Tetracyclic Triterpene Synthesis. Part 1. Stereospecific Conversion of 6-Methoxy-1-tetralone into 7-Methoxy-*trans*-3a,9b-dimethyl-1,3,3a,4,5,-9b-hexahydrobenz[*e*]inden-2-one

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Both *cis*- and *trans*-3a,9b-dimethyl derivatives of 7-methoxy-1,3,3a,4,5,9b-hexahydrobenz[*e*]inden-2-one have been synthesised stereospecifically from 6-methoxy-1-tetralone. The *trans*-compound is a possible intermediate for the synthesis of triterpenes of the lanostane–cycloartane group.

THE present work [1] † stemmed from the hope that 6-methoxy-1-tetralone (1), a compound well known in the field of steroid synthesis, might serve as a starting point for the synthesis of terpenes of the lanostane–cycloartane group. We describe here the stereospecific conversion of this compound into 7-methoxy-*trans*-3a,9b-dimethyl-1,3,3a,4,5,9b-hexahydrobenz[*e*]inden-2-one (30), a compound of B–C–*trans*–D type [2] possessing a carbonyl group suitably positioned for the introduction of a side chain at the future C-17 position.

The tetralone (1) had already been transformed into compound (12) by two routes.[3,4] In one,[3] 6-methoxy-1-tetralone (1) was alkylated with 2,3-dichloropropene; the monoalkyl ketone (2) was further alkylated to produce (3). Hydrolysis of (3) then gave (11) which on cyclisation formed the unsaturated ketone (12). Our attempts to achieve monoalkylation [5,6] of the tetralone [(1) ⟶ (2) as well as (1) ⟶ (9)] gave low yields. Also, methylation of the hydroxymethylene ketone (4) as well as the procedure [6] (4) ⟶ (5) ⟶ (9) were troublesome partly owing to the pronounced tendency of compound (4) to revert to the starting ketone (1). We therefore prepared the methyltetralone (9) by the route [4,7] (1) ⟶ (6) ⟶ (7) ⟶ (8) ⟶ (9), this then being followed by the sequence (9) ⟶ (10) ⟶ (11) ⟶ (12). As expected the glyoxylate (6) existed entirely in the enolic form, but for the β-oxo-ester (7)

† A different numbering system was applied in ref. 1. *E.g.* the title indenone was named 3-methoxy-*trans*-6a,9a-dimethylhexahydrobenz[*e*]inden-8-one in ref. 1.

[1] Preliminary communication, R. A. Packer and J. S. Whitehurst, *J.C.S. Chem. Comm.*, 1975, 757.

[2] L. Velluz, J. Valls, and G. Nominé, *Angew. Chem. Internat. Edn.*, 1965, **4**, 181.

[3] P. T. Lansbury, E. J. Nienhouse, D. J. Scharf, and F. R. Hilfiker, *J. Amer. Chem. Soc.*, 1970, **92**, 5649.

[4] R. E. Juday, B. Bukwa, K. Kaiser, and G. Webb, *J. Medicin. Chem.*, 1970, **13**, 314.

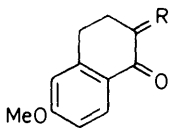
[5] P. J. Hattersley, I. M. Lockhart, and M. Wright, *J. Chem. Soc.* (C), 1969, 217.

[6] A. P. G. Kieboom and H. van Bekkum, *Synthesis*, 1970, 476.

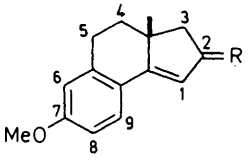
[7] W. E. Bachmann and D. G. Thomas, *J. Amer. Chem. Soc.*, 1942, **64**, 94.

the n.m.r. spectrum clearly showed that the keto form was the one preferentially adopted.

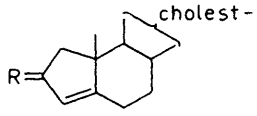
It has been reported [8] that A-norcholest-3(5)-en-2-one (15) undergoes reduction with lithium aluminium hydride to yield stereoselectively the allylic alcohol (16).



