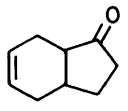
Regiochemical Control in the Alkylation of Tetrahydroindanones

Thomas V. Lee* and Judy Toczek
Department of Organic Chemistry, The University, Bristol BS8 1TS

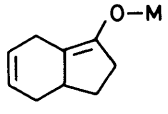
The first regiospecific alkylation of the 3a,4,7,7a-tetrahydroindanone (**1**) has been achieved, by use of a phenylthio group acting as a directing group for enolate anion generation or as a blocking group which permits the formation of the regioisomeric enolate anion. The stereochemical outcome of the process has been determined for alkylation with methyl iodide, allyl bromide, and methyl bromoacetate. Additionally the alkylation of the enolate anion has been compared to that of the equivalent *O*-silylated enolate. The difference in stereochemistry may reflect a balance between steric and stereoelectronic effects.

The stereochemical outcome of the alkylation of perhydroindan derivatives has been studied by House.[1] However, direct regiochemical control in the alkylation of the system has only recently been achieved.[2] Although the two enolate anions (**2**) and (**4**) obtained from 3a,4,7,7a-tetrahydroindan-1-one (**1**) have been generated separately by a multi-step procedure, it is not possible to do this directly from the parent ketone. This paper describes a method for regiospecifically alkylating the indanone (**1**) with various alkylating agents. The stereochemical consequences of the alkylations have also been determined so as to enhance further the potential of the perhydroindan system in organic synthesis.

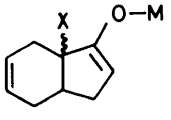
Additionally, we report upon the acid-catalysed alkylation of the *O*-silylated enolate (**3**) with methyl chloro(phenylthio)acetate (**7**)[3] and describe how the stereochemical outcome of this reaction compares with the basic enolate anion alkylation.



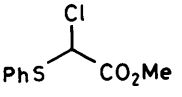
(**1**)



(**2**) M = Li
(**3**) M = $SiMe_3$



(**4**) X = H, M = Li
(**5**) X = SPh, M = Li
(**6**) X = H, M = $SiMe_3$



(**7**)

The key to controlling the regiochemistry of the alkylation involves the use of the phenylthioindanone (**8**). The phenylthio group can be used as a directing group, in a dissolved metal reduction, to generate the enolate anion (**2**). Alternatively, reaction of (**8**) with a strong base will generate the enolate anion (**5**), with the phenylthio group acting as a blocking group which can be subsequently removed.

Thus, reaction of an excess of buta-1,3-diene and 2-phenylthiocyclopent-2-enone[4] in a sealed glass tube at 180 °C for 24 h gave, after purification by rapid filtration through a bed of silica gel, 60% of the indanone (**8**). Upon treatment with lithium metal in anhydrous liquid ammonia the ketone (**8**) formed the enolate anion (**2**) (Scheme. The anion maintains its regiochemical integrity at −20 °C so allowing a regiospecific alkylation with methyl bromoacetate to give an 87% isolated yield of the oxoester (**9**). Gas chromatographic analysis indicated that the *cis* to *trans* ratio about the bridgehead was 94:6 in agreement with the observations of House.† Under these conditions no trace of di-or poly-alkylated products was observed.

Similarly reaction of the enolate anion (**2**) with allyl bromide produced a 69% yield of the ketone (**10**) with a *cis* to *trans* ratio of 95:5 as determined by gas chromatography.‡ However, in this case 11% of the diallylated ketone (**12**) was formed which, presumably reflecting the reduced reactivity of allyl bromide in these reactions, allows partial enolization of the ketone (**10**). As was expected, alkylation with methyl iodide led to difficulties with polyalkylation, with the optimum conditions found to give 60% of the monoalkylated ketone (**11**) and 14% of the dimethyl ketone (**13**). The ketone (**11**) showed a bridgehead isomer ratio of 66:34, as determined by gas chromatography.

