Reactions of 3-Phenylthiobut-3-en-2-one. Part 4.[1] Novel and Efficient Synthesis of 7-Hydroxycalamenene, Ferruginol, and D-Homoestrone

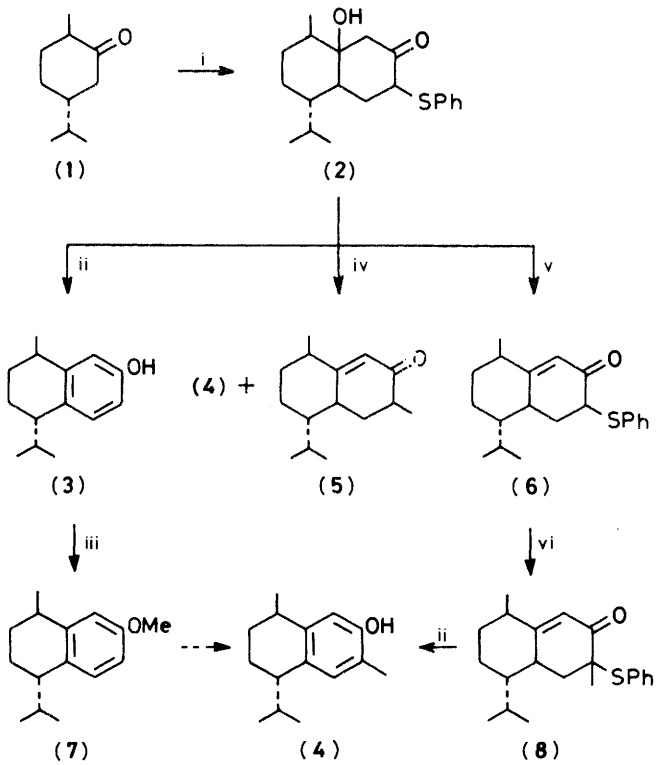
Ken Takaki,* Masakatsu Ohsugi, Michikazu Okada, Masateru Yasumura, and Kenji Negoro
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Saijo, Higashi-Hiroshima 724, Japan

The annelation reaction of 3-phenylthiobut-3-en-2-one with carvomenthone (**1**) gives 8a-hydroxy-4α-isopropyl-1-methyl-6-phenylthioperhydronaphthalen-7-one (**2**), which is converted into 7-hydroxycalamenene (**4**) by subsequent dehydration, methylation, and aromatisation in good yield. Ferruginol (**13**) and D-homoestrone (**16**) are prepared similarly by this annelation method starting from naphthalenone (**9**) and phenanthrenone (**14**), respectively. In addition, the reactions of 3-phenylthiobut-3-en-2-one with (**14**) and with cyclohex-2-en-1-one in the presence of liquid ammonia afford annelated pyridine derivatives, the azachrysene (**21**), and the tetrahydroquinoline (**23**).

There is currently a significant amount of interest in the development of aromatic annelations, methods for building up fused aromatic products starting from alicyclic compounds, which enjoy some advantages over the classical pathways from aromatic starting materials.[2] In previous parts of this series, we have described a new method of constructing simple fused phenols from cycloalkanones and 3-phenylthiobut-3-en-2-one.[3] Several natural products containing β-phenol units could, in principle, be prepared by this method, because aromatic rings can easily be regioselectively attached to readily available cycloalkanones. In order to show the generality of this reaction, we report here an efficient synthesis of 7-hydroxycalamenene (**4**),[4] a sesquiterpene of the cadinane family, ferruginol (**13**),[5] a diterpene of the abietane family, and D-homoestrone (**16**)[6] as typical examples, and also the pyridine annelation of 3-phenylbut-3-en-2-one.

