 1 Anionic annulation of thiophthalide **4a–c** onto Michael acceptors

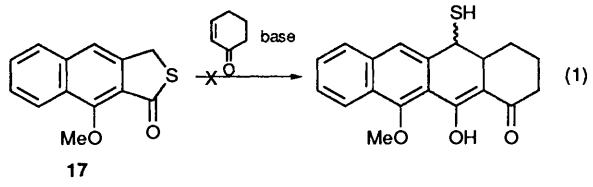
Compd.	Acceptor*	Product(s)		Yield (%)
4a			**7**	26
4a			**9**	43
4a	CYH		**10** + **11** (1 : 3)	27[a]
4a	CYH		**10** + **11** (1 : 1)	42[b]
4b	CYH		**12**	31
4c	CYH		**13**	35
4c	CYH		**14**	14[c]
4b			**15**	23

* CYH = cyclohex-2-enone. [a] The ratio of the products was 1:3. [b] This was performed in the presence of CuI. [c] After the reaction was carried out according to the general procedure, the reaction mixture was heated at reflux for 3 h.

corresponding *C*-silylated product, possibly because of loss of the trimethylsilyl group during aqueous work-up.

In our next approach, we felt it necessary to increase the reactivity of the thiolactone group by using a thiophilic catalyst. Of known thiophilic reagents,[19] CuI was chosen in the hope that it would not only activate the thiolactone group of the thiophthalide but also facilitate initial Michael addition *via* a cuprate intermediate. Indeed, higher yields of the annulated products **10** and **11** were obtained when the reaction of **4a** with **5a** was performed in the presence of cuprous iodide (see Table 1), but, the improvement was only marginal.

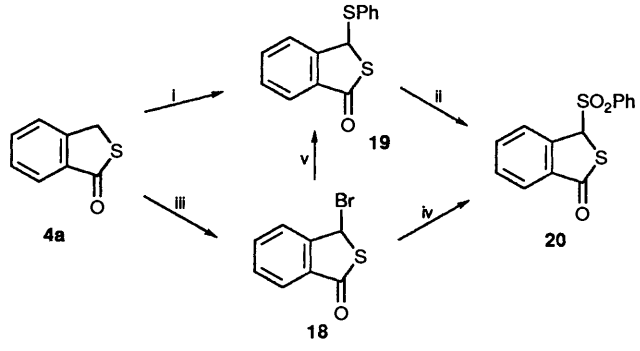
In further efforts to extend the scope of thiophthalide annulation in assembling a tetracyclic structure, the benzo analogue **17** [eqn. (1)] of thiophthalide was allowed to react with cyclohex-2-enone **5a** under a variety of conditions: namely, LDA, Bu^{t}OLi, Bu^{t}OK or LDA and CuI. Unfortunately, these reactions gave only unchanged thiophthalide **17**, no annulated product being detected.



17

Annulation with 3-Monosubstituted Thiophthalides **18–20**.—Although factors affecting annulation with 1,4-dipolar synthon equivalents, in general, were taken into consideration in the work already described, since the yields of annulation with thiophthalides **4a–c** were low it occurred to us that with such compounds a second Michael addition at C-3 could be a problem. Consequently, we investigated the reactivity of such compounds towards electron-deficient alkenes, choosing to prepare 3-phenylsulfonylthiophthalide **20**, in line with Hauser's work [7] on 3-phenylsulfonylphthalide.

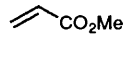
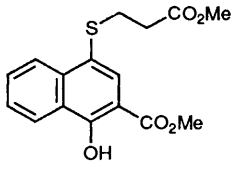
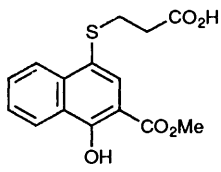
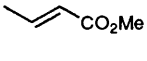
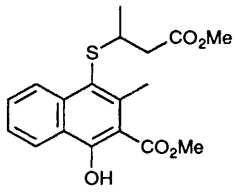
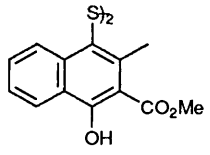
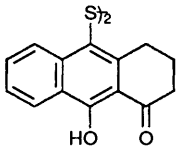
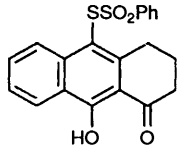
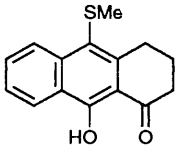
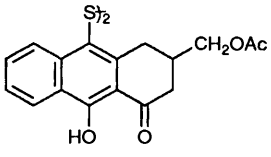
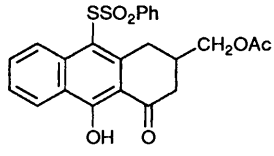
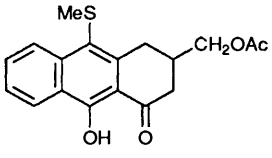
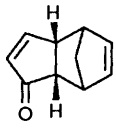
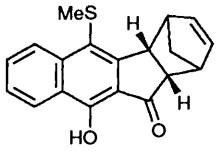
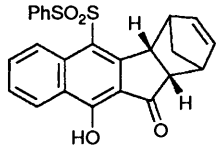
Three different sequences of reactions (see Scheme 7) were examined with a view to preparing the sulfone **20** inexpensively, and on a multigram scale. The best route consisted of (i) benzylic bromination of thiophthalide **4a**, (ii) nucleophilic displacement of bromine in **18** by thiophenoxide ion and (iii) selective oxidation of **19** by H_2O_2/AcOH, a sequence of reactions providing **20** in 70–90% overall yield.