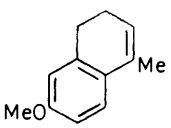
(1) R = H_2
(2) R = H, $CH_2CCl{:}CH_2$
(3) R = Me, $CH_2CCl{:}CH_2$
(4) R = CHOH
(5) R = CHOBz
(6) R = H, $COCO_2Me$
(7) R = H, CO_2Me
(8) R = Me, CO_2Me
(9) R = H, Me
(10) R = Me, $CH_2C{:}CH$
(11) R = Me, CH_2COMe



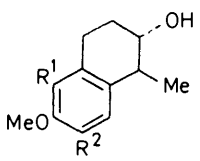
(12) R = O
(13) R = β-H, α-OH
(14) R = β-H, α-OEt



(15) R = O
(16) R = β-H, α-OH



(17)



(18) $R^1 = R^2 = H$
(19) R^1 = Me, R^2 = H
(20) $R^1 = R^2$ = Cl

By analogy we hoped that the ketone (12) would yield the alcohol (13). This reduction had in fact been reported [3] as giving a diastereoisomeric mixture of alcohols but in our experience only one compound, presumably (13), was obtained. It was intended to employ the hydroxy-group in this compound to introduce stereospecifically a cyclopropane bridge [9] at the double bond by a Simmons–Smith reaction and then by a subsequent metal–ammonia reduction of the derived ketone to generate the desired α-oriented methyl group. Addition of the allylic alcohol (13) to the zinc–methylene iodide reagent [10] in diethyl ether gave an immediate blue solution. The colour did not develop, however, if the reaction mixture contained 1,2-dimethoxyethane, which is known to complex with zinc iodide.[11] All the allylic alcohol had been consumed after 90 min; nevertheless cyclopropanation was not achieved. The u.v. absorption of the product showed that little, if any, attack on the double bond had occurred. One pure compound was obtained which evidently, from its spectral properties, was the ethyl ether (14). The corresponding carbon–carbon double bond in the ketone (12) was resistant to attack by lithium dimethylcuprate as well as by dimethylsulphoxonium methylide.

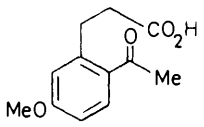
Attention was therefore directed to the preparation of the isomeric compounds (26) and (27). 6-Methoxy-1-tetralone (1) by reaction with methylmagnesium iodide gave 7-methoxy-4-methyl-1,2-dihydronaphthalene (17). Treatment of this compound with perbenzoic acid followed by hydrochloric acid gave the tetralone [12] (22), but the procedure was capricious and the yield mediocre (50%); oxidation with perphthalic acid [13] was, in our hands, even less satisfactory (16%). A better route was found which involved hydroboration followed by alkaline hydrogen peroxide oxidation. The product (18) on Pfitzner–Moffatt oxidation [14] gave the tetralone (22) (80%), the overall yield from 6-methoxy-1-tetralone being 61%.

Other oxidations of the alcohol (18) proceeded differently. Treatment with chromium trioxide in aqueous acetone produced almost quantitatively the oxo-acid (21). However, even after a 3 day contact with chromium trioxide in aqueous pyridine *ca.* 56% of the original material (18) was recovered in pure form. Oxidation of the similarly constituted tetralol (19) with chromium trioxide in either acetic acid or pyridine is reported to produce [15] the corresponding methoxynaphthol. Interestingly, the pyridine–chlorine complex [16] reacted with (18) to give the 5,7-dichloro-derivative (20); thorough examination of the product failed to reveal any carbonyl compound. Oxidation with the dimethyl sulphide–*N*-chlorosuccinimide complex [17] did give the tetralone (22) (30% yield); attempted oxidation of the tetralol under standard Oppenauer conditions was unsuccessful.

Alkylation of 6-methoxy-1-methyl-2-tetralone (22) with 3-bromopropyne gave compound (23) which after hydration [mercury(II) acetate in acetic acid–formic acid] gave the diketone (24). Hot methanolic 2% potassium hydroxide under nitrogen cyclised this to the unsaturated ketone (26). Reduction of this compound with aluminium hydride [18] in tetrahydrofuran furnished, stereospecifically, the allylic alcohol (27). Unlike its isomer, this compound underwent the Simmons–Smith

[8] R. Heckendon and Ch. Tamm, Abstracts of 2nd Internat. Conference on Hormonal Steroids, Milan, 1966, p. 227; *Helv. Chim. Acta*, 1967, **50**, 1964.
[9] S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, 1961. **83**, 3235; W. G. Dauben, G. J. Fonken, and D. S. Noyce, *ibid.*, 1956, **78**, 2579; W. G. Dauben and G. H. Berezin, *ibid.*, 1963, **85**, 468; W. G. Dauben and A. C. Ashcraft, *ibid.*, p. 3673.
[10] J. M. Denis, C. Girard, and J.-M. Conia, *Synthesis*, 1972, 549.
[11] H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Amer. Chem. Soc.*, 1964, **86**, 1347.
[12] F. H. Howell and D. A. H. Taylor, *J. Chem. Soc.*, 1958, 1248.
[13] G. Stork, A. Meisels, and J. E. Davies, *J. Amer. Chem. Soc.*, 1963, **85**, 3419.
[14] K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, 1965, **87**, 5661, 5670.
[15] G. Traverso, A. A. Bothner-By, G. P. Pollini, and A. Barco, *Gazzetta*, 1966, **96**, 1186.
[16] J. Wicha and A. Zarecki, *Tetrahedron Letters*, 1974, **35**, 3059.
[17] E. J. Corey and C. U. Kim, *J. Amer. Chem. Soc.*, 1972, **94**, 7586.
[18] H. C. Brown and H. M. Hess, *J. Org. Chem.*, 1969, **34**, 2206; E. Wiberg, *Angew. Chem.*, 1951, **63**, 485; H. C. Brown and N. M. Yoon, *J. Amer. Chem. Soc.*, 1966, **88**, 1464.