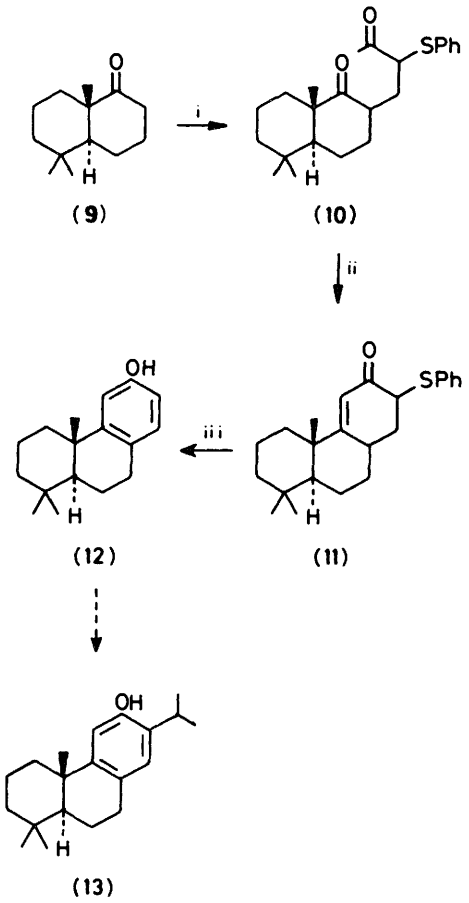
The synthesis of 7-hydroxycalamenene (**4**) is shown in Scheme 1. Carvomenthone (*p*-menthan-2-one) (**1**), prepared from l-carvone (*p*-mentha-6,8-dien-2-one) by catalytic hydrogenation and therefore a mixture of C-2 methyl epimers, was converted into the lithium enolate on treatment with lithium di-isopropylamide under kinetic conditions; this reacted with 3-phenylthiobut-3-en-2-one to give the ketol (**2**) in 88% yield. Aromatisation of compound (**2**) (81%) and subsequent methylation (81%) afforded the phenol derivative (**7**) as described previously.[3] Although compound (**7**) could be converted into the calamenene (**4**) by the literature method,[7] direct alkylation of (**2**), by using the phenylsulphenyl group, before aromatisation seemed to offer a convenient means of placing the methyl substituent at C-3. Thus the ketol (**2**) was treated with sodium hydride and then lithium di-isopropylamide, followed by methyl iodide, to give the calamenene (**4**) in 41% yield together with methylated enone (**5**) † (37%). A more practical synthesis of (**4**) was accomplished by quantitative dehydration on treatment with aluminium oxide, followed by kinetic methylation of (**6**) (98%), and aromatisation of (**8**) (100%). The n.m.r. spectrum of (**4**) shows two signals due to the C-8 methine proton at 6.63 and 6.56 p.p.m., in a ratio of 2:1, the former being assignable to the naturally occurring *cis*-calamenene and the latter to the *trans*-isomer.[4] This ratio probably results from that of carvomenthone (**1**), since epimerisation of the methyl group could be suppressed under the conditions described above.

Many synthetic methods for C-aromatic tricyclic diterpenoids have been reported; however, most of them are based on cyclisation of B-rings starting from C-aromatic precursors and therefore specific conditions are necessary to control the stereochemistry of the A–B ring conjunctions.[8] Our strategy makes it possible to start with decalone derivatives, whose preparation has been well established[9] (Scheme 2). The reaction of 4,4,8aβ-trimethyl-4aα-perhydronaphthalen-8-one (**9**) with 3-phenylthiobut-3-en-2-one afforded the diketone (**10**) in 71% yield, which cyclised to the enone (**11**) (82%) on treatment with ethanolic potassium hydroxide. Unfortunately, the kinetic enolate of (**11**) failed to react with isopropyl iodide, in contrast to the reaction of (**6**) with methyl iodide, presumably owing to steric hindrance. Thus, aromatisation of (**11**) gave the phenanthrol (**12**) in 91% yield; an isopropyl group was then



Scheme 1. *Reagents:* i, LDA, then 3-phenylthiobut-3-en-2-one; ii, toluene-*p*-sulphonic acid; iii, Me_2SO_4; iv, NaH, LDA, then MeI; v, Al_2O_3; vi, LDA then MeI

† The structures of these minor by-products, (**5**) and (**17**), were assigned on the basis of their i.r. and n.m.r. spectra, but they have not been investigated further.