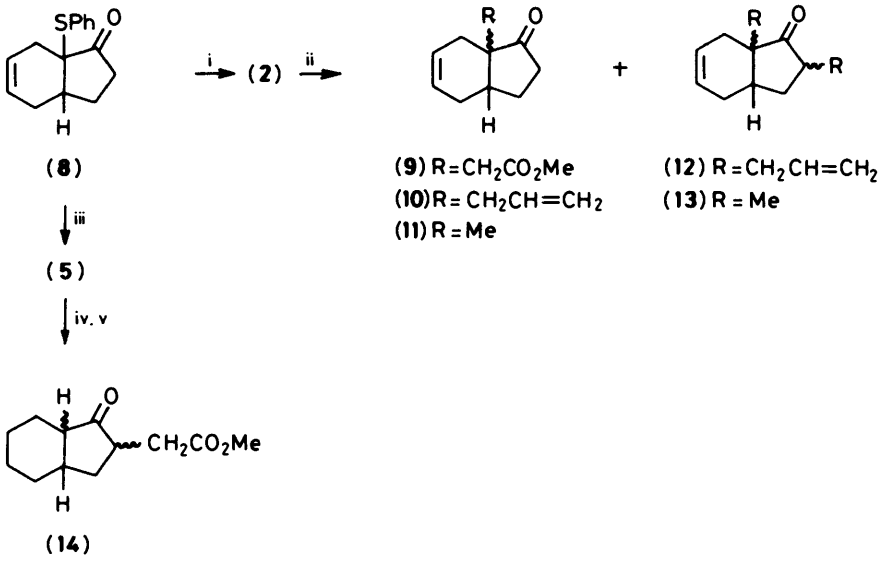
In contrast, the opposite regiochemistry can readily be obtained by treating the indanone (**8**) with lithium diisopropylamide to generate the enolate anion (**5**). Alkylation with methyl bromoacetate followed by reduction, with zinc in acetic acid, gave the oxo ester (**14**) with a *cis* to *trans* ratio of 3:2 in an overall yield of 65%. This is presumably the thermodynamic ratio obtained under these typically equilibrating conditions.

By comparison the Lewis acid-catalysed alkylation of the *O*-silylated enolate (**3**) prepared as a 93:7 mixture with its isomer (**6**), using the chloro ester (**7**) gave a 48:52 *cis* to *trans* ratio, as determined by gas chromatography of the crude mixture. The same ratio was observed after purification (67% yield) of the products, which could then be characterised spectroscopically and by conversion into the known oxo esters, *cis* and *trans* (**9**), by Raney nickel reduction. Additionally, Raney nickel reduction of the crude product prior to separation gave a mixture of *cis* and *trans* (**9**) in the ratio of 48:52, using the same gas chromatography conditions as in the enolate anion reaction.

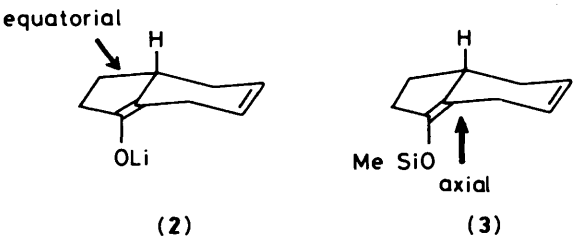
This difference in stereoselectivity between the enolate anion and enol reaction may be due to a contrast between steric and stereoelectronic control in the transition state. Thus, as is well known,[5] for an enolate anion such as (**2**) the preferred transition state involves introduction of the electrophile equatorial to the non-oxygenated ring, due to steric constraints. However, for the enol ether (**3**) it would appear that, possibly due to stereoelectronic control, the axial approach is enhanced resulting in a greater yield of the *trans* product. Such stereoelectronic control has previously been observed for enamines,[6] but further work is

† The structure of the two isomers of (**9**) were confirmed by g.l.c. separation and comparison with authentic spectra.

‡ The stereochemistry of the major isomer of (**10**) was confirmed by converting it into *cis*-(**9**) by a sequence of selective ozonolysis of the allyl group and oxidation to a carboxylic acid, followed by methylation (CH_2N_2).



Scheme. i, $Li/NH_3(l)$; ii, R–X (see text), iii, lithium di-isopropylamide; iv $BrCH_2CO_2Me$; v, Zn/AcOH.



necessary to see if this is a general phenomenon for *O*-silylated enolates, as is work to explain the rôle of Lewis acids in these reactions.