reaction and gave the cyclopropane alcohol (28) in which it was expected [9] that the cyclopropane ring and the



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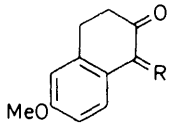
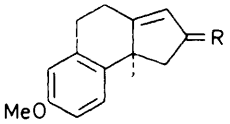
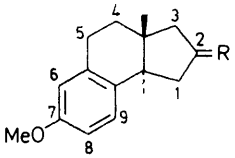


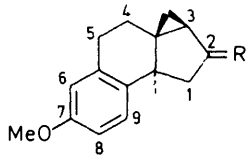
(22) R = H, Me
(23) R = Me, $CH_2C{:}CH$
(24) R = Me, CH_2COMe
(25) R = Me, $CH_2CCl{:}CH_2$



(26) R = O
(27) R = α-H, β-OH



(30) R = O
(31) R = SCH_2CH_2S
(32) R = H_2



(28) R = β-OH, α-H
(29) R = O

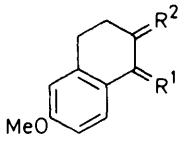
hydroxy-group would be *cis*-oriented. The corresponding ketone (29) underwent reduction by lithium–ammonia to yield the tricyclic ketone (30).

A detailed n.m.r. study of the ketone (30) did not provide sufficient evidence to satisfy us that it was the desired *trans*-compound. It was felt that if the ketone of opposite configuration (40) were prepared spectral comparison might lead unequivocally to assignment of its configuration. For the preparations of the ketone (40), 6-methoxy-2-methyl-1-tetralone (9) was alkylated with 2,3-dichloropropene. The product (3) was treated with methylmagnesium iodide. The tertiary alcohol (33) first formed lost water during work-up to give the olefin (34). Boiling formic acid converted this compound into a mixture of three products, one of which was separated easily from the other two by p.l.c. It was clearly a ketone isomeric with the ketone (30). The remaining two compounds were separated from each other by preparative g.l.c. and proved to be the chloro-olefins (43) and (44). These chloro-olefins, either separately or together, were converted into the ketone (40) by dissolution in cold concentrated sulphuric acid.

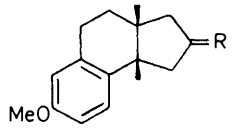
The i.r. carbonyl absorption for both ketones both occurred at 1 738 cm^{-1}. The configurations of these compounds were first deduced from n.m.r. spectroscopy (following paper) and subsequently were established chemically. In 1974, Wirthlin, Wehrli, and Jeger [19] published the results of a degradative study of dehydroabietic acid which, *inter alia*, led to the two optically active ketones (45) and (46). Through the kindness of these authors we secured a small amount of the *cis*-ketone (46). Transformation of this into its ethylene thioacetal (47) followed by desulphurisation (Raney nickel) produced the indene (48). The racemic ketones (30) and (40) likewise were transformed into their corresponding thioacetals (31) and (41) and thence into the racemic compounds (32) and (42). The n.m.r. spectrum of compound (42) was identical with that of compound (48); therefore, ketone (30) was the desired *trans*-compound.

The formic acid cyclisation [(34) ⟶ (40)] was the method of choice. Hot trifluoroacetic acid carried the conversion only to the chloro-olefin stage (yield *ca.* 40%); at room temperature there appeared to be no reaction. Attempted cyclisation using either concentrated sulphuric acid or phosphorus pentoxide in methanesulphonic acid [20] produced complex mixtures.