Scheme 7 *Reagents and conditions:* i, LDA, PhSSPh or $PhSSO_2Ph$; ii, H_2O_2 (30%), AcOH, 50 °C; iii, *N*-bromosuccinimide, CCl_4, heat; iv, $PhSO_2Na$, DMF; v, PhSH, Et_3N

As expected, the reagent **20** underwent clean deprotonation at C-3 with lithium *tert*-butoxide at −60 °C to form a yellow solution of the anion **21** which smoothly reacted with a variety of Michael acceptors in tandem Michael–Dieckmann fashion to afford the annulated products (see Table 2). Treatment of **20** with methyl acrylate under the above reaction conditions furnished the annulated products **22a** and **22b**, respectively, in an unoptimized combined yield of 51%, clearly indicating the higher efficiency of the reagent **20** over the thiophthalide **4a**. Similar trends were found with other Michael acceptors (see Table 2). The product from cyclohex-2-enone (entry 3), after acidic work-up, was the disulfide **24a**, the structure of which was established on the basis of ^{1}H NMR evidence. In contrast, the corresponding disulfide **26a** from 5-acetoxymethylcyclohex-2-

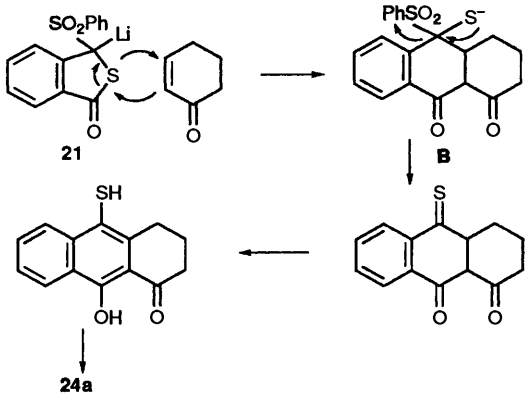
Table 2 Annulation[a] of 3-phenylsulfonylthiophthalide **20** with Michael acceptors

Entry	Acceptor	Products (% yield)		Total yield (%)	
1			**22a** (43)		**22b** (8) 51
2			**23a** (42)		**23b** (12) 54
3	**5a**		**24a** (65)		**24b** (5) 70
4	**5a**		**25** (72)	**24b** (trace)	72
5	**5b**		**26a** (25)		**26b** (4) 29
6	**5b**		**27** (38)		**26b** (7) 45
7		**28** 	**29a** (60)		**29b** (11) 71

[a] For entries 4, 6 and 7, the reaction mixture was treated with iodomethane before it was worked up.

enone **5b** provided an unusually complex ^{1}H NMR spectrum. These reactions were then reexamined with methyl iodide being used to quench them, work-up and product identification then being simpler. The minor product **24b** was, however, still obtained. While it is possible that these products could be formed from intermolecular transfer of SO_2Ph group of the unchanged sulfone **20** to thiolate of the annulated product, no products arising from the conjugate base of thiophthalide **4a** were identified. Therefore, it seems that the thiosulfonate by-products are formed *in situ* by internal nucleophilic attack of S^- on a SO_2Ph group in **B** (Scheme 8) followed by aerial oxidation. Similarly, the cyclohexenone **5b** reacted with **20** to afford the product **27** in good yield. The tricyclo enone **28**[20] also provided the annulated product **29a** in good yield.

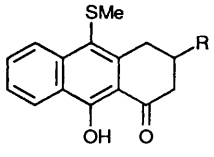
During our work with the sulfone **20**, we noted that its annulation was sluggish compared to that of the thiophthalide **4a**, occurring only at room temperature (annulated products, on TLC examination, exhibit fluorescent spots). Since this, we thought, was due to steric hindrance caused by SO_2Ph group[21] in **20**, we then examined the reactivity of 3-phenylthiothiophthalide **19** where less steric hindrance during the initial Michael addition is likely. We found it to be an excellent annulating agent giving the products **25** and **24a** in 90% combined yield. Similarly, with the 5-substituted cyclohexen-



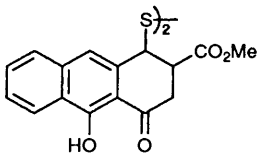
Scheme 8

Table 3 Annulation of 3-(phenylthio)thiophthalide **19** with the cyclohexenones **5**

Entry	Acceptor	Products (% yield)	Total yield (%)
1	**5a**	**25a** (70) + **24** (20)	90
2	**5c**	**30a** (56) + **30b** (15) + **30c** (8.5)	79.5
3	**5b**	**27** (38) + **31** (39)	77



30a R = CO_2Me
30c R = CO_2H
31 R = CH_2OH



30b

ones **5b** and **5c** the sulfide **19** gave the corresponding products in consistently excellent yields (Table 3). TLC examination of these reactions showed that the annulation occurs even at low temperature (~ −40 °C). Suppression of by-product formation [compounds **24a** and **30b** (entry 1 and 2, Table 3)] could be avoided by using an excess of MeI for a longer reaction period (entry 3). It is noteworthy that the ester substituents in the Michael acceptors do not affect the overall annulation process (entry 2 and 3). The hydrolysed by-products **30c** and **31** are possibly formed during the work-up or *via* transesterification. The structures of **24a** and **30b** were further confirmed by their desulfurization to **6a** and **6c**, respectively. In order to utilize the more readily accessible 3-bromothiophthalide **18** as a substitute for **19**, it was treated with the cyclohexenone **5a** in the presence of LDA at −60 °C. But, this reaction resulted in a complicated mixture of products.

Thus, the synthetic viability and effectiveness of reagents **19** and **20** as 1,4-dipolar synthon equivalents in anionic [4 + 2] cycloaddition have been established. The now ready availability of 5-acetyloxymethylcyclohex-2-enone **5b** in optically active forms,[22] makes it a potentially important olivin intermediate.

