# Polarized Ketene Dithioacetals. Part 42.[1] Studies on the Reactions of Alkyl and Aryl Grignard Reagents with α-Oxoketene Dithioacetals

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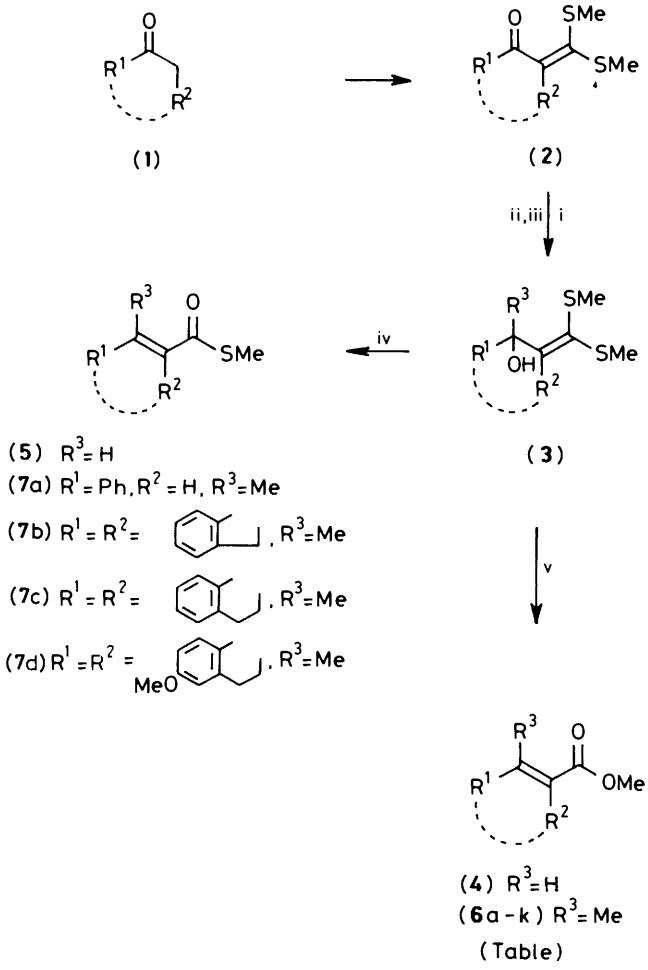
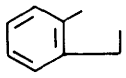
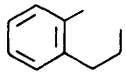
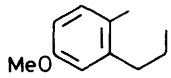
The oxoketene dithioacetals (**2a—k**) derived from a variety of cyclic and acyclic active methylene ketones undergo 1,2-addition with methylmagnesium iodide to give the alcohol acetals (**3a—k**) which, on subsequent boron trifluoride—ether catalysed methanolysis, yield methyl β-methyl-α,β-unsaturated esters (**6a—k**) in 51—70% overall yields. Also the alcohols (**3a**) and (**3i—k**) underwent partial hydrolysis in the presence of boron trifluoride—ether and water to yield β-methyl-α,β-unsaturated *S*-methyl esters (**7a—d**) in 41—60% yield. Under similar conditions however, the oxoketene dithioacetals (**2l—q**) derived from higher homologues of acetophenone yielded the corresponding 2-alkyl-3-methylinden-1-ones (**8a—f**) in 50—62% overall yields. The reactions of cyclic oxoketene dithioacetals (**2g**), (**2h**), and (**2j**) with higher alkyl Grignard reagents afforded the alcohols (**13a—f**), formed by sequential 1,4 and 1,2 addition, which on subsequent methanolysis yielded the corresponding 1-(2-alkylcycloalk-1-enyl)alkan-1-ones (**14a—f**) in 48—58% overall yields. Similarly the phenylmagnesium bromide underwent sequential 1,4 and 1,2 addition to the oxoketene dithioacetals (**2a—c**), (**2h**) and (**2j**) to yield the alcohols (**13g—k**), which upon subsequent methanolysis yielded either 1,3,3-triarylprop-2-en-1-ones (**14g—i**) or phenyl (2-phenylcycloalk-1-enyl) ketones (**14j—k**) in 53—71% yield.

We recently reported a new general method for the conversion of easily available ketones into the stereoselective and regiospecific α,β-unsaturated *O*-methyl/*S*-methyl esters *via* the oxoketene dithioacetals (**2**).[2] It is now known that the compounds (**2**) undergo exclusive 1,2 reduction with sodium borohydride to give the corresponding alcohol acetals (**3**; $R^3 = H$) in high yields. Subsequent methanolysis of compounds (**3**) in the presence of boron trifluoride–ether yielded the corresponding α,β-unsaturated *O*-methyl esters (**4**; $R^3 = H$) in good yields (Scheme 1). Also, the compounds (**3**) have been partially hydrolysed in the presence of boron trifluoride–ether and water to afford the corresponding *S*-methyl esters (**5**; $R^3 = H$) in good yields (Scheme 1). The reaction was found to be general with aliphatic, aromatic, cyclic, and acyclic ketones. In continuation of this work, it was considered that the utility of this transformation would be further enhanced if an alkyl or aryl group could be added in place of hydride ion, since this would constitute a useful general route for the conversion of easily available active methylene ketones into β-alkyl/aryl-α,β-unsaturated esters. The reported methods for such transformations involve stereoselective conversion of active methylene ketones to either enol acetates,[3] alkyl thioenolates,[4] enol phosphates[5] or β-halogeno esters[6] through their respective β-keto esters. These esters were subsequently treated with lithium dialkylcuprates to give the corresponding β-alkylene esters in good yields. The scope and limitations of these reactions have been discussed.[5] Knowing that the oxoketene dithioacetals (**2**) undergo exclusive 1,2 reduction[2] with sodium borohydride, we considered this class of compounds to be excellent candidates for the synthesis of β-alkyl/aryl-α,β-substituted ene esters. We also found that α-oxoketene dithioacetals (**2**) had been reported to react with methyl-lithium to give the alcohol acetals (**3**), which on hydrolysis with hydrofluoboric acid and mercuric oxide yielded the corresponding β-methyl-α,β-unsaturated *S*-methyl esters.[7] No attempts were made however to prepare the corresponding *O*-alkyl esters from these alcohol acetals. In continuation of our studies on oxoketene dithioacetals, we now report our results on the reaction of compounds (**2**) with alkyl and aryl Grignard reagents and subsequent methanolysis of the