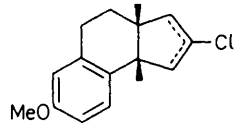
The possibility of preparing the ketone (40) by cyclisation of the acetylene (36) with acid was also explored. The unsaturated linkages in this molecule could conceivably give rise to cyclic products (five- or six-membered) by way of ' bent ' vinylium ions, *e.g.* (49). The



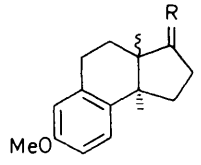
(33) R^1 = Me, OH, R^2 = Me, $CH_2CCl{:}CH_2$
(34) R^1 = CH_2, R^2 = Me, $CH_2CCl{:}CH_2$
(35) R^1 = Me, OH, R^2 = Me, $CH_2C{:}CH$
(36) R^1 = CH_2, R^2 = Me, $CH_2C{:}CH$
(37) R^1 = Me, + charge, R^2 = Me, $CH_2C{:}CH$
(38) R^1 = H, Me, R^2 = Me, $CH_2C{:}CH$
(39) R^1 = Me, $CH_2CCl{:}CH_2$, R^2 = Me, OH



(40) R = O
(41) R = SCH_2CH_2S
(42) R = H



(43) Δ^2
(44) Δ^1



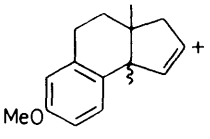
(45) *trans*, R = O
(46) *cis*, R = O
(47) *cis*, R = SCH_2CH_2S
(48) *cis*, R = H_2

intermediacy of such species in not in doubt. Thus the acetylene (50) on acetolysis gives six-membered as well

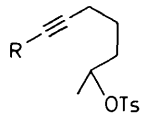
[19] T. Wirthlin, H. Wehrli, and O. Jeger, *Helv. Chim. Acta*, 1974, **57**, 351.

[20] P. E. Eaton, G. R. Carlson, and J. T. Lee, *J. Org. Chem.*, 1973, **38**, 4051.

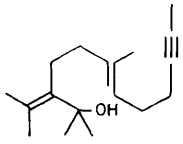
as five-membered ring compounds; the lower homologue (51) gives acyclic and six-membered ring products but no five-membered compound.[21] Also, cyclisation of the alcohol (52) leads to *trans*-decalin or *trans*-perhydroindane structures, depending on conditions.[22] Compound (36) was readily made by the action of a methyl Grignard reagent on the ketone (10), the intermediary alcohol (35) undergoing dehydration exactly as for the analogue (33). This compound could not be induced to react with trifluoroacetic acid. However treatment with cold formic acid gave an immediate green solution, which perhaps contained the ion (37); the solution on heating



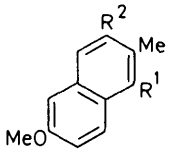
(49)



(50) R = Me
(51) R = H



(52)



(53) R^1 = Me, R^2 = $CH_2CCl{:}CH_2$
(54) R^1 = $CH_2CCl{:}CH_2$, R^2 = Me

gave as major product (60%) compound (38) as a diastereoisomeric mixture. A close analogy for this reduction seems to be the triphenylmethanol–triphenylmethane conversion.[23] No products of cyclisation were detected.

Methylmagnesium iodide reacted stereoselectively with compound (25), obtained by alkylation of the tetralone (22) with 2,3-dichloropropene, noticeably more slowly than with the isomeric ketone (3), and gave a single alcohol corresponding to formula (39). This compound on treatment with formic acid gave a mixture of products which did not include any of the compounds (30), (40), (43), and (44). The major component (*ca.* 40% of the mixture) was a naphthalene possessing methoxy, chloroallyl, and methyl substituents. The n.m.r. spectrum showed two methyl singlets at δ 2.54 and 2.42. N.m.r. evidence from other methylnaphthalenes [24] clearly indicates that the δ 2.42 signal corresponds to a β-methyl group (*i.e.* position 2- or 3-) and mechanistic considerations lead to two likely structures, (53) and (54). The n.m.r. spectrum showed, as the furthest downfield signal, a doublet (1H) due to H-8 (δ 7.92, *J* 10 Hz); representative values for the corresponding proton (δ value, compound number) in other compounds are 7.79 (1); 7.54 (34); 7.18 (25); 7.55 (12); and 6.99 (17). It seems unlikely that the low field doublet can be reconciled with the presence of a methyl group at C-1. However, the chlorine atom of a chloropropenyl group at C-1 (54) could approach H-8 and thus bring about the observed deshielding.