Experimental

M.p.s and b.p.s are uncorrected. Unless otherwise stated, ^1H NMR spectra were recorded at 90 MHz (Varian) and 100 MHz (JEOL) for solutions in ^2H chloroform with tetramethylsilane as the internal standard. Chemical shifts are reported as δ values and ^1H–^1H coupling constants are in Hz. IR spectra were obtained on a Perkin-Elmer model-883 as a KBr pellet or neat liquid and the characteristic peaks presented in cm^{-1}. Mass spectral and analytical data were obtained from CDRI, Lucknow and RSIC, Madras.

All solvents used for reactions were purified before use. Benzene, toluene, ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone under an atmosphere of dry argon, and dichloromethane from CaH_2. *tert*-Butyl alcohol was distilled from sodium. Commercial solutions of butyllithium in hexane were titrated by Gilman double titration method. All chromatographic solvents were distilled prior to use. In most cases, mixtures of ethyl acetate and light petroleum (b.p. 60–80 °C) were used as eluents. Column chromatography was performed on silica gel (60–120 mesh, S.D. fine chemicals). TLC was performed on GF_{254} silica gel (S.D. fine chemicals). Preparation of lithium *tert*-butoxide was carried out by addition of butyllithium (Fluka) to a stirred solution of *tert*-butyl alcohol in THF under an Ar atmosphere at 0 °C. All the thiophthalides except **18**–**20** used in this study were prepared according to recently reported procedures.[13]

5-(Acetoxymethyl)cyclohex-2-enone **5b**.—To a well-stirred suspension of $LiAlH_4$ (3.25 g, 85.6 mmol) in dry ether (250 cm^3) at room temperature was added dropwise a solution of 6-oxabicyclo[3.2.1]oct-3-en-7-one[23] (8.5 g, 68.5 mmol) in dry ether (250 cm^3). When the addition was complete, the reaction mixture was heated at reflux for 1 h and then cooled to 0 °C. Water (3.3 cm^3), aqueous sodium hydroxide (15%; 3.3 cm^3) and water (10 cm^3) were successively added to the mixture to decompose the excess of hydride reagent after which the resulting white precipitate was filtered off and washed with ether (2 × 50 cm^3). The combined filtrate and the washings were dried (Na_2SO_4) and concentrated to give essentially pure 5-hydroxymethylcyclohex-2-en-1-ol (8.7 g, 97%) as a thick colourless oil; δ_H 5.95–5.6 (m, 2 H), 4.45–4.20 (m, 1 H), 3.58 (br d, 2 H), 2.3–1.75 (m, 4 H), 1.8 (br s, 2 H) and 1.48–1.12 (m, 1 H).

To a magnetically stirred solution of 5-hydroxymethyl cyclohex-2-enol (4.4 g, 34 mmol) in chloroform (250 cm^3) was added powdered freshly prepared manganese dioxide (22 g, 253 mmol) and the stirring was continued for 12 h at room temperature. Manganese dioxide was filtered off and the filtrate was concentrated to an oily residue which was purified by column chromatography to give 5-hydroxymethylcyclohex-2-enone[24] as a light brown liquid (3.6 g, 83%); ν_{max}(KBr)/cm^{-1} 3440, 1677 and 1250; δ_H 7.2–6.7 (m, 1 H), 5.95 (d, 1 H), 3.75–3.2 (m, 2 H), 3.0 (br s, 1 H) and 2.95–1.90 (m, 5 H). This material was used in the next step without further purification. Substitution of MnO_2 with $BaMnO_4$[25] in the above reaction also gave the product (78.5%).

Dry pyridine (18 cm^3) was added to a solution of 5-hydroxymethylcyclohex-2-enone (3.0 g, 23 mmol) in freshly distilled acetic anhydride (12 cm^3) at room temperature. After 6 h at ambient temperature the contents of the flask were poured into water (50 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined extracts were washed with aqueous saturated copper sulfate (5 × 30 cm^3) and brine (1 × 50 cm^3), dried (Na_2SO_4) and evaporated to provide a brownish residue. This was distilled (b.p. 110 °C/0.4 mmHg) to give **5b** as a pale yellow liquid (2.5 g, 62%); ν_{max}(KBr)/cm^{-1} 1743, 1677, 1583 and 1242; δ_H 7.05–6.80 (m, 1 H), 6.05–5.8 (br d, 1 H), 4.1–3.8 (br d, 2 H), 2.35–2.10 (m, 5 H) and 2.0 (s, 3 H); *m/z* 108 (M − 60).

Methyl 3-Oxocyclohex-4-enecarboxylate **5c**.—To a well

stirred solution of 6-oxabicyclo[3.2.1]oct-3-en-7-one (1.0 g, 8.06 mmol) in dry methanol (25 cm^3) at room temperature was added a catalytic amount of potassium carbonate (0.2 g) Stirring was continued for 12 h. Methanol was removed after which the mixture was evaporated under reduced pressure and the resulting residue was taken up in ethyl acetate (30 cm^3). The precipitated potassium carbonate filtered off and the filtrate was washed with water (10 cm^3) and brine (5 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure to furnish methyl 3-hydroxycyclohex-1-enecarboxylate as a clear colourless liquid (1.0 g, 79.5%); ν_{max}(KBr)/cm^{-1} 3427, 1731, 1654 and 1259; δ_H 5.7 (br s, 2 H), 4.53–4.0 (m, 1 H), 3.65 (s, 3 H), 2.9–2.0 (m, 4 H) and 1.8–1.3 (m, 1 H).