**Scheme 1.** *Reagents:* i, $H^-(NaBH_4)$; ii, $R^3MgI$; iii, $NH_4Cl$; iv, $BF_3$·$Et_2O$–$H_2O$; v, $BF_3$·$Et_2O$–MeOH

**Table.** Preparation of β-methyl-α,β-unsaturated esters (**6**).

| Starting acetal | Unsaturated ester | $R^1$ | $R^2$ | Refluxing time (h)[a] | Yield[b] (%) | Properties |
|---|---|---|---|---|---|---|
| (**2a**) | (**6a**) | Ph | H | 13 | 56 | Viscous semisolid (29 °C)[c,16] |
| (**2b**) | (**6b**) | *p*-$MeC_6H_4$ | H | 9 | 51 | Light yellow solid, m.p. 43—44 °C (45—45.5 °C[c,16] |
| (**2c**) | (**6c**) | *p*-$MeOC_6H_4$ | H | 10 | 57 | Light yellow solid, m.p. 52—53 °C |
| (**2d**) | (**6d**) | *p*-$ClC_6H_4$ | H | 10 | 58 | Pale yellow viscous oil |
| (**2e**) | (**6e**) | Et | Me | 12 | 69 | Liquid, 161—162 °C (163 °C)[c,19] |
| (**2f**) | (**6f**) | Me | Bu | 14 | 50 | Pale yellow oil |
| (**2g**) | (**6g**) | $-(CH_2)_3-$ | | 10 | 66 | Colourless liquid, b.p. 65—68 °C/5 mm (55 °C/2 mm)[c,20] |
| (**2h**) | (**6h**) | $-(CH_2)_4-$ | | 8 | 69 | Colourless liquid,[20] b.p. 85—90 °C/5 mm |
| (**2i**) | (**6i**) |  | | 12 | 65 | White solid, m.p. 63—4 °C (64 °C)[c,21,22] |
| (**2j**) | (**6j**) |  | | 15 | 70 | Pale yellow viscous semisolid |
| | | | | 15 | 65 | White solid, m.p. 72—73 °C |
| (**2k**) | (**6k**) |  | 15 | 65 | | White solid, m.p. 72—73 °C |

[a] Refluxing time of methanolysis. [b] Yield of pure isolated product calc. from (**2**). [c] Reported m.p., b.p. and references for spectral data.

resulting carbinols to give either β-methyl-α,β-unsaturated esters or 1,3-dialkyl (or diaryl)alk-2-en-1-ones.