The above studies have clearly demonstrated how one can achieve the regio- and stereo-specific alkylation of tetrahydroindanones so enhancing their synthetic utility.[7] Furthermore, they have indicated that additional studies on the stereochemical outcome of the alkylation of *O*-silylated enolates would be beneficial to our understanding of these reactions.

Experimental

All m.p.s and b.p.s are uncorrected. The i.r. spectra were recorded on a Pye-Unicam SP3-100 or a Perkin-Elmer 1420 spectrophotometer. The ^1H n.m.r. were determined at 60 MHz on a Varian T-60 spectrometer and at 200 MHz on a Varian XL200 spectrometer, using Me_4Si as an internal standard. Mass spectra were obtained on an AEI MS902 spectrometer. $MgSO_4$ was used for drying solutions in organic solvents, and all solvents were dried and distilled prior to use. Merck silica gel (230—400 mesh) was used for column chromatography and light petroleum refers to the 60—80 °C boiling fraction. Ether refers to diethyl ether. All reactions utilising reactive intermediates were performed under a dry nitrogen atmosphere.

2-*Phenylthiocyclopent-2-enone*.—Following procedures described earlier[4,8] benzenesulphenyl chloride (317 g, 2.21 mol) was added dropwise to a solution of cyclopentanone (56 g, 670 mmol) in dry acetonitrile (900 ml) at room temperature (21 °C). After being stirred for 2.5 h the solution was evaporated to give a dark brown solid (310 g). Column chromatography of this, eluting with ether and light petroleum, gave the thioenone (2.4 g, 59%) as orange crystals, m.p. 63—65 °C (lit.,[4] m.p. 64—65 °C); $\nu_{max.}(CCl_4)$ 3 050, 2 950, 2 870, 1 710 (C=O), 1 660 (C=C), and 1 580 cm^{-1} (aromatic C=C); $\delta(CCl_4)$ 7.5 (5 H, m, Ph), 7.0 (1 H, dd, *J* 2 and 3 Hz, 3-H), and 2.7—2.4 (4 H, m, 4-H_2, 5-H_2); *m/z* 190 (100%, M^+), 134 (62), and 71 (60).

7a-*Phenylthio*-3aR,7aR-3a,4,7,7a-*tetrahydroindan*-1-*one* (**8**).—Buta-1,3-diene (41 ml, 474 mmol) was condensed into a Carius tube containing the thioenone (9.0 g, 47 mmol) and hydroquinone (0.15 g, 1.4 mmol) and the sealed tube was heated at 175 °C for 24 h. The crude product (27 g) was purified by dry flash chromatography,[9] followed by flash chromatography, [10] eluting with a mixture of ether and light petroleum to afford the phenylthioindanone (**8**) (7.6 g, 66%) as a yellow oil; $\nu_{max.}$(thin film) 3 030, 2 950, 1 730 (C=O), 1 660 (C=C), and 1 580 cm^{-1} (aromatic C=C); $\delta(CCl_4)$, 7.35 (5 H, m, Ph), 5.6 (2 H, m, 5-H, 6-H), and 2.8—1.5 (9 H, m, alkyl); *m/z* 244 (71%, M^+), 135 (74, M − SPh), and 110 (100).

7a-*Methoxycarbonylmethyl*-3aS,7aR-3a,4,7,7a-*tetrahydroindan*-1-*one* (**9**).—Lithium (0.75 g, 106 mmol) was added to dry ammonia (100 ml) at −78 °C under nitrogen, to give a dark blue solution. This was stirred for 10 min after which a solution of the phenylthioindanone (**8**) (2.60 g, 10 mmol) in anhydrous THF (120 ml) was added, and the mixture stirred for a further 15 min. The ammonia was removed under reduced pressure over 20 min when methyl bromoacetate (21.2 g, 138 mmol) was rapidly added at −20 °C. After 2 min the reaction was quenched with saturated aqueous ammonium chloride (30 ml) and washed with ether (3 × 50 ml). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate (2 × 50 ml) and aqueous sodium chloride (2 × 50 ml), dried, and evaporated to give a yellow oil. Purification by flash chromatography, using light petroleum–ether gave the oxo ester (**9**) (1.9 g, 87%) as a colourless liquid;[1] $\nu_{max.}$ (CCl_4), 3 020, 2 920, 1 745 (C=O), and 1 660 cm^{-1} (C=C); $\delta(CCl_4)$, 5.60 (2 H, m, 5-H, 6-H), 3.60 (3 H, s, OMe), and 2.7—1.6 (11 H, m, alkyl); *m/z* 208 (45%, M^+), 135 (73, 134 (100), 92 (93), and 91 (93). G.l.c. analysis[1] of the crude product gave a ratio of 94:6 for the *cis* and *trans* isomers.