Pulverized solid manganese dioxide (2.0 g, 22.4 mmol) at room temperature was added to a stirred solution of methyl 3-hydroxycyclohex-1-enecarboxylate (0.5 g, 3.2 mmol) in chloroform (30 cm^3) and stirring continued for 24 h. The mixture was then filtered, concentrated and the residue distilled under reduced pressure (108–110 °C/0.3 mm) to furnish **5c** [26] as a clear pale yellow liquid (0.45 g, 91%); ν_{max}(KBr)/cm^{-1} 1737, 1682 and 1248; δ_H 7.1–6.85 (m, 1 H), 6.05 (br d, 1 H), 3.7 (s, 3 H), 3.25–2.8 (m, 1 H) and 2.75–2.55 (m, 4 H).

General Procedure for Annulation with Thiophthalides **4**, **19** *and* **20**.—To a stirred solution of lithium *tert*-butoxide (7.0 mmol) at −60 °C ($CHCl_3$/liquid N_2 bath) was added a solution of a thiophthalide (3.3 mmol) in THF (30 cm^3). The resulting yellowish solution was stirred at −60 °C for 15–20 min after which a Michael acceptor (1.2–1.5 equiv. unless otherwise stated) was added to it neat with washing (THF) into the reaction vessel. The cooling bath was removed after *ca.* 3 h at −60 °C and the reaction mixture brought to room temperature. The starting thiophthalide and the initial Michael adduct had similar UV characteristics on TLC while the annulated products exhibited blue fluorescence on TLC under UV light. After the reaction had reached a steady state as indicated by TLC, it was acidified with 10% HCl (3 cm^3) at 0 °C. The resulting solution was concentrated under reduced pressure to remove THF and the residue was extracted with ethyl acetate (2 × 50 cm^3). The combined extracts were then washed with water (30 cm^3), saturated aqueous $NaHCO_3$ (25 cm^3) and brine (20 cm^3) and dried (Na_2SO_4). Removal of solvent yielded a slightly coloured material which was purified by column chromatography to furnish the corresponding products. Occasionally, final purifications were achieved by preparative TLC. For entries 4, 6 and 7 (Table 2) and entries 1–3 (Table 3) prior to acid work-up, iodomethane (16 mmol) was introduced into the reaction flask and the resulting mixture was stirred at room temperature for 24 h. Lithium *tert*-butoxide as base (3 equiv.) was used for annulation with compounds **19** and **20**.

Cuprous Iodide-catalysed Reaction of **4a** *with* **5a**.—To a stirred solution of LDA [diisopropylamine (9 mmol) and BuLi (9 mmol) in THF (25 cm^3)] at −60 °C, was slowly added a solution of **4a** (500 mg, 3.3 mmol) in THF (5 cm^3). The reaction mixture was stirred at −60 °C for 30 min after which CuI (630 mg, 3.3 mmol) was introduced into the reaction flask. After the resulting mixture had been stirred at −60 °C for 1 h cyclohexenone **5a** (634 mg, 6.6 mmol) was then added to it and reaction continued for a further 1 h. The cooling bath was then removed and the reaction mixture allowed to come to room temperature under ambient conmditions. After 3.5 h room temperature, the reaction was quenched with 2 mol dm^{-3} HCl (15 cm^3) and the resulting mixture was concentrated under reduced pressure to give a light-coloured solution. This was extracted with ethyl acetate (3 × 50 cm^3). The combined extracts were washed successively with water (2 × 25 cm^3) and brine (2 × 25 cm^3), dried (Na_2SO_4) and concentrated. At this point insoluble material was precipitated and this was filtered off. The filtrate on concentration, and purification by column chromatography produced **10** and **11** (1:1 ratio) in 42% yield.

Methyl 1-*Hydroxy*-4-(2-*methoxycarbonylethylthio*)-3,4-*dihydronaphthalene*-2-*carboxylate* **7**.—The thiophthalide **4a** (13.3 mmol) and freshly distilled methyl acrylate (28 mmol) were allowed to react under the conditions described in the general procedure to provide **7** as a viscous oil; ν_{max}(neat)/cm^{-1} 1739, 1650 and 764; δ_H 12.4 (s, 1 H), 8.00–7.72 (m, 1 H), 7.5–7.24 (m, 3 H), 4.02 (dd, 1 H, *J* 4.0, *J* 4.5), 3.85 (s, 3 H), 3.66 (s, 3 H) and 3.00–2.40 (m, 6 H); *m*/*z* 322 (M^+), 262, 203 and 171 (100).

2-*Cyano*-4-(2-*cyanoethylthio*)-3,4-*dihydronaphthalen*-2(1H)-*one* **9**. This compound was prepared in a similar fashion to **7** from **4a** and acrylonitrile as a pale yellow crystalline solid; m.p. 124–125 °C (dichloromethane–light petroleum); ν_{max}(KBr)/cm^{-1} 2251 and 1689; δ_H(400 MHz) 8.09 (dd, 1 H, *J* 1.4, *J* 7.9), 7.63 (dt, 1 H, *J* 1.5, *J* 7.5), 7.5–7.4 (m, 2 H), 4.60 (dd, 1 H, *J* 3.0, *J* 3.2), 4.56 (dd, 1 H, *J* 4.0, *J* 13.0) and 3.00–2.75 (m, 6 H); δ_C 186.7, 140.8, 135.1, 129.8, 129.7, 129.1, 128.5, 117.9, 116.6, 42.5, 36.5, 32.0, 27.4 and 19.2; *m*/*z* 256 (M^+) and 170 (100) (Found; C, 65.5; H, 4.7; N, 10.9. Calc. for $C_{14}H_{12}N_2OS$: C, 65.62; H, 4.68; N, 10.93%).