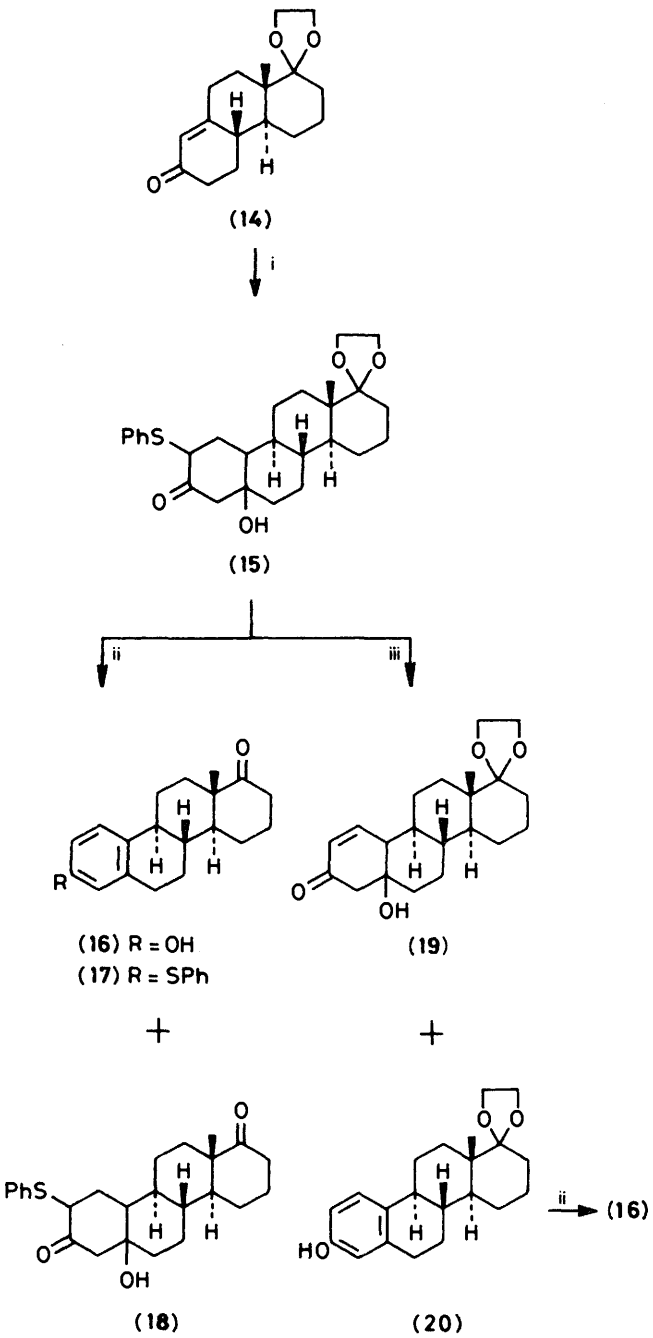


Scheme 2. *Reagents:* i, LDA, then 3-phenylthiobut-3-en-2-one; ii, KOH–EtOH; iii, toluene-*p*-sulphonic acid

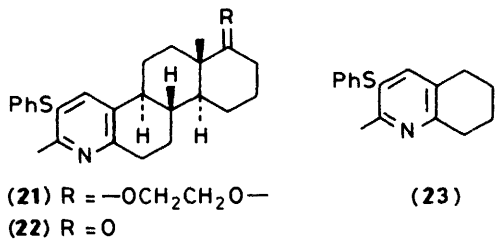
introduced at C-7, by the reported method,[5] to give ferruginol (**13**).

The tricyclic enone (**14**), prepared from Wieland–Miescher ketone,[10] was reduced with lithium in liquid ammonia, and then treated with 3-phenylbut-3-en-2-one in THF to afford the ketol (**15**) in 88% yield (Scheme 3). Treatment of the ketol (**15**) with toluene-*p*-sulphonic acid gave D-homoestrone (**16**), the sulphenylated ketone (**17**),* and the diketone (**18**) in 50, 18, and 18% yields, respectively. The ketone (**17**) was probably formed by the reaction of compound (**16**) with diphenyl disulphide, generated during aromatisation, in the presence of acid;[11] accordingly, the use of more drastic conditions in order to consume the diketone (**18**) would cause an increase in the yield of (**17**). Alternatively, oxidation of compound (**15**) with *m*-chloroperbenzoic acid and subsequent heating afforded the products (**19**) and (**20**) in 44 and 26% yield, respectively. D-Homoestrone (**16**) was obtained in 56% yield from this mixture by aromatisation and removal of the protective group, without the formation of the ketone (**17**).