7a-*Allyl*-3aS,7aR-3a,4,7,7a-*tetrahydroindan*-1-*one* (**10**).—The above procedure was followed using phenylthioindanone (**8**) (0.5 g, 2 mmol) and allyl bromide (3.7 g, 30 mmol) to give a yellow oil. Purification by flash chromatography, eluting with pentane–ether, gave the ketone (**10**) (0.25 g, 69%) as a colourless

liquid, b.p. 55—60 °C/0.1 mmHg (Found: C, 81.90; H, 9.20. $C_{12}H_{16}O$ requires C, 81.77; H, 9.15%). $\nu_{max.}$(CCl_4), 3 060, 3 020, 1 740 (C=O), 1 660 and 1 640 cm^{-1} (C=C); δ(CCl_4), 5.7 (2 H, m, 5-H, 6-H), 5.5—4.8 (3 H, m, allyl), and 2.7—1.7 (11 H, m, alkyl); *m/z* 176 (10%, M^+), 135 (100, $M - CH_2{=}CH{-}CH_2$), 134 (90), and 79 (95). G.l.c. analysis of the crude product indicated a 95:5 ratio for the *cis* and *trans* isomers. The dialkylated ketone (**12**) (0.05 g, 11%) was also isolated as a colourless liquid; δ(CCl_4), 5.7 (2 H, m, 5-H, 6-H), 5.5—4.8 (6 H, m, 2 × allyl), and 2.7—1.7 (12 H, m, alkyl); *m/z* 216 (20%, M^+), 188 (18, $M - C_2H_4$), 175 (94, $M - CH_2{=}CH{-}CH_2$), 91 (100), and 79 (86), that was not characterised further.

7a-*Methyl*-3aS,7aS-3a,4,7,7a-*tetrahydroindan*-1-*one* (**11**).—The previous procedure for the synthesis of the oxo ester (**9**) was followed, using the phenylthioindanone (**8**) (0.5 g, 2 mmol) and methyl iodide (4.37 g, 30 mmol). The reaction was quenched after 4.5 min to give a yellow oil. Flash chromatography using pentane–ether gave the monoalkylated ketone (**11**) (0.19 g, 60%) as a colourless liquid, b.p. 22 °C/0.1 mmHg (Found: C, 79.85; H, 9.25. $C_{10}H_{14}O$ requires C, 79.96; H, 9.39%); $\nu_{max.}$(CCl_4), 3.020, 2 920, 1 738 (C=O), and 1 650 cm^{-1} (C=C); δ(CCl_4), 5.7 (2 H, m, 5-H, 6-H), 2.4—1.6 (9 H, m, alkyl), 1.0 and 0.8 (3 H, s, Me); *m/z* 150 (31%, M^+), 136 (32, $M + H - Me$), 135 (20, $M - Me$), and 79 (100). G.l.c. analysis of the crude product gave a ratio of 2:1 for the bridgehead isomers. The dialkylated ketone (**13**) (0.048 g, 14%) was also isolated as a colourless liquid, b.p. 21 °C/0.1 mmHg (Found: C, 80.40; H, 9.80. $C_{11}H_{16}O$ requires C, 80.45; H, 9.80%). $\nu_{max.}$(CCl_4), 3 030, 2 920, 1 738 (C=O), and 1 650 cm^{-1} (C=C); δ(CCl_4), 5.5 (2 H, m, 5-H, 6-H), 2.6—1.4 (8 H, m, alkyl), 1.65 (3 H, d, *J*6 Hz, Me), and 1.0 (3 H, s, Me); *m/z* 164 (82%, M^+), 149 (46, $M - Me$), and 79 (100).