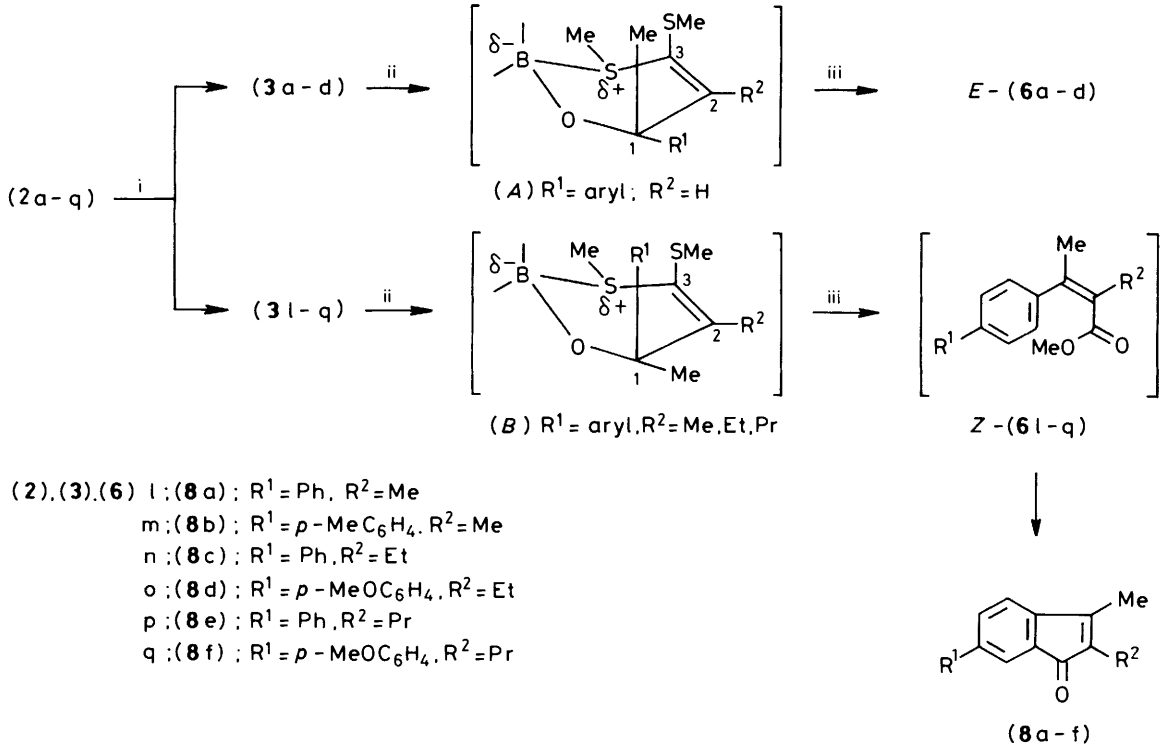
## Results and Discussion

Treatment of methylmagnesium iodide with (**2a**) gave the corresponding alcohol acetal (**3a**) in almost quantitative yield (Scheme 1) by 1,2-addition; there was no 1,4-addition product formed. The alcohol (**3a**) underwent smooth methanolysis in the presence of boron trifluoride–ether to yield the corresponding *E*-methyl β-methylcinnamate (**6a**) (Scheme 1) in 56% yield. Similarly the dithioacetals (**2b—d**), derived from the substituted acetophenones, on sequential 1,2 addition and methanolysis afforded the corresponding ene esters (**6b—d**) in 51—58% overall yields (Table). The ketene dithioacetals (**2e**) and (**2f**) derived from diethyl ketone and heptan-2-one, respectively, also gave the corresponding ene esters (**6e**) and (**6f**) in good yields. Similarly the dithioacetals (**2g—k**) derived from the corresponding cyclic ketones, yielded under similar reaction conditions, the respective ene esters (**6g—k**) in 65—70% overall yields (Scheme 1) (Table). Some of the alcohol acetals, (**3a**) and (**3i—k**) were hydrolysed in the presence of boron trifluoride–ether and water to give the corresponding, and hitherto unreported, β-methyl-α,β-unsaturated *S*-methyl esters (**7a—d**) in 41—60% overall yields (Scheme 1). Interestingly, the dithioacetals (**21**) (derived from propiophenone), when treated with methylmagnesium iodide, failed to give the expected ene ester (**6l**) upon solvolysis of the alcohol (**3l**), the product isolated (55%) being characterised as 2,3-dimethylinden-1-one (**8a**) (Scheme 2).[8] Similarly, the dithioacetal (**2m**) and its higher homologues (**2n—q**) gave the corresponding inden-1-ones (**8b—f**) in 50—62% overall yields. The inden-1-ones (**8a—f**) are apparently derived by intramolecular cyclocondensation of the corresponding *Z*-β-methyl α-alkylcinnamates (**6l—q**)[9] which could not be isolated.

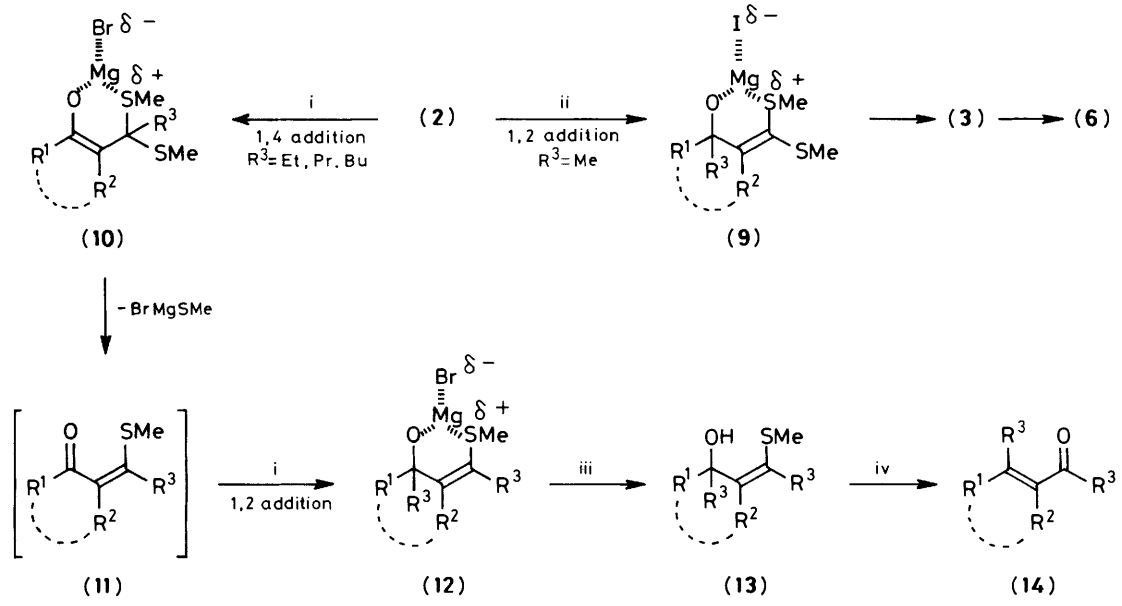
The reactions of higher alkyl Grignard reagents (ethyl-, propyl-, and butyl-magnesium bromides) with (**2a**) were found to be unsatisfactory; no characterizable compounds could be isolated. However, the cyclic ketene dithioacetals (**2h**) derived from cyclohexanone when treated with ethylmagnesium bromide gave, upon methanolysis of the corresponding carbinol (**13a**), 1-(2-ethylcyclohex-1-enyl)propan-1-one (**14a**) (48%) (Scheme 3). It is apparent that (**13a**) is derived from (**2h**) through the preferential 1,4-addition followed by 1,2-addition of the Grignard reagent. Similarly, propyl- and butyl-magnesium bromides, when treated with (**2h**), gave the corresponding α,β-unsaturated ketones (**14b**) and (**14c**) in 50 and 55% yields respectively (Scheme 3). Under identical conditions, (**2g**) and (**2j**) reacted with propyl- and butyl-magnesium bromides to give the corresponding β-alkyl-α,β-unsaturated ketones (**14d—f**) in 50—55% overall yields (Scheme 3).