The reaction of ene-1,5-diones with ammonia sources is the most useful of the recently reported methods for pyridine synthesis; however, the problem of low yields is often encountered in the preparation of annelated pyridines by this method.[12] In the course of the D-homoestrone synthesis described above, we found that the pyridine derivative (**21**) was one of the main products (52%), together with (**15**) (20%), when



Scheme 3. *Reagents:* i, Li–NH_3, then 3-phenylthiobut-3-en-2-one; ii, toluene-*p*-sulphonic acid; iii, *m*-chloroperbenzoic acid, then boiling benzene



cyclisation of the lithium enolate of compound (**14**) with 3-phenylthiobut-3-en-2-one was carried out in the presence of ammonia. The structures of (**21**) and its derivative (**22**) were

* The structures of these minor by-products, (**5**) and (**17**), were assigned on the basis of their i.r. and n.m.r. spectra, they have not been investigated further.

determined unambiguously. The analogous reaction of cyclohex-2-en-1-one with 3-phenylthiobut-3-en-2-one gave the tetrahydroquinoline (**23**) in 41% yield. Although the optimum conditions have not been established, this result shows a possible use for 3-phenylthiobut-3-en-2-one for pyridine annelation.

Experimental

M.p.s were measured with a Yanagimoto micro melting point apparatus and are uncorrected. I.r. spectra were recorded for Nujol mulls (solids) or liquid films with a Hitachi 215 spectrophotometer. ^{1}H N.m.r. spectra were obtained for solutions in $CDCl_3$ unless otherwise stated, on a JEOL PMX-60 instrument, and chemical shifts are reported in p.p.m. on the δ scale from internal Me_4Si. Mass spectra were taken with a Hitachi RMU-6D mass spectrometer at 70 eV. Microanalyses were determined on a Yanagimoto CHN-Corder. G.l.c. analyses were performed on a KOR-70 instrument equipped with f.i.d. and on a G-80 instrument with a thermal conductivity detector using a 2 m × 3 mm i.d. column of 10% OV-17 and 10% SE-30 on Chromosorb W. Column chromatography was carried out on Wakogel C-300 (silica gel). Ether refers to diethyl ether.

8a-*Hydroxy*-5α-*isopropyl*-8-*methyl*-3-*phenylthioperhydronaphthalen*-2-*one* (**2**).—Carvomenthone (**1**) (12.0 g, 78 mmol), prepared from l-carvone by catalytic hydrogenation,[3] was added to a stirred solution of lithium di-isopropylamide (86 mmol) in dry tetrahydrofuran (THF) (140 ml) at −78 °C under N_2, and stirring was continued for 2 h. 3-Phenylthiobut-3-en-2-one (13.9 g, 78 mmol) in dry THF (80 ml) was added dropwise to the mixture, and the resulting solution was stirred for 2 h at −78 °C, for 6 h at room temperature, and for 2 h at 40 °C. After addition of 10% hydrochloric acid (20 ml), the mixture was extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give a yellow oil (26.9 g). The oily residue (10 g) was chromatographed on silica gel (benzene–ether, 1:1) to afford the *ketol* (**2**) as a colourless solid (8.48 g, 88%), m.p. 157—159 °C (benzene–hexane); $\nu_{max.}$ 3 450, 1 710 cm^{-1}; δ[$(CD_3)_2SO$] 0.90—1.07 (m, 9 H), 1.07—3.10 (m, 12 H), 3.33 (s, 0.7 H, OH), 3.83 (br, 1 H), 4.20 (s, 0.3 H, OH), and 7.13—7.83 (m, 5 H) (Found: C, 72.5; H, 8.4. $C_{20}H_{28}O_2S$ requires C, 72.26; H, 8.49%).

3,8-*Dimethyl*-5α-*isopropyl*-4,4a,5,6,7,8-*hexahydronaphthalen*-2(3H)-*one* (**5**).—The ketol (**2**) (407 mg, 1.23 mmol) in dry THF (5 ml) was added at 0 °C under N_2 to a suspension of sodium hydride (32.5 g, 1.35 mmol), previously washed with ether, in dry THF (5 ml), and stirring was continued until the evolution of H_2 had ceased. Lithium di-isopropylamide (1.35 mmol) in dry THF (5 ml) was added at 0 °C and the mixture was stirred for an additional 1 h, then treated with methyl iodide (200 mg, 1.41 mmol), stirred for 4 h at 0 °C, and neutralised with 10% hydrochloric acid. The organic layer was extracted with ether, dried ($MgSO_4$), and evaporated under reduced pressure. The crude mixture was separated by preparative t.l.c. (on SiO_2, benzene) to give 7-hydroxycalamenene (**4**) (110 mg, 41%), R_F 0.27, and the enone (**5**) as a liquid (100 mg, 37%), R_F 0.15, $\nu_{max.}$ 1 675, 1 620 cm^{-1}; δ 0.56—2.73 (m, 23 H), 5.70—6.00 (m, 1 H).