2-*Methoxycarbonylmethyl*-3aS,7aS-3a,4,7,7a-*tetrahydroindan*-1-*one* (**14**).— Butyllithium (1.46 M solution in hexane 1.54 ml) was added to a solution of di-isopropylamine (0.32 ml, 2.3 mmol) in dry THF (10 ml) under nitrogen at −60 °C. After 10 min the phenylthioindanone (**8**) (0.5 g, 2 mmol) in anhydrous THF (3 ml) was added, followed after 15 min by methyl bromoacetate (0.94 g, 6 mmol). The mixture was warmed to −12 °C before quenching with saturated aqueous ammonium chloride (5 ml). The mixture was extracted with ether (3 × 20 ml) washed with saturated aqueous sodium hydrogen carbonate (2 × 25 ml) and aqueous sodium chloride (2 × 25 ml), dried, and concentrated. Flash chromatography using chloroform–light petroleum gave the alkylated phenylthioindanone (0.42 g, 87%) as a yellow liquid; $\nu_{max.}$(CCl_4), 3 040, 2 960, 1 835 (C=O), and 1 660 cm^{-1} (C=C); δ(CCl_4), 7.4 (5 H, m, Ph), 5.6 (2 H, m, 5-H, 6-H), 3.7 (3 H, s, OMe), and 2.7—1.7 (10 H, m, alkyl); *m/z* 316 (22%, M^+), 207 (46, M − SPh), 175 (83), 110 (98), and 71 (100).

A solution of the alkylated phenylthioindanone (0.79 g, 2.5 mmol) in glacial acetic acid (8 ml) was added dropwise to a mixture of zinc powder (1.1 g, 17 mmol) in glacial acetic acid (10 ml) and the resulting mixture was vigorously stirred at 70 °C for 5 h. After cooling, the zinc was filtered off and the filtrate diluted with chloroform (50 ml) and washed with saturated aqueous potassium carbonate (2 × 25 ml). The organic layer was washed with water (2 × 50 ml), dried, and evaporated to give a pale yellow liquid. Purification by flash chromatography, eluting with chloroform and subsequent distillation under reduced pressure gave the oxo ester (**14**) (0.37 g, 79%) as a colourless liquid, b.p. 120 °C/0.5 mmHg (Found: C, 69.1; H, 7.75. $C_{12}H_{16}O_3$ requires C, 69.20; H, 7.75%). $\nu_{max.}$(CCl_4), 3 025, 2 950, 1 735 (C=O), 1 650 cm^{-1} (C=C); δ(CCl_4), 5.7 (2 H, m, 5-H, H-6), 3.65 (3 H, s, OMe), and 2.8—1.6 (11 H, m, alkyl); *m/z* 208 (14%, M^+), 178 (22), 177 (24), 134 (35), and 116 (100).

A sample of the crude alkylated phenylthioindanone was similarly reduced and the crude product analysed by g.l.c. to give a ratio of 3:2 for presumably the *cis* and *trans* isomers.

3-*Trimethylsiloxy*-1,2,7,7a-*tetrahydroindene* (**3**).—Method A. The procedure described earlier for the synthesis of the oxo ester (**9**) was followed using the phenylthioindanone (**8**) (0.45 g, 1.8 mmol). After the removal of ammonia, triethylamine (0.11 ml, 0.8 mmol) and trimethylsilyl chloride (0.46 ml, 3.7 mmol) were added to the solution of lithium enolate at −7 °C. The mixture was allowed to warm to room temperature (21 °C) and stirred for 45 min. The crude mixture was filtered through Celite and the filtrate evaporated. Purification by column chromatography using chloroform gave the *O-silylated enolate* (**3**) (0.16 g, 36%) (see Method B for spectral data).

3aS,7aS-3a,4,7,7a-*Tetrahydroindan*-1-*one* (**1**).—*Method B.* A solution of the phenylthioindanone (**8**) (2 g, 8 mmol) in glacial acetic acid (15 ml) was slowly added to a mixture of zinc powder (3.6 g, 55 mmol) in glacial acetic acid (30 ml). The mixture was vigorously stirred at 70 °C for 5 h, and the cooled mixture was treated as for the preparation of (**14**). Purification by column chromatography, eluting with dichloromethane gave the indanone (**1**)[1] (0.66 g, 60%) as a pale yellow, sweet smelling liquid; $\nu_{max.}$(CCl_4), 3 020, 2 920, 1 740 (C=O), and 1 650 cm^{-1} (C=C); δ(CCl_4) 5.7 (2 H, m, 5-H, 6-H) and 2.6—1.7 (10 H, m, alkyl); *m/z* 136 (100%, M^+), 92 (81), and 79 (95).