The reaction of (**2**) with phenylmagnesium bromide was examined next. Thus, (**2a**) was treated with 3 equiv. of phenylmagnesium bromide, to give a white solid (90%), characterized as the alcohol (**13g**) (see Scheme 3). The structure of (**13g**) was confirmed by its methanolysis which afforded the corresponding 1,3,3-triphenylprop-2-en-1-one (**14g**) (Scheme 3) in 71% yield. Use of 1.2 equiv. of phenylmagnesium bromide gave (**13g**) in only 30% yield, together with unchanged starting material (**2a**); none of the 1,2 addition product was observed, the preference of phenylmagnesium bromide being for 1,4-addition. Similarly the other dithioacetals (**2b**), (**2c**), (**2h**), and (**2j**) reacted with phenylmagnesium bromide, to yield, after methanolysis, the corresponding β-phenyl-α,β-unsaturated ketones (**14h—k**) (Scheme 3) in 53—68% overall yields.

The reason for the above-described preference for 1,2 addition of methylmagnesium iodide appears to be kinetic, since longer reaction times and higher temperatures resulted in the formation of complex reaction mixtures.[10a] Several of the substituted indenones prepared in this work have been recently prepared by coupling of *O*-di-iodobenzene with dialkylacetylene in the presence of carbonyl nickel.[8] The methanolysis of the




**Scheme 2.** *Reagents:* i, MeMgI–$Et_2O$; ii, $BF_3$·$Et_2O$; iii, MeOH




**Scheme 3.** *Reagents:* i, $R^3MgBr$; ii, $R^3MgI$; iii, $NH_4Cl$; iv, $BF_3$·$Et_2O$–MeOH

alcohol acetals (**3a**—**k**) and (**3l**—**q**) probably involves boat-like transition states *A* and *B*, respectively (Scheme 2). In the case of the alcohols (**3a**—**d**) ($R^1$ = Aryl; $R^2$ = H) derived from acetophenones, the bulkier aryl group occupies the quasiequatorial position, while the methyl group is present in axial position (*A*); this leads to the formation of *E*-cinnamates (**6a**—**d**) exclusively. However when $R^2$ is a bulkier alkyl group (Me, Et, Pr) as in the case of the alcohols (**3l**—**q**) derived from higher homologues of acetophenones, the less bulky methyl group occupies the quasiequatorial position (to minimize the steric interaction between 1,2-substituents), while the aryl group is present in the axial position (*B*); this results in the formation of *Z*-cinnamates (**6l**—**q**) which are the actual precursors for the indenones (**8a**—**f**).[2,10b]

The reaction of higher alkyl and aryl Grignard reagents with compounds (**2**) affords complex (**10**) *via* 1,4 addition;[11] this, on elimination of methylthiomagnesium bromide, yields the methylthioalkenyl ketones (**11**)*,† (Scheme 3). Subsequent *in situ* 1,2 addition of Grignard reagents to compounds (**11**) and methanolysis of the resulting alcohol (**13**), gave the corresponding ketone (**14**) in moderate yields. It is worth noting that the conjugate 1,4-additions of dialkylcuprates to oxoketene dithioacetals have been extensively studied; this affords a useful method for the synthesis of β-alkyl-β-alkylthio- or β,β-dialkyl-α,β-unsaturated ketones in high yield.[13] The organocuprates appear to be better regioselective reagents for 1,4-addition. However in the present reaction, the oxoketene dithioacetals undergo sequential 1,2- and 1,4-addition to yield novel 1,3-dialkyl-(or aryl)-α,β-unsaturated ketones in moderate to high yields *via* 1,3-alkylative (or arylative) carbonyl transpositions.[14]

## Experimental

M.p.s were determined on a Thomas Hoover melting point apparatus and are uncorrected. $^1$H-N.m.r. spectra were recorded on a Varian EM-390 spectrophotometer using tetramethylsilane (TMS) as internal standard. I.r. spectra were recorded on a Perkin-Elmer 297 spectrometer. All the Grignard reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Boron trifluoride–ether was distilled (125—126 °C) before use. T.l.c. (silica gel BDH) was used for monitoring the reactions. All the α-oxoketene dithioacetals (**2a**—**q**) required for the present investigation were prepared by standard procedures reported earlier.[15] Ether refers to diethyl ether.

*General Procedure for the Reaction of Grignard Reagents with* (**2**): 3,3-*Bismethylthio*-1-*methyl*-1-*phenylprop*-2-*en*-1-*ol* (**3a**).—To an ice-cooled solution (−5 to 0 °C) of methylmagnesium iodide [0.03 mol prepared from magnesium turnings (0.69 g) and methyl iodide (4.26 g)] in dry ether (50 ml), a solution of (**2a**) (0.01 mol) in dry benzene (20 ml) was added dropwise (2—3 min). The reaction mixture was then stirred for 45 min, before being decomposed with saturated aqueous ammonium chloride (50 ml) and extracted with ether (2 × 100 ml). The combined extracts were washed with water (60 ml), dried ($Na_2SO_4$) and evaporated to give the crude alcohol acetal (**3a**) (2.15 g, 90%), as a viscous oil; $\nu_{max.}$(neat) 3 428br cm$^{-1}$ (OH). The crude alcohol (**3a**) was used for subsequent methanolysis since on attempted purification of (**3a**) by column chromatography (neutral alumina), it decomposed.