5α-*Isopropyl*-8-*methyl*-3-*phenylthio*-4,4a,5,6,7,8-*naphthalen*-2(3H)-*one* (**6**).—The ketol (**2**) (500 mg, 1.51 mmol) was dissolved in benzene (200 ml) and treated with activated alumina (50 g; 300 mesh) at reflux temperature for 10 h. The mixture was filtered and concentrated to give the enone (**6**) as a liquid (472 mg, 100%), $\nu_{max.}$ 1 670, 1 610 cm^{-1}; δ 0.67—2.83 (m, 19 H), 3.67—4.10 (m, 1 H), 5.77—6.00 (m, 1 H), and 7.03—7.60 (m, 5 H).

3,8-*Dimethyl*-5α-*isopropyl*-3-*phenylthio*-4,4a,5,6,7,8-*hexahydronaphthalen*-2(3H)-*one* (**8**).—The enone (**6**) (0.94 g, 3.0 mmol) in dry THF (10 ml) was added at −78 °C to a solution of lithium di-isopropylamide (3.3 mmol) and hexamethyl phosphoramide (HMPA) (0.59 g, 3.3 mmol) in dry THF (15 ml) under N_2, and stirred for 1 h at −78 °C. To the mixture was added methyl iodide (0.47 g, 3.3 mmol) and stirring was continued for 1 h at −78 °C and then for 1 h at room temperature. The mixture was poured into saturated aqueous ammonium chloride, extracted with ether, dried ($MgSO_4$), and concentrated. The crude mixture was chromatographed on silica gel (benzene) to afford the naphthalenone (**8**) as a liquid (0.96 g, 98%), $\nu_{max.}$ 1 670, 1 620 cm^{-1}; δ 0.70—2.80 (m, 19 H), 1.32 (s, 3 H), 5.83 (br, 1 H), and 7.03—7.67 (m, 5 H).

7-*Hydroxycalamenene* (**4**).—The naphthalenone (**8**) (656 mg, 2.0 mmol) in benzene (50 ml) was treated with toluene-*p*-sulphonic acid monohydrate (95 mg, 0.5 mmol) at reflux temperature for 4 h. After neutralisation with sodium hydrogen carbonate, the mixture was extracted with benzene, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography on silica gel (benzene) to give the *calamenene* (**4**) as a colourless oil (435 mg, 100%), $\nu_{max.}$ 3 370, 1 615, and 1 585 cm^{-1}; δ 0.71, 0.76, 0.98, 1.00 (four d, *J* 6.5, 6.5, 7.0, 7.0 Hz, total 6 H), 1.21 (d, *J* 7.0 Hz, 3 H), 1.38—2.08 (m, 5 H), 2.20 (s, 3 H), 2.32—3.00 (m, 2 H), 4.78 (br, 1 H, OH), 6.56 (br, s, 0.33 H), 6.63 (br s, 0.67 H), and 6.92 (br s, 1 H); *m/z* 218 (M^+) (Found: C, 82.6; H, 9.9. $C_{15}H_{22}O$ requires C, 82.51; H, 10.16%).

5,5,8aβ-*Trimethyl*-2-(3-*oxo*-2-*phenylthiobutyl*)-4aα-*perhydronaphthalen*-1-*one* (**10**).—The naphthalenone (**9**)[9] (4.30 g, 22.2 mmol) in dry THF (20 ml) was added at −78 °C to a solution of lithium di-isopropylamide (24.4 mmol) in dry THF (50 ml) with stirring under N_2. After being stirred for 2 h at −78 °C, 3-phenylthiobut-3-en-2-one (3.95 g, 22.2 mmol) in dry THF (50 ml) was added to the mixture. The reaction mixture was stirred for 1 h at −78 °C, for 4 h at room temperature, and for 2 h at 40 °C, then neutralised with 10% hydrochloric acid, extracted with ether, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed on silica gel (benzene) to give the diketone (**10**) as an oil (5.89 g, 71%), $\nu_{max.}$ 1 705, 1 585 cm^{-1}; δ 0.73—2.17 (m, with s at δ 0.77, 0.87, 0.93, 1.10, 1.23, total 23 H), 2.20 and 2.27 (two s, 3 H), 3.70—4.07 (m, 1 H), 7.10—7.60 (m, 5 H).