(10RS)-9-*Hydroxy*-10-*mercapto*-3,4,4a,10-*tetrahydroanthracen*-1(2H)-*one* **10**. This compound was prepared from **4a** and **5a** according to the general procedure; m.p. 104–106 °C; ν_{max}(KBr)/cm^{-1} 1605; δ_H(270 MHz) 16.60 (s, 1 H), 7.99 (d, 1 H, *J* 7.7), 7.98 (d, 1 H, *J* 7.7), 7.60 (t, 1 H, *J* 7.6), 7.40 (t, 1 H, *J* 7.6), 3.84 (dd, 1 H, *J* 9.3, 12.7), 2.8–2.56 (m, 2 H), 2.56–2.4 (m, 2 H), 2.1–2.0 (m, 1 H), 1.8–1.55 (m, 1 H), 1.63 (d, 1 H, *J* 9.3) and 1.45–1.25 (m, 1 H); δ_C 189.8, 181.4, 142.5, 132.9, 131.2, 127.7, 127.4, 126.4, 107.8, 45.5, 42.3, 32.7, 29.6 and 20.7; *m*/*z* 246 (M^+) and 212 (100).

(10SR)-9-*Hydroxy*-10-*mercapto*-3,4,4a,10-*tetrahydroanthracen*-1(2H)-*one* **11**.—Semi-solid; ^1H NMR data were extracted from a sample containing a trace of the aromatized product **6a**; δ_H 16.20 (s, 1 H), 8.08–7.8 (br d, 1 H), 7.6–7.2 (m, 3 H), 4.12 (dd, 1 H, *J* 4.0, 8.0), 3.4–2.9 (m, 1 H), 2.6–2.2 (m, 2 H), 2.2–1.55 (m, 4 H) and 1.5 (d, 1 H, *J* 8.0).

(10S)-9-*Hydroxy*-10-*mercapto*-8-*methoxy*-3,4,4a,10-*tetrahydroanthracene*-1(2H)-*one* **12**. This compound was prepared according to the general procedure given above from **4b** and **5a**; m.p. 145–146 °C; ν_{max}(KBr)/cm^{-1} 1608 and 1598; δ_H(300 MHz) 16.48 (s, 1 H), 7.42 (t, 1 H, *J* 8.0), 6.91 (d, 1 H, *J* 8.1), 6.86 (d, 1 H, *J* 8.1), 4.03 (dd, 1 H, *J* 3.7, 7.5), 3.94 (s, 3 H), 3.1 (m, 1 H), 2.43 (m, 2 H), 1.98 (m, 2 H), 1.83–1.68 (m, 2 H) and 1.54 (d, 1 H, *J* 7.5); δ_C 185.7, 185.0, 160.4, 148.4, 134.1, 119.1, 111.6, 104.9, 82.3, 56.2, 44.6, 37.4, 31.5, 26.8 and 20.6; *m*/*z* (CI, isobutane) 277 (100), 243 and 215.

5-*Methoxy*-3-(3-*oxocyclohexyl*)*benzo*[c]*thiophen*-1(3H)-*one* **13**. This compound was prepared according to the general procedure from **4c** and **5a**; m.p. 191–193 °C; ν_{max}(KBr)/cm^{-1} 1711, 1666 and 1598; δ_H 7.7 (d, 1 H, *J* 7.5), 7.1–6.8 (m, 2 H), 4.98 (d, 1 H, *J* 4.0), 3.9 (s, 3 H) and 2.9–1.45 (m, 9 H); *m*/*z* (CI, isobutane) 277 (100), 243 and 180.

9-*Hydroxy*-6-*methoxy*-3,4-*dihydroanthracen*-1(3H)-*one* **14**. This compound was prepared from **4c** and **5a** following the general procedure by using LDA. Prior to work-up, the mixture was heated at reflux for 3 h; m.p. 120–122 °C; ν_{max}(KBr)/cm^{-1} 1620br; δ_H(400 MHz) 14.20 (s, 1 H), 8.26 (d, 1 H, *J* 8.9), 7.05 (dd, 1 H, *J* 2.3, 8.9), 6.94 (s, 1 H), 6.92 (d, 1 H, *J* 2.3), 3.91 (s, 3 H), 2.98 (t, 2 H, *J* 5.7), 2.72 (t, 2 H, *J* 6.3) and 2.11 (tt, 2 H, *J* 6.3); *m*/*z* 276 (M^+) (Found: C, 65.4; H, 5.1. Calc. for $C_{15}H_{14}O_3$: C, 65.21; H, 5.07%).

3-*Acetoxymethyl*-9-*hydroxy*-8-*methoxy*-3,4-*dihydroanthracen*-1(2H)-*one* **15**. This compound was prepared from **4b** and **5b** according to the general procedure; m.p. 142–143 °C; ν_{max}(KBr)/cm^{-1} 1736, 1624 and 1579; δ_H(270 MHz) 15.09 (s,

1 H), 7.49 (t, 1 H, *J* 8.0), 7.20 (d, 1 H, *J* 8.0), 6.98 (s, 1 H), 6.81 (d, 1 H, *J* 8.0), 4.11 (d, 2 H, *J* 5.5), 4.02 (s, 3 H), 3.06 (br d, 1 H, *J* 15.0), 2.9–2.7 (m, 2 H), 2.67–2.5 (m, 2 H) and 2.09 (s, 3 H); *m/z* 314 (M^+, 100), 254 and 241 (Found: C, 68.9; H, 5.8. Calc. for $C_{18}H_{18}O_5$: C, 68.79; H, 5.73%).