The alcohol acetals (**3b**—**d**) and (**3g**—**k**) were similarly obtained from their respective oxoketene dithioacetals (**2b**—**d**) and (**2g**—**k**) in nearly quantitative yields. In the case of dithioacetals (**2e**—**f**) and (**2l**—**q**), the reactions were carried out at 5—10 °C for a longer reaction period (3 h), to afford the corresponding alcohol acetals (**3e**—**f**) and (**3l**—**q**) in nearly quantitative yields. The alcohol acetal (**3l**) was stable to purification by column chromatography over neutral alumina (hexane as eluant) and was obtained as a viscous oil (90%); $\nu_{max.}$(neat) 3 422br cm$^{-1}$ (OH); (no carbonyl); $\delta_H(CCl_4)$ 1.53 (s, 3H, Me); 1.90 (s, 3 H, Me); 2.18 (s, 3 H, SMe); 2.27 (s, 3 H, SMe); 4.62 (s, 1 H, OH, exch. with $D_2O$), and 7.04—7.40 (m, 5 H, ArH) (Found: C, 61.6; H, 7.3; $C_{13}H_{18}OS_2$ requires C, 61.41; H, 7.09%).

The reactions of the oxoketene dithioacetals (**2g**), (**2h**), and (**2j**) with higher alkyl Grignard reagents (*e.g.*, EtMgBr, PrMgBr, and BuMgBr) were also carried out under conditions identical with those described for (**3a**). Work-up of the reaction mixture afforded the crude alcohol acetals (**13a**—**f**), which were used as such for subsequent methanolysis. Similarly the reaction of (**2a**—**c**), (**2h**), and (**2j**) with phenylmagnesium bromide under identical conditions (5—10 °C) yielded the crude alcohol acetals (**13g**—**k**) in nearly quantitative yield. The alcohol (**13g**) was purified by column chromatography over neutral alumina (hexane as eluant) as a white solid; 80%; m.p. 115—116 °C; $\nu_{max.}$(KBr) 3 448br cm$^{-1}$ (OH), no carbonyl; $\delta_H(CDCl_3)$ 1.90 (s, 3 H, SMe); 4.58 (s, 1 H, OH, exchangeable with $D_2O$), 6.48 (s, 1 H, olef. H), and 7.01—7.68 (m, 15 H, ArH) (Found: C, 79.2; 5.85. $C_{22}H_{20}OS$ requires C, 79.51; H, 6.02%).

*General Procedure for Boron Trifluoride–Ether catalysed Methanolysis of Alcohol Acetals* (**3a**—**g**) *and* (**13a**—**k**); E-*Methyl*-β-*Methylcinnamate* (**6a**).—Boron trifluoride–ether (6 ml) was added to a solution of the crude alcohol acetal (**3a**) obtained from (**2**) (0.01 mol) and the reaction mixture was stirred for 5 min. It was then diluted with absolute methanol (50 ml) and refluxed for 8—22 h (Table). The mixture was cooled, poured over ice–water (100 ml) and extracted with chloroform (2 × 75 ml). The combined extracts were washed with saturated aqueous $NaHCO_3$ (60 ml) and water (2 × 50 ml), dried ($Na_2SO_4$), and evaporated to give the crude compound (**6a**); this was purified by column chromatography over silica-gel using hexane–benzene (9:1) as eluant to give a pale yellow viscous oil (56%) (lit.,[16] m.p. 29 °C) (i.r. and n.m.r. data as reported[17,18]).

The other β-methyl α,β-unsaturated esters, (**6b**—**k**), which were similarly obtained under identical conditions (Table), were either purified by silica-gel column chromatography [hexane–benzene (9:1) as eluant] or by distillation [(**6e**), (**6g**), and (**6h**)]. The methanolysis of carbinols (**3l**—**q**) and (**13a**—**k**) under similar conditions yielded the inden-1-ones (**8a**—**f**) and α,β-unsaturated ketones (**14a**—**k**), which were purified by silica-gel column chromatography using hexane–benzene (9:1) as eluant. All the known esters were characterised by comparison of their b.p., m.p., and n.m.r./i.r. spectral data with those reported. The spectral and analytical data for unknown esters, ketones and indenones and for those known ones whose spectral data are not reported in the literature are given below.

*E*-Methyl β-methyl-*p*-methylcinnamate (**6b**), $\nu_{max.}$(KBr) 1 716, 1 634, and 1 610 cm$^{-1}$; $\delta_H(CCl_4)$ 2.24 (s, 3 H, *p*-Me), 2.45 (d, *J* 1.5 Hz, 3 H, Me), 3.61 (s, 3 H, OMe), 6.01 (q, *J* 1.5 Hz, 1 H, olef. H), and 7.14 and 7.35 (dd, $A_2B_2$, 4 H, ArH).