1,1,4aβ-*Trimethyl*-7-*phenylthio*-1,2,3,4,4a,8,8a,9,10,10a-*decahydro*-10aα-*phenanthren*-6(7H)-*one* (**11**).—The diketone (**10**) (5.0 g, 13.4 mmol) was added to a 3M ethanolic solution of potassium hydroxide (6.7 ml) and stirred at room temperature for 2.5 h. The mixture was neutralised with 10% hydrochloric acid, extracted with ether, dried ($MgSO_4$), concentrated, and chromatographed on silica gel (benzene–ether, 1:1) to yield the enone (**11**) as an oil (3.94 g, 82%), $\nu_{max.}$ 1 670, 1 600 cm^{-1}; δ 0.88 (s, 6 H), 1.00—2.53 (m, with s at δ 2.17, 17 H), 3.60—3.90 (m, 1 H), 5.73—6.20 (m, 1 H), and 7.13—7.67 (m, 5 H).

1,1,4aβ-*Trimethyl*-1,2,3,4,4a,9,10,10a-*octahydro*-10aα-*phenanthren*-6-*ol* (**12**).—A solution of the enone (**11**) (1.0 g, 2.8 mmol) and toluene-*p*-sulphonic acid monohydrate (114 mg, 0.6 mmol) in benzene (50 ml) was refluxed for 2 h. The mixture was cooled, washed with aqueous sodium hydrogen carbonate, extracted with benzene, dried ($MgSO_4$), and concentrated. The reaction mixture was separated by column chromatography on alumina (benzene–ethanol, 95 : 5) to give the *phenanthrol* (**12**) as a solid (0.62 g, 91%), m.p. 110—111 °C (hexane); $\nu_{max.}$ 3 300, 1 610, and 1 585 cm^{-1}; δ 0.96 (s, 6 H), 1.17 (s, 3 H), 1.23—2.46 (m, 9 H), 2.60—3.00 (m, 2 H), 5.23 (br, 1 H, OH), and 6.40—6.97 (m, 3 H); *m/z* 244 (M^+) (Found: C, 83.5; H, 10.0. $C_{17}H_{24}O$ requires C, 83.55; H, 9.90%).

1,1-*Ethylenedioxy*-6a-*hydroxy*-12aβ-*methyl*-9-*phenylthio*-4aα,4bβ,10bα-*perhydrochrysen*-8-*one* (**15**).—A solution of the phenanthrenone (**14**) (2.58 g, 9.3 mmol) and t-butyl alcohol (0.85 ml) in dry THF (40 ml) was added dropwise to dry liquid ammonia (500 ml) containing lithium (0.19 g, 27.5 mmol) at −78 °C under argon, and stirring was continued for an additional 30 min. The mixture was treated with isoprene to consume the excess of lithium, allowed to stand at room temperature, and then evaporated under reduced pressure to dryness. The residual powder was dissolved in dry THF (50 ml) and cooled again to −78 °C. Then 3-phenylthiobut-3-en-2-one (2.12 g, 11.9 mmol) in dry THF (30 ml) was added to the solution, which was stirred for 10 min at −78 °C, for 30 min at room temperature, and for 2.5 h at 40 °C. After addition of aqueous ammonium chloride, the organic layer was extracted with ether, dried ($MgSO_4$), and concentrated. Separation by column chromatography on silica gel (benzene–ether, 3:1) afforded the ketol (**15**) as a white solid (3.74 g, 88%), m.p. 202—203 °C (benzene); $\nu_{max.}$(KBr) 3 340, 1 700 cm^{-1}; δ[$(CD_3)_2SO$] 0.92 (br s, 3 H), 1.05—1.90 (m, 20 H), 1.95—2.05 (m, 2 H), 3.50—4.10 (m, 5 H), 4.37 (br, 1 H, OH), and 7.00—7.50 (m, 5 H).