3-*Bromobenzo*[c]*thiophene*-1(3H)-*one* **18**.—*N*-Bromosuccinimide (0.32 g, 95%, 1.7 mmol) was added to a solution of the thiophthalide **4a** (0.25 g, 1.7 mmol) in distilled CCl_4 (30 cm^3) and the mixture refluxed while the flask was irradiated by a 100 W bulb. After completion of the reaction, the reaction mixture was cooled to 0 °C, filtered and the residue washed thoroughly with cold CCl_4 (30 cm^3). Concentration of the combined filtrate and washings provided a solid which was recrystallized (benzene–light petroleum) to give **18** as a crystalline solid (0.381 g, 99%); m.p. 82–84 °C; ν_{max}(KBr)/cm^{-1} 1700, 1586 and 606; δ_H(CCl_4) 7.9–7.3 (m, 4 H) and 6.75 (s, 1 H).

3-*Phenylthiobenzo*[c]*thiophene*-1(3H)-*one* **19** *from* **18**.—To a stirred solution of compound **18** (0.38 g, 1.7 mmol) in dry THF (30 cm^3) at room temperature under an argon atmosphere were added dry triethylamine (0.23 cm^3, 1.7 mmol) and thiophenol (0.17 cm^3, 1.7 mmol). Stirring of the mixture was continued until completion (2 h) of the reaction when THF was removed. The residue obtained was dissolved in diethyl ether (50 cm^3) and the solution washed successively with aqueous NaOH (5%; 20 cm^3), water (20 cm^3) and brine (20 cm^3) and then dried (Na_2SO_4). After concentration of the solution the crude material was purified by column chromatography to give a solid which was recrystallized (benzene–light petroleum) to afford white crystalline compound **19** (0.386 g, 90%); m.p. 57 °C; ν_{max}(KBr)/cm^{-1} 1691; δ_H 7.9–7.2 (m, 9 H) and 6.15 (s, 1 H); 258 (M^+) and 149 (100) (Found: C, 65.4; H, 3.9. Calc. for $C_{14}H_{10}OS_2$: C, 65.11; H, 3.9%).

Compound **19** *from* **4a**.—*Method A*. To a stirred solution of LDA (prepared from 4.3 mmol of diisopropylamine and 3.9 mmol of BuLi) in THF (20 cm^3) was added a solution of the thiophthalide **4a** (0.5 g, 3.4 mmol) in THF (10 cm^3) at −78 °C under an argon atmosphere. The resulting yellow solution was transferred using a cannula to a magnetically stirred solution of diphenyl disulfide (0.74 g, 3.4 mmol) in THF (10 cm^3) at −78 °C. After 2 h the reaction was quenched by addition of aqueous HCl (5%, 3.5 cm^3) to the reaction mixture which was then added to 5% aqueous HCl (50 cm^3) and extracted into diethyl ether (3 × 30 cm^3). The combined extracts were washed with aqueous NaOH (5%; 2 × 25 cm^3), water (25 cm^3) and brine (25 cm^3) and then dried (Na_2SO_4) and evaporated. The residue was purified by column chromatography to give pure **19** (0.258 g, 30%).

Method B. A repeat reaction using phenyl benzenethiosulfonate[27] instead of diphenyl disulfide gave compound **19** in 30–35% yield.

3-*Phenylsulfonylbenzo*[c]*thiophene*-1(3H)-*one* **20** *from* **18**.—To a stirred suspension of sodium benzenesulfinate (0.738 g, 4.5 mmol) in THF (5 cm^3) were added compound **18** (1.0 g, 4.4 mmol) and tetrabutylammonium iodide (81 mg, 0.22 mmol) successively. The reaction mixture was heated at reflux for 30 min after which it was cooled and diluted with ice–water (20 cm^3). On storage in refrigerator the mixture gave a pale yellow solid which was filtered off, washed with cold light petroleum and recrystallized (light petroleum–ether) to give **20** (0.465 g, 50%) as white crystalline solid; m.p. 165–167 °C; ν_{max}(KBr)/cm^{-1} 1686, 1319 and 1154; δ_H 8.15 (d, 1 H, *J* 7), 7.85–7.20 (m, 8 H) and 6.0 (s, 1 H); *m/z* 290 (M^+), 197 and 149 (100) (Found: C, 58.5; H, 3.7. Calc. for $C_{14}H_{10}O_3S_2$: C, 58.0; H, 3.5%).

Compound **20** *from* **19**.—*Method A*. To a solution of compound **19** (1.0 g, 3.87 mmol) in acetic acid (10 cm^3) was added H_2O_2 (20%; 10 cm^3, 60 mmol) at room temperature and the mixture was heated to 50 °C. The mixture was stirred at this temperature for 5–15 min after which it was brought back to room temperature and stirred for 36 h. A precipitated white solid was filtered off and dissolved in distilled $CHCl_3$ and the solution dried (Na_2SO_4) and evaporated. Purification of the residue by chromatography gave homogeneous material which was recrystallized ($CHCl_3$–light petroleum) to give white needles of compound **20** (1.0 g, 90%) having the same melting point as the product obtained in the previous experiment.

Method B. To a well stirred solution of compound **19** (0.17 g, 0.66 mmol) in ethanol (7 cm^3) and water (5 cm^3) was added magnesium monoperoxyphthalate hydrate (80%; 0.408 g, 0.66 mmol) at room temperature. The precipitated solid was filtered off after 2 h, washed thoroughly with water (10 cm^3) and purified by column chromatography to give compound **20** (0.105 g, 55%).

Compounds **22**–**30** were prepared according to the general procedure.

Compound **22a**. M.p. 82–84 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1741 and 1667; δ_H(270 MHz) 12.05 (s, 1 H), 8.44 (m, 2 H), 8.08 (s, 1 H), 7.72 (br t, 1 H), 7.57 (br t, 1 H), 4.01 (s, 3 H), 3.63 (s, 3 H), 3.06 (t, 2 H, *J* 7.4), 2.55 (t, 2 H, *J* 7.4); *m/z* 320 (M^+) and 288 (100) (Found: C, 60.3; H, 5.1. Calc. for $C_{16}H_{16}O_5S$: C, 60.0; H, 5.04%).