A mixture of the indanone (**1**) (1.00 g, 3.4 mmol) and trimethylsilyl chloride (0.99 g, 9.2 mmol) in acetonitrile (15 ml) and a solution of triethylamine (0.92 g, 9.2 mmol) in acetonitrile (5 ml) were simultaneously added to a solution of sodium iodide (1.37 g, 9.1 mmol) in acetonitrile (20 ml), under nitrogen at room temperature. After being stirred for 1 h, the reaction mixture was poured into ice-cold water–pentane (1:1; 80 ml). The aqueous layer was washed with pentane (3 × 20 ml) and the combined organic extracts dried and evaporated. Column chromatography of the residue, eluting with chloroform, afforded a mixture of the *O*-silylated enolates (**3**) and (**6**) (1.05 g, 69%) as a pale yellow liquid, b.p. 110 °C/6 mmHg; $\nu_{max.}$(CCl_4), 3 020, 2 950, 1 690 and 1 650 cm^{-1} (C=C); δ(CCl_4) 5.5 (2 H, m, 5-H, 6-H), 5.0 (≪1 H, m, 2-H), 2.7—0.9 (9 H, m, alkyl), and 0.1 (9 H, s, $SiMe_3$) (Found: M^+, 208.1287. $C_{12}H_{20}OSi$ requires M, 208.1283), *m/z* 208 (1%, M^+), 136 (100, $M + H - SiMe_3$), and 79 (97). G.l.c.* analysis of the crude product indicated a ratio of 93:7 for the *O*-silylated enolates (**3**) and (**6**) which was in agreement with n.m.r. analysis of the mixture.

Phenylthioalkylation of the O-Silylated Enolate (**3**).—A catalytic amount of anhydrous zinc bromide was added to a stirred solution of the *O*-silylated enolates (**3**) and (**6**) (0.98 g, 4.8 mmol) in the presence of methyl chloro(phenyl)thioacetate (**7**) (1.11 g, 5 mmol) in dichloromethane (20 ml), under nitrogen at room temperature (22 °C). Water was added after 2 h and the aqueous layer was washed with dichloromethane (3 × 10 ml). The combined organic extracts were dried and evaporated to afford a yellow liquid, which was purified by flash chromatography using ether–light petroleum to give the alkylated phenylthioindanone, with different isomers being isolated in 3 fractions. (a) As a white solid (0.268 g, 18%), m.p. 41—44 °C; $\nu_{max.}$($CDCl_3$) 3 020, 2 950, 1 730 (C=O) and 1 660 cm^{-1} (C=C); δ($CDCl_3$) 7.6 (5 H, m, Ph), 6.0 (2 H, m, 5-H, 6-H), 3.7 (3 H, s, OMe), and 3.0—1.8 (10 H, m, alkyl) (Found: M^+, 316.1137. $C_{18}H_{20}O_3S$ requires M, 316.1133), *m/z* 316 (17%, M^+), 207 (92, M − SPh), and 135 (100, M − SPh − $CHCO_2CH_3$).

* This determination was obtained using a 2 m 5% APL on Celite column, at 140 °C and a flow rate of 20 ml min^{-1}.

(b) As a pale yellow liquid (0.32 g, 21%); $\nu_{max.}(CDCl_3)$ 3 020, 2 950, 1 730br (C=O), and 1 660 cm^{-1} (C=C); $\delta(CDCl_3)$ 7.35 (5 H, m, Ph), 5.6 (2 H, m, 5-H, 6-H), 3.6 (s, OMe, 54% of total ester signal), 3.5 (s, OMe, 46% of total ester signal), and 2.8—1.7 (10 H, m, alkyl) (Found: M^+, 316.1135. $C_{18}H_{20}O_3S$ requires M, 316.1133), m/z 316 (12%, M^+), 182 (100), and 135 (82).