Aromatisation of the Ketol (**15**) *by Treatment with Acid.*—A solution of the ketol (**15**) (0.74 g, 1.6 mmol) and toluene-*p*-sulphonic acid monohydrate (45 mg, 0.2 mmol) in dioxane (10 ml) containing water (2 ml) was refluxed for 4 h. After being cooled, the mixture was extracted with ether, washed with aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$), and concentrated to give a residue (0.74 g). Separation by column chromatography on silica gel (benzene, benzene–ether 3:1) afforded three solid compounds. The first product was 3,4,4a,4b,5,6,10b,11,12,12a-decahydro-12aβ-methyl-8-phenylthio-4aα,4bβ,10bα-chrysen-1(2*H*)-one (**17**) (0.11 g, 18%), m.p. 196—198 °C (benzene); $\nu_{max.}$ 1 700 cm^{-1}; δ 1.05 (s, 3 H), 1.23—2.53 (m, 17 H), and 6.90—7.70 (m, 8 H).

The second product was D-homoestrone (**16**) (0.23 g, 50%), m.p. 220—222 °C (benzene–ethanol) (lit.,[6] 220—223 °C); $\nu_{max.}$ 3 350, 1 695 cm^{-1}; δ 1.12 (s, 3 H), 1.24—2.95 (m, 17 H), 4.62 (br, 1 H, OH), 6.40—6.75 (m, 2 H), and 7.01—7.15 (m, 1 H) (Found: M^+, 284.1775. $C_{19}H_{24}O_2$ requires *M*, 284.1777).

The third product was 6a-hydroxy-12aβ-methyl-9-phenylthio-4aα,4bβ,10bα-perhydrochrysene-1,8-dione (**18**) (0.12 g, 18%), m.p. 195—197 °C (benzene–ethanol); $\nu_{max.}$ 3 450, 1 700 cm^{-1}; δ 1.13 (s, 3 H), 1.25—2.50 (m, 22 H), 3.14—3.38 (br, 1 H, OH), 3.71—3.96 (m, 1 H), and 7.16—7.43 (m, 5 H) (Found: M^+, 412.2084. $C_{25}H_{32}O_3S$ requires *M*, 412.2070).

Aromatisation of the Ketol (**15**) *by Oxidative Elimination.*—To a cooled solution of (**15**) (0.35 g, 0.77 mmol) in CH_2Cl_2 (30 ml) was added *m*-chloroperbenzoic acid (80%, 0.19 g, 0.88 mmol) in CH_2Cl_2 (10 ml). After being stirred at room temperature for 2 h, the mixture was treated with 10% aqueous sodium sulphite, extracted with CH_2Cl_2, washed with 5% aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated to give a residue (0.36 g). The crude residue was dissolved in benzene (25 ml) and refluxed for 5 h in the presence of calcium carbonate (0.10 g). The mixture was filtered and evaporated under reduced pressure to afford a viscous oil, which was solidified by the addition of ether. The solid mixture (0.25 g) was composed of (**19**), (**20**), and (**15**) in a ratio of 1.8:1:1 (44, 26, and 19% yields, respectively), determined by h.p.l.c.

1,1-*Ethylenedioxy*-6a-*hydroxy*-12aβ-*methyl*-1,2,3,4,4a,4b,5,6,6a,10a,10b,11,12,12a-*tetradecahydro*-4aα,4bβ,10bα-*chrysen*-8(7H)-*one* (**19**) was isolated as a solid, m.p. 195—197 °C (precipitated from Me_2SO–acetone); δ 1.01 (br s, 3 H), 1.15—1.80 (m, 17 H), 2.00—2.50 (m, 3 H), 3.90 (br, 4 H), 4.25 (br, 1H, OH), 5.77—6.03 (m, 1 H), and 6.86—7.10 (m, 1 H) (Found: M^+, 346.2117. $C_{21}H_{30}O_4$ requires *M*, 346.2142).