E-*Methyl* β-*methyl*-p-*methoxycinnamate* (**6c**), $\nu_{max.}$(KBr) 1 717, 1 633, and 1 605 cm$^{-1}$; $\delta_H(CCl_4)$ 2.45 (s, 3 H, Me); 3.65 (s, 3 H, OMe); 3.75 (s, 3 H, OMe); 6.02 (br s, 1 H, olef. H), and 6.80 and 7.40 (dd, $A_2B_2$, 4 H, ArH) (Found: C, 69.6, H, 6.35. $C_{12}H_{14}O_3$ requires C, 69.90; H, 6.79%).

E-*Methyl* β-*methyl*-p-*chlorocinnamate* (**6d**), $\nu_{max.}$(neat) 1 716, 1 632, and 1 592 cm$^{-1}$; $\delta_H(CCl_4)$ 2.49 (d, *J* 1.5 Hz, 3 H, Me);

* Our attempts to isolate β-methylthioalkenyl ketones (**11**) in these reactions were unsuccessful.

† The alkylthiomethylene ketones are known to undergo ready 1,2-addition with organolithium compounds.[12]

3.66 (s, 3 H, OMe); 6.01 (q, *J* 1.5 Hz, 1 H, olef. H), and 7.15 and 7.44 (dd, $A_2B_2$, 4 H, ArH) (Found: C, 62.35; H, 4.95. $C_{11}H_{11}ClO_2$ requires C, 62.70; H, 5.22%).

*Methyl 2-butyl-3-methylbut-2-enoate* (**6f**), $\nu_{max.}$(neat) 1 723 and 1 645 $cm^{-1}$; $\delta_H(CCl_4)$ 0.85 (t, 3 H, $CH_2Me$); 1.25—1.46 [m, 4 H, $(CH_2)_2$]; 1.73 (s, 3 H, Me); 1.88 (s, 3 H, Me); 2.12—2.45 (m, 2 H, $CH_2$), and 3.59 (s, 3 H, OMe) (Found: C, 70.85; H, 10.3. $C_{11}H_{18}O_2$ requires C, 70.58; H, 10.58%).

*Methyl 1-methyl-3,4-dihydronaphthalene-2-carboxylate* (**6j**), $\nu_{max.}$(neat) 1 715, 1 620, and 1 570 $cm^{-1}$; $\delta_H(CCl_4)$ 2.30 (s, 3 H, Me), 2.40—2.64 [m, 4 H, $(CH_2)_2$], 3.61 (s, 3 H, OMe), 6.95—7.49 (m, 4 H, ArH) (Found: C, 77.0; H, 7.3. $C_{13}H_{14}O_2$ requires C, 77.22; H, 6.93%).

*Methyl 6-methoxy-1-methyl-3,4-dihydronaphthalene-2-carboxylate* (**6k**), $\nu_{max.}$(KBr) 1 710, 1 615, and 1 570 $cm^{-1}$; $\delta_H(CCl_4)$ 2.35 (s, 3 H, Me); 2.40—2.70 [m, 4 H, $(CH_2)_2$]; 3.67 (s, 3 H, OMe); 3.70 (s, 3 H, OMe); 6.53—7.24 (m, 3 H, ArH) (Found: C, 72.1; H, 7.15. $C_{14}H_{16}O_3$ requires C, 72.41; H, 6.89%).

2,3-Dimethylinden-1-one (**8a**). Refluxed for 16 h, orange-red solid (55%), m.p. 78—79 °C (lit.,[8] m.p. 77—78 °C); i.r. and n.m.r. data as reported.[8]

2,3,6-Trimethylinden-1-one (**8b**). Refluxed for 15 h, orange-red solid, m.p. 66—67 °C (lit.,[23] 72—73 °C); 60% $\nu_{max.}$(neat) 1 705, 1 620, and 1 596 $cm^{-1}$; $\delta_H(CCl_4)$ 1.75 (s, 3 H, Me); 2.05 (s, 3 H, Me); 2.30 (s, 3 H, Me); 6.70—7.42 (m, 3 H, ArH) (Found: C, 83.4; H, 7.3. Calc. for $C_{12}H_{12}O$: C, 83.72; H, 6.97%); *m/z* 172 ($M^+$).

2-Ethyl-3-methylinden-1-one (**8c**). Refluxed for 18 h, red viscous oil (50%); i.r. and n.m.r. data as reported.[8]

*2-Ethyl-6-methoxy-3-methylinden-1-one* (**8d**). Refluxed for 18 h, orange viscous oil (57%); $\nu_{max.}$(neat) 1 704, 1 625, and 1 600 $cm^{-1}$; $\delta_H(CCl_4)$ 1.0 (t, 3 H, $CH_2Me$); 2.01 (s, 3 H, Me); 2.18 (q, 2 H, $CH_2Me$); 3.72 (s, 3 H, OMe), and 6.45—6.94 (m, 3 H, ArH) (Found: C, 77.45; H, 7.3. $C_{13}H_{14}O_2$ requires C, 77.22; H, 6.93%); *m/z* 202 ($M^+$).

3-Methyl-2-propylinden-1-one (**8e**). Refluxed for 15 h, red viscous oil (62%); i.r. and n.m.r. data as reported.[8]

*6-Methoxy-3-methyl-2-propylinden-1-one* (**8f**). Refluxed for 18 h, red viscous oil (56%), $\nu_{max.}$(neat) 1 705, 1 620, and 1 600 $cm^{-1}$; $\delta_H(CCl_4)$ 0.91 (t, 3 H, $CH_2Me$), 1.05—1.65 (m, 2 H, $CH_2CH_2Me$), 2.02 (s, 3 H, Me), 2.1—2.31 (t, 2 H, $CH_2CH_2Me$), 3.73 (s, 3 H, OMe), and 6.48—6.95 (m, 3 H, ArH) (Found: C, 77.3; H, 7.75. $C_{14}H_{16}O_2$ requires C, 77.77; H, 7.40%); *m/z* 216 ($M^+$).