(c) As a pale yellow liquid (0.34 g, 23%); $\nu_{max.}(CDCl_3)$, 3 020, 2 950, 1 730 (C=O), 1 635 cm^{-1} (C=C); $\delta(CDCl_3)$ 7.4 (5 H, m, Ph), 5.85 (2 H, m, 5-H, 6-H), 3.7 (3 H, s, OMe), and 3.1—1.8 (10 H, m, alkyl) (Found: M^+, 316.1132. $C_{18}H_{20}O_3S$ requires M, 316.1133), m/z 316 (9%, M^+), 182 (100), and 135 (82). This constituted an overall yield of 67% for the alkylated phenylthioindanone.

cis *and* trans-7a-*Methoxycarbonylmethyl*-3a,4,7,7a-*tetrahydroindan*-1-*one* (**9**).—The three fractions obtained from the alkylation of the *O*-silylated enolates (**3**) and (**6**) were individually dissolved in acetone (1 ml) and stirred with Raney nickel at room temperature (20 °C) for 2 h. The mixtures were filtered, dried, and evaporated. The percentage of *cis* and *trans*-isomers of the oxo ester (**9**) was determined by g.l.c.[1] analysis: (a) cis (100%), (b) cis (54%), trans (46%), and (c) trans (100%). The combined weights for the two isomers gave an overall yield of *cis* (48%) and *trans* (52%).

A sample of the crude alkylated phenylthioindanone (0.5 g) was similarly reduced with Raney nickel. G.l.c.[1] analysis of the crude product gave a ratio of 48:52 for the *cis* and *trans* isomers. Purification by flash chromatography, using ether–light petroleum gave the oxo ester (**9**). The *cis* isomer (0.045 g, 27%) was isolated as a colourless liquid; $\nu_{max.}(CCl_4)$, 3 020, 2 920, 1 745 (C=O), and 1 660 cm^{-1} (C=C); $\delta(CCl_4)$, 5.60 (2 H, m, 5-H, 6-H), 3.60 (3 H, s, OMe), and 2.7—1.6 (11 H, m, alkyl); m/z 208 (45%, M^+), and 134 (100). The *trans* isomer (0.053 g, 31%) was obtained as a colourless liquid; $\nu_{max.}(CCl_4)$, 3 020, 2 950, 1 748 (C=O), and 1 640 cm^{-1} (C=C); $\delta(CCl_4)$, 5.65 (2 H, m, 5-H, 6-H), 3.50 (3 H, s, PMe), and 2.7—1.6 (11 H, m, alkyl). The oxo ester (**13**) (0.019 g, 5%) was also isolated as a colourless liquid; $\nu_{max.}(CDCl_3)$, 3 025, 2 950, 1 735 (C=O), and 1 650 cm^{-1} (C=C); $\delta(CDCl_3)$, 5.7 (2 H, m, 5-H, 6-H), 3.65 (3 H, s, OMe), and 2.8—1.6 (11 H, m, alkyl); m/z 208 (14%, M^+) and 116 (100).

Acknowledgements

We thank the S.E.R.C. (studentship to J. T.) for their support of this work. We are indebted to Professor H. O. House for kindly providing us with authentic spectra of the *cis* and *trans* tetrahydroindanone (**9**).

References

1 H. O. House and C. J. Blankley, *J. Org. Chem.*, 1967, **32**, 1741.
2 T. V. Lee and J. Toczek, *J. Chem. Soc., Chem. Commun.*, 1982, 968.
3 T. V. Lee and J. Okonkwo, *Tetrahedron Lett.*, 1983, **24**, 323; I. Fleming and J. Iqbal, *ibid.*, 1983, **24**, 327.
4 H. J. Monteiro, *J. Org. Chem.*, 1977, **42**, 2324.
5 H. O. House, 'Modern Synthetic Reactions,' Benjamin 1972, p. 586.
6 J. M. Conia and P. Briet, *Bull. Soc. Chim. Fr.*, 1966, 3881.
7 T. V. Lee and J. Toczek, *Tetrahedron Lett.*, 1985, **26**, 473.
8 S. Knapp, R. Lis, and P. Michna, *J. Org. Chem.*, 1981, **46**, 624.
9 L. M. Harwood, *Aldrichimica Acta*, 1985, **18**, 25.
10 W. Clark Still, M. Kahn, and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.

Received 24*th March* 1986; *Paper* 6/569