The crude solid mixture (50 mg) in benzene was treated with toluene-*p*-sulphonic acid monohydrate (5 mg, 0.03 mmol) at reflux temperature for 2 h. After being cooled, the mixture was diluted with ether, washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated. Separation by h.p.l.c. afforded D-homoestrone (**16**) (20 mg, 56%), the dione (**18**) (10 mg), and 6a-hydroxy-12aβ-methyl-3,4,4a,4b,5,6,6a,10a,10b,11,12,12a-dodecahydro-4aα,4bβ,10bα-chrysene-1,8-(2*H*, 7*H*)-dione (10 mg, 26%), m.p. 199—201 °C; δ 1.16 (s, 3 H), 1.30—2.50 (m, 20 H), 4.25 (br, 1 H, OH), 5.77—6.03 (m, 1 H), and 6.86—7.10 (m, 1 H).

1,1-*Ethylenedioxy*-8,12aβ-*dimethyl*-9-*phenylthio*-1,2,3,4,4a,4b,5,6,10b,11,12,12a-*dodecahydro*-4aα,4bβ,10bα-7-*azachrysene* (**21**).—A solution of the phenanthrenone (**14**) (9.70 g, 35.1 mmol) and t-butyl alcohol (3.1 ml) in dry THF (150 ml) was added at −78 °C to dry liquid ammonia (1 l) containing lithium (0.70 g, 101 mmol) under argon. After 30 min, the excess of lithium was quenched with isoprene and then a large portion of the ammonia was evaporated on standing at room temperature. To the residual solution was added 3-phenylthiobut-3-en-2-one (7.85 g, 44.1 mmol) in dry THF (90 ml) at −78 °C and stirring was continued at −78 °C for 1 h, at room temperature for 3 h, and at 40 °C for 2.5 h. The mixture was poured into aqueous ammonium chloride, extracted with ether, dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (benzene) to yield two solid compounds. The first product was the *azachrysene* (**21**) (7.99 g, 52%), m.p. 127—128 °C (benzene); δ 0.99 (s, 3 H), 1.20—2.40 (m, 15 H), 2.54 (s, 3 H), 2.80—3.20 (m, 2 H), 3.92 (br, 4 H), 7.00—7.30 (m, 5 H), and 7.54 (br, 1 H); *m/z* 435 (M^+) (Found: C, 74.3; H, 7.45; N, 3.2. $C_{27}H_{33}NO_2S$ requires C, 74.44; H, 7.64; N, 3.21%).

The second product was the ketol (**15**) (3.17 g, 20%).

8,12aβ-*Dimethyl*-9-*phenylthio*-3,4,4a,4b,5,6,10b,11,12,12a,-*decahydro*-4aα,4bβ,10bα-7-*azachrysen*-1(2H)-*one* (**22**).—A solution of the acetal (**21**) (0.13 g, 0.3 mmol), toluene-*p*-sulphonic acid monohydrate (11 mg, 0.06 mmol), and water (2 ml) in dioxane (5 ml) was refluxed for 6 h. The mixture was extracted with ether, washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated. The crude oil was purified by h.p.l.c. to give the *azachrysenone* (**23**) as a colourless solid (0.10 g, 86%), m.p. 49—51 °C (benzene); $\nu_{max.}$ 1 715 cm^{-1}; δ 1.11 (s, 3 H), 1.40—2.40 (m, 15 H), 2.54 (s, 3 H), 2.80—3.20 (m, 2 H), 7.00—7.30 (m, 5 H), and 7.53 (br, 1 H) (Found: C, 76.75; H, 7.2; N, 3.3; M^+, 391.1980. $C_{25}H_{29}NOS$ requires C, 76.68; H, 7.46; N, 3.58%; *M*, 391.1968).

2-*Methyl*-3-*phenylthio*-5,6,7,8-*tetrahydroquinoline* (**23**).—Cyclohex-2-en-1-one (1.15 g, 12.0 mmol) was treated with 3-phenylthiobut-3-en-2-one (2.33 g, 13.1 mmol) as described in the synthesis of (**21**) to afford the *quinoline* (**23**) as a liquid (1.26 g, 41%), b.p. 245—250 °C at 0.2 mmHg; δ 1.70—2.25 (m, 6 H), 2.50—3.22 (m, 5 H), and 7.08—7.50 (m, 6 H) (Found: C, 74.9; H, 7.1; N, 5.6; M^+, 255.1061. $C_{16}H_{17}NS$ requires C, 75.27; H, 6.71; N, 5.49; *M*, 255.1080).

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