*Cyclohex-1-enyl-2-ethylpropan-1-one* (**14a**). Refluxed for 13 h, pale yellow viscous oil, (48%); $\nu_{max.}$(neat) 1 697 and 1 627 $cm^{-1}$; $\delta_H(CCl_4)$ 0.64—1.09 (2 t, 6 H, 2 Me); 1.20—1.76 [m, 4 H, ring $(CH_2)_2$], and 1.87—2.48 [m, 8 H, 2 ($CH_2Me$) and 2 ring-$(CH_2)$] (Found: C, 79.1; H, 11.1. $C_{11}H_{18}O$ requires C, 79.51; H, 10.84%).

*Cyclohex-1-enyl-2-propylbutan-1-one* (**14b**). Refluxed for 10 h, pale yellow viscous oil (50%); $\nu_{max.}$(neat) 1 695 and 1 620 $cm^{-1}$; $\delta_H(CCl_4)$ 0.79—1.27 (2 t, 6 H, 2 Me), 1.33—1.76 (m, 4 H, 2 $CH_2CH_2Me$), and 1.88—2.62 [m, 12 H, 2 $CH_2CH_2Me$ and ring $(CH_2)_4$] (Found: C, 80.8; H, 11.7. $C_{13}H_{22}O$ requires C, 80.41; H, 11.34%).

*2-Butylcyclohex-1-enylpentan-1-one* (**14c**). Refluxed for 10 h, pale yellow viscous oil (55%); $\nu_{max.}$(neat) 1 715 and 1 632 $cm^{-1}$; $\delta_H(CCl_4)$ 0.61—1.09 (2 t, 6 H, 2 Me), 1.14—1.84 [m, 12 H, 2 $CH_2(CH_2)_2Me$ and ring $(CH_2)_2$], and 1.90—2.51 [m, 8 H, 2 $CH_2(CH_2)_2Me$ and 2 ring $(CH_2)$] (Found: C, 80.8; H, 11.45. $C_{15}H_{26}O$ requires C, 81.08; H, 11.71%).

2-Butylcyclopent-1-enylpentan-1-one (**14d**). Refluxed for 12 h, pale yellow viscous oil (lit.,[24] b.p. 144—145 °C/16 mmHg) (53%); $\nu_{max.}$(neat) 1 715 and 1 640 $cm^{-1}$; $\delta_H(CCl_4)$ 1.00—1.15 (2 t, 6 H, 2 Me), 1.23—1.56 [m, 8 H, 2 $CH_2(CH_2)_2Me$], 1.64—1.94 (m, 2 H, ring $CH_2CH_2$-$CH_2$), and 2.24—2.85 [m, 8 H, 2 $CH_2(CH_2)_2Me$ and 2 ring $(CH_2)$)] (Found: C, 80.55; H, 11.15; Calc. for $C_{14}H_{24}O$: C, 80.76; H, 11.53%).

*3,4-Dihydro-2-naphthyl-1-propylbutan-1-one* (**14e**). Refluxed for 8 h, pale yellow viscous oil (50%); $\nu_{max.}$(neat) 1 682 and 1 610 $cm^{-1}$; $\delta_H(CCl_4)$ 0.64—1.06 (2 t, 6 H, 2 Me), 1.8—1.85 (m, 4 H, 2 $CH_2CH_2Me$), 2.15—2.76 [m, 8 H, 2 $CH_2CH_2CH_3$ and ring $(CH_2)_2$], and 6.94—7.44 (m, 4 H, ArH) (Found: C, 84.0; H, 9.3. $C_{19}H_{22}O$ requires C, 84.29; H, 9.09%).

*1-Butyl-3,4-dihydro-2-naphthylpentan-1-one* (**14f**). Refluxed for 10 h, pale yellow viscous oil (55%); $\nu_{max.}$(neat) 1 678 and 1 600 $cm^{-1}$; $\delta_H(CCl_4)$ 0.73—1.10 (2 t, 6 H, 2 Me), 1.15—1.70 [m, 8 H, 2 $CH_2(CH_2)_2Me$], 1.80—2.73 [m, 8 H, 2 $CH_2CH_2CH_2Me$ and ring $(CH_2)_2$], and 6.92—7.48 (m, 4 H, ArH) (Found: C, 84.15; H, 9.4. $C_{19}H_{26}O$ requires C, 84.44; H, 9.62%).

1,3,3-Triphenylprop-2-en-1-one (**14g**). Refluxed for 8 h, light yellow crystalline solid (71%) m.p. 87—88 °C (lit.,[25] 88 °C); $\nu_{max.}$(KBr) 1 660 and 1 602 $cm^{-1}$; $\delta_H(CDCl_3)$ 6.93—7.48 (m, 14 H, ArH and olef. H), 7.62—7.94 (m, 2 H, ArH); *m/z* 284 ($M^+$).

*E/Z-1,3-Diphenyl-3-(p-tolyl)prop-2-en-1-one* (**14h**).Refluxed for 9 h, light yellow solid (64%) m.p. 106—107 °C (lit.,[25] 108—109 °C); $\nu_{max.}$(KBr) 1 660 and 1 590 $cm^{-1}$; $\delta_H(CCl_4)$ 2.14 (s, 1.5 H, *p*-Me), 2.24 (s, 1.5 H, *p*-Me), 6.69—7.30 (m, 13 H, ArH and olef. H), and 7.52—7.83 (m, 2 H, ArH); *m/z* 298 ($M^+$).