Compound **22b**. M.p. 150 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1708 and 1655; δ_H 12.1 (s, 1 H), 8.4 (d, 2 H, 7), 8.02 (s, 1 H), 7.6 (m, 1 H), 7.15 (s, 1 H), 3.95 (s, 3 H), 3.01 (br t, 2 H) and 2.53 (br t, 2 H). On diazomethane treatment **22b** gave **22a**.

Compound **23a**. M.p. 100 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1728, 1651 and 1615; δ_H(270 MHz) 12.55 (s, 1 H), 8.64 (d, 1 H, *J* 8.0), 8.41 (d, 1 H, *J* 8), 7.66 (br t, 1 H), 7.47 (br t, 1 H), 4.00 (s, 3 H), 3.56 (s, 3 H), 3.4 (1 H), 2.97 (s, 3 H), 2.48 (m, 2 H) and 1.24 (d, 3 H, *J* 6.5); δ_C 172.8, 171.8, 162.3, 141.7, 138.5, 130.5, 126.9, 125.3, 124.4, 124.3, 121.4, 107.8, 52.4, 51.5, 41.6, 40.5, 22.6 and 20.6; *m/z* 348 (M^+), 316 and 216 (100) (Found: C, 62.3; H, 5.7. Calc. for $C_{18}H_{20}O_5S$: C, 62.06; H, 5.8%).

Compound **23b**. M.p. 137–139 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1648 and 1569; δ_H(270 MHz) 12.58 (s, 1 H), 8.40–8.1 (m, 2 H), 7.5–7.3 (m, 2 H), 3.89 (s, 3 H) and 2.31 (br s, 3 H); δ_C 172.6, 163.0, 142.4, 137.8, 130.1, 126.6, 125.3, 124.2, 124.0, 123.5, 107.4, 52.3 and 21.8; *m/z* 494 (M^+), 248, 215 (100) and 171.

Compound **24a**. M.p. 229 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1619, 1574 and 761; δ_H 14.74 (s, 1 H), 8.4–8.08 (m, 1 H), 8.08–7.88 (m, 1 H), 7.68–7.24 (m, 2 H), 3.2–2.68 (m, 2 H), 2.54 (t, 2 H, *J* 6) and 2.00–1.36 (m, 2 H); *m/z* (CI) 487 (M^+ + 1), 486 (M) and 243 (Found: C, 69.4; H, 4.57. Calc. for $C_{28}H_{22}O_4S_2$: C, 69.10; H, 4.56%).

Compound **24b**. M.p. 185 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1625, 1572, 1321 and 1141; δ_H 15.15 (s, 1 H), 8.65–8.5 (m, 1 H), 8.05–7.85 (m, 1 H), 7.7–7.4 (m, 7 H), 3.2 (br s, 2 H), 2.7 (t, 2 H, *J* 6.5) and 2.0 (m, 2 H); *m/z* 384 (M^+) and 243 (100). Satisfactory analysis could not be obtained.

Compound **25**. M.p. 76 °C (benzene–light petroleum); ν_{max}(KBr)/cm^{-1} 1617; δ_H 14.70 (s, 1 H), 8.66 (d, 1 H, *J* 8), 8.5 (d, 1 H, *J* 8), 7.76 (br t, 1 H), 7.5 (br t, 1 H), 3.48 (t, 2 H, *J* 7), 2.76 (t, 2 H, *J* 7), 2.24 (s, 3 H), 2.16 (t, 2 H, *J* 7); *m/z* 258 (M) and 91 (100) (Found: C, 69.9; H, 5.7. Calc. for $C_{15}H_{14}O_2S$: 69.8; H, 5.50%).

Compound **26a**. M.p. 195 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1739, 1623, 1572 and 1233; δ_H 14.68 (s, 1 H), 8.8–7.2 (m, 4 H), 4.2 (m, 7 H) and 2.06 (s, 3 H); *m/z* 630 (M^+), 316 and 255 (100).

Compound **26b**. M.p. 148 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1741, 1627, 1575, 1320 and 1139; δ_H 14.88

(s, 1 H) 8.8–8.24 (m, 1 H), 8.24–7.12 (m, 8 H), 4.08 (br s, 2 H), 3.64–3.24 (m, 1 H), 3.12–2.12 (m, 4 H) and 2.08 (s, 3 H).

Compound **27**. M.p. 102–103 °C (benzene–light petroleum); ν_{max}(KBr)/cm^{-1} 1733, 1624 and 1576; δ_H 14.6 (s, 1 H), 8.68 (d, 1 H, *J* 8), 8.52 (br d, 1 H, *J* 8), 7.8 (br t, 1 H, *J* 8), 7.52 (br t, 1 H, *J* 8), 4.2 (d, 2 H, *J* 5), 3.86 (br d, 1 H, *J* 15), 3.2–2.4 (m, 4 H), 2.26 (s, 3 H) and 2.14 (s, 3 H); *m/z* 331 (M^+ + 1, 100) (Found: C, 66.1; H, 5.48. Calc. for $C_{18}H_{18}O_4S$: C, 65.50; H, 5.5%).