*E/Z-3-(p-Methoxyphenyl)-1,3-diphenylprop-2-en-1-one* (**14i**). Refluxed for 8 h, light yellow viscous semisolid (61%); $\nu_{max.}$(neat) 1 662 and 1 595 $cm^{-1}$; $\delta_H(CCl_4)$ 3.54 (s, 1.5H, *p*-MeO), 3.62 (s, 1.5 H, *p*-MeO), 6.81—7.40 (m, 13 H, ArH and olef. H), and 7.68—7.93 (m, 2 H, ArH) (Found: C, 84.35; H, 5.25. $C_{22}H_{18}O_2$ requires C, 84.07; H, 5.73%); *m/z* 314 ($M^+$).

1-Benzoyl-2-phenylcyclohex-1-ene (**14j**). Refluxed for 10 h, light yellow crystals (53%) m.p. 90—91 °C (light petroleum) (lit., [26] 91—92 °C); $\nu_{max.}$(KBr) 1 710 and 1 600 $cm^{-1}$; $\delta_H(CCl_4)$ 1.70—2.06 [m, 4 H, $(CH_2)_2$], 2.32—2.73 [m, 4 H, 2 $CH_2$], and 6.88—7.60 (m, 10 H, ArH).

*2-Benzoyl-1-phenyl-3,4-dihydronaphthalene* (**14k**). Refluxed for 8 h, light yellow viscous semisolid (65%); $\nu_{max.}$(neat) 1 712 and 1 605 $cm^{-1}$; $\delta_H(CCl_4)$ 2.40—2.90 [2 t, 4 H, $(CH_2)_2$], and 6.60—7.69 (m, 14 H, ArH) (Found: C, 88.75, H, 6.1. $C_{23}H_{18}O$ requires C, 89.03; H, 5.80%); *m/z* 310 ($M^+$).

*General Procedure for Boron Trifluoride–Ether catalysed partial Hydrolysis of the Alcohol Acetals* (**3a**) and (**3i—k**). S-*Methyl β-methylthiocinnamate* (**7a**).—Boron trifluoride–ether (5 ml) was added to the crude alcohol (**3a**) (2.15 g, 0.009 mol), in ether (50 ml), and the reaction mixture was stirred at room temperature for 5 min. It was then diluted with distilled water (5 ml), refluxed for 6 h, cooled, poured into cold water (75 ml) and extracted with chloroform (2 × 75 ml). The combined extracts were washed with saturated aqueous $NaHCO_3$ (60 ml) and water (60 ml), and then dried ($Na_2SO_4$) and evaporated to give the crude thiocinnamate (**7a**) which was further purified by column chromatography over silica gel (hexane as eluant); it was a pale yellow viscous oil (41%), $\nu_{max.}$(neat) 1 672 and 1 608 $cm^{-1}$; $\delta_H(CCl_4)$ 2.35 (s, 3 H, SMe), 2.54 (s, 3 H, Me); 6.32 (s, 1 H, olef. H), and 7.16—7.66 (m, 5 H, ArH) (Found: C, 68.9; H, 6.55. $C_{11}H_{12}OS$ requires C, 68.75; H, 6.25%).

The thioesters (**7b—d**) were similarly obtained under identical conditions.

S-*Methyl 1-methyl-1-indene-2-thiocarboxylate* (**7b**). Refluxed for 10 h, light yellow crystals (55%), m.p. 78—79 °C; $\nu_{max.}$(KBr) 1 644 and 1 588 $cm^{-1}$; $\delta_H(CCl_4)$ 2.37 (s, 3 H, SMe), 2.55 (t, *J* 1.5 Hz, 3 H, Me), 3.64 (q, *J* 1.5 Hz, 2 H, $CH_2$), and 7.13—7.58 (m, 4 H, ArH) (Found: C, 70.2; H, 6.1. $C_{12}H_{12}OS$ requires C, 70.58; H, 5.88%).

S-*Methyl 1-methyl-3,4-dihydronaphthalene-2-thiocarboxylate* (**7c**). Refluxed for 12 h, light yellow crystals (60%), m.p. 43—44 °C; $\nu_{max.}$(KBr) 1 665 and 1 610 $cm^{-1}$; $\delta_H(CCl_4)$ 2.40 (br s, 6 H, SMe and Me), 2.54—2.85 [m, 4 H, $(CH_2)_2$], and 7.00—7.49

(m, 4 H, ArH) (Found: C, 71.85; H, 6.15. $C_{13}H_{14}OS$ requires C, 71.55; H, 6.42%).

S-*Methyl* 6-*methoxy*-1-*methyl*-3,4-*dihydronaphthalene*-2-*thiocarboxylate* (**7d**). Refluxed for 10 h, pale yellow viscous oil (58%); $\nu_{max.}$(neat) 1 663 and 1 614 $cm^{-1}$; $\delta_H(CCl_4)$ 2.35 (s, 6 H, SMe and Me), 2.50—2.84 [m, 4 H, $(CH_2)_2$], 3.80 (s, 3 H, OMe), and 6.51—7.43 (m, 3 H, ArH) (Found: C, 68.1; H, 6.8. $C_{14}H_{16}O_2S$ requires C, 67.74; H, 6.45%); *m/z* 248 ($M^+$).

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