Compound **29a**. M.p. 150–152 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1669 and 1626; δ_H 10.40 (br s, 1 H), 8.56 (d, 1 H, *J* 8), 8.40 (br d, 1 H, *J* 8), 7.78 (br t, 1 H), 7.52 (br t, 1 H), 5.96 (m, 1 H), 5.56 (m, 1 H), 4.20 (m, 1 H), 3.72 (br s, 1 H), 3.6–3.2 (m, 2 H), 2.36 (s, 3 H) and 1.8 (br s, 2 H); *m/z* 309 (M^+ + 1) and 242 (100) (Found: C, 73.7; H, 5.30. Calc. for $C_{19}H_{16}O_2S$: C, 74.0; H, 5.23%).

Compound **29b**. M.p. 160–162 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1674, 1626, 1325 and 1143; δ_H 8.22–8.16 (m, 1 H), 8.0–7.07 (m, 8 H), 5.88 (m, 1 H), 5.44 (br s, 1 H), 3.9 (m, 1 H), 3.6 (br s, 1 H), 3.6–3.5 (m, 2 H) and 1.68 (m, 2 H); a good mass spectrum could not be recorded.

Compound **30a**. M.p. 120–122 °C (benzene–light petroleum); ν_{max}(KBr)/cm^{-1} 1734, 1625 and 1574; δ_H 14.52 (s, 1 H), 8.62 (d, 1 H, *J* 8.5), 8.47 (d, 1 H, *J* 8.2), 7.77 (t, 1 H, *J* 7.5), 7.45 (t, 1 H, *J* 7.5), 3.98 (dd, 1 H, *J* 4, 16.8), 3.75 (s, 3 H), 3.53 (dd, 1 H, *J* 9.6, 16.8), 3.29–3.17 (m, 1 H), 3.1–2.95 (m, 2 H) and 2.26 (s, 3 H); *m/z* 316 (M^+, 100) (Found: C, 65.0; H, 5.1. Calc. for $C_{17}H_{16}O_4S$: C, 64.60; H, 5.1%).

Compound **30b**. M.p. 163–165 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 1736 and 1621; δ_H 14.60(s), 14.54(s), 8.58–8.30 (m, 1 H), 8.2–7.9 (m, 1 H), 7.6–7.3 (m, 2 H), 3.7 (br s, 5 H) and 3.0–2.5 (m, 3 H); *m/z* 602 (M^+) and 301 (100).

Compound **30c**. M.p. 174 °C; ν_{max}(KBr)/cm^{-1} 1705, 1623 and 1575; δ_H 14.48 (s, 1 H), 8.60 (m, 2 H), 7.68 (m, 2 H), 5.6 (br s, 1 H), 4.16–2.7 (m, 5 H) and 2.24 (s, 3 H).

Compound **31**. M.p. 131–132 °C (chloroform–light petroleum); ν_{max}(KBr)/cm^{-1} 3412, 1622 and 1571; δ_H(300 MHz) 14.62 (s, 1 H), 8.65 (d, 1 H, *J* 8.5), 8.47 (d, 1 H, *J* 8.2), 7.75 (t, 1 H, *J* 7.5), 7.55 (t, 1 H, *J* 7.5), 3.95 (d, 1 H, *J* 6.2), 3.8 (m, 2 H), 3.2–2.8 (m, 3 H), 2.8–2.55 (m, 1 H), 2.52–2.3 (m, 1 H) and 2.25 (s, 3 H).

Raney Nickel Degradation of the Anthracenones **10–12**, **24a** *and* **30b**.—To a well-stirred solution of the anthracenone (0.8 mmol) in hot ethanol (30 cm^3) or acetone (30 cm^3) was added freshly prepared Raney nickel (2 g) at room temperature. After being stirred at room temperature for 5 h, the reaction mixture was filtered and the residue was thoroughly washed with chloroform (3 × 20 cm^3). The filtrate and washings were combined and concentrated to give a yellow residue which was then extracted with chloroform (50 cm^3). The extract was concentrated under reduced pressure to give a pale yellow semi-solid which on purification by preparative thin layer chromatography yielded the anthracenones **6** in 60–70% yield.

Compound **6a**. M.p. 93–94 °C (lit.,[8] m.p. 93.5–94 °C); ν_{max}(KBr)/cm^{-1} 1626 and 1574; δ_H 14.20 (s, 1 H), 8.38 (br d, 1 H), 7.85–7.25 (m, 3 H), 7.04 (s, 1 H), 2.96 (t, 2 H, *J* 7.6), 2.72 (t, 2 H, *J* 7.6) and 2.12 (m, 2 H).

Compound **6b**. M.p. 154 °C (lit.,[28] m.p. 153–154 °C); ν_{max}(KBr)/cm^{-1} 1622 and 1583; δ_H(400 MHz) 15.21 (s, 1 H), 7.48 (t, 1 H, *J* 8.0), 7.20 (d, 1 H, *J* 8.0), 6.98 (s, 1 H), 6.80 (d, 1 H, *J* 8.0), 4.03 (s, 3 H), 2.99 (t, 2 H, *J* 5.8), 2.76 (t, 2 H, *J* 6.0) and 2.20–2.00 (m, 2 H).

Compound **6c**. M.p. 116–118 °C; ν_{max}(KBr)/cm^{-1} 1721 and 1627; δ_H 14.01 (s, 1 H), 8.38 (d, 1 H, 7.5), 7.67–7.57 (m, 2 H), 7.45 (t, 1 H, 7.5), 7.06 (s, 1 H), 3.73 (s, 3 H), 3.33–3.19 (m, 3 H) and 2.99–2.97 (m, 2 H); δ_C 202.33, 173.0, 163.36, 137.61, 135.22, 130.59, 126.99, 126.98, 125.36, 124.55, 124.50, 116.84, 52.15, 40.54, 39.98 and 32.66; *m/z* 270 (Found: C, 71.2; H, 5.3. Calc. for $C_{16}H_{14}O_4$: C, 71.11; H, 5.22%).

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