EXPERIMENTAL

U.v. absorption spectra refer to solutions in 95% ethanol. N.m.r. spectra were recorded for solutions in deuteriochloroform with tetramethylsilane as internal reference. T.l.c. was carried out using pre-coated silica gel F254 plates (Merck). Preparative layer chromatography (p.l.r.) was performed using 20 × 20 cm glass plates coated with 40 g of Kieselgel GF254 (Merck); each plate was heated to 100 °C for 2 h and then cooled before use. Products were located under u.v. light. G.l.c. was carried out using a Pye Argon instrument with a glass column (1.2 m × 6 mm) packed with 3% silicone OV1 on GasChrom Q (60—80 mesh) unless otherwise stated (column temperatures in the range 140—200 °C; argon flow rate normally 60 cm^3 min^{-1}). Petroleum refers to the fraction of b.p. 60—80 °C. Benzene and diethyl ether were dried by storage over sodium. Before use, bis-(2-methoxyethyl) ether (diglyme) and tetrahydrofuran were distilled from lithium aluminium hydride, t-butyl alcohol from sodium, and methanol from magnesium and iodine under dry nitrogen. Dimethyl sulphoxide was distilled from calcium hydride and stored over a 4 Å molecular sieve. Liquid ammonia was distilled from sodium.

Elemental analyses are available as Supplementary Publication No. SUP 22230 (3 pp.) *

2-[Hydroxy(methoxycarbonyl)methylene]-6-methoxy-1-tetralone [enol form of (6)] [7] had $\lambda_{max.}$ 351 nm (ε 14 000), $\nu_{max.}$ ($CHCl_3$) 3 450 and 1 738 cm^{-1}, δ 6.66 (2 H, m), 7.86 (1 H, d, *J* 8 Hz), 15.63br (1 H, exchanges with D_2O).

6-Methoxy-2-methoxycarbonyl-1-tetralone (7) [7] had $\lambda_{max.}$ 276 nm (ε 14 000), $\nu_{max.}$ ($CHCl_3$) 1 738 and 1 674 cm^{-1}, δ 6.65 (2 H, m), 7.85, (1 H, d, *J* 8 Hz), and 12.54 (v. weak, exchanges with D_2O).

6-Methoxy-2-methoxycarbonyl-2-methyl-1-tetralone (8) [7] had $\lambda_{max.}$ 277 nm (ε 17 300), $\nu_{max.}$ ($CHCl_3$) 1 731 and 1 673 cm^{-1}, δ 1.48 (3 H, s), 6.72 (2 H, m), and 8.01 (1 H, d, *J* 8 Hz).

6-Methoxy-2-methyl-1-tetralone [25] (9) was prepared from compound (8) (12 g) by heating with potassium hydroxide (40 g) in methanol (140 cm^3) for 2 h (yield 8.7 g); $\lambda_{max.}$ 273 nm (ε 14 200), $\nu_{max.}$ (film) 1 674 cm^{-1}, δ 1.17 (3 H, d, *J* 7 Hz), 6.66 (2 H, m), and 7.86 (1 H, d, *J* 8 Hz).

6-Methoxy-2-methyl-2-(prop-2-ynyl)-1-tetralone [4] (10) had $\lambda_{max.}$ 275 nm (ε 15 200), $\nu_{max.}$ (film) 3 315, 2 130, and 1 670 cm^{-1}, δ 1.16 (3 H, s), 2.01 (3 H, m, 3-H_2 and C≡CH), 6.58 (2 H, m), and 7.83 (1 H, d, *J* 8 Hz).

2-Acetonyl-2-methyl-6-methoxy-1-tetralone (11) had m.p.

* For details of Supplementary Publications see Notice to Author No. 7, *J.C.S. Perkin I*, 1976, Index issue.

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100° (lit.,[3] 97—98°; lit.,[4] b.p. 137° at 0.05 mmHg), $\lambda_{max.}$ 274 nm (ε 17 600), $\nu_{max.}$ ($CHCl_3$) 1 705 and 1 670 cm^{-1}, δ 1.20 (3 H, s), 2.10 (3 H, s), 6.69 (2 H, m), and 7.96 (1 H, d, *J* 8 Hz).

7-Methoxy-3a-methyl-3,3a,4,5-tetrahydrobenz[*e*]inden-2-one (12)[3,4] had $\lambda_{max.}$ 317 nm (ε 15 100), $\nu_{max.}$ ($CHCl_3$) 1 685 cm^{-1}, δ 1.21 (3 H, s), 6.12 (1 H, s, C=CH), 6.75 (2 H, m), and 7.55 (1 H, d, *J* 8 Hz).

7-*Methoxy*-3a-*methyl*-3,3a,4,5-*tetrahydro*-2H-*benz*[e]*inden*-2-*ol* (13) was prepared by addition of the ketone (12) (1 g) in ether (2 cm^3) to lithium aluminium hydride (42 mg) in ether (5 cm^3) and refluxing the mixture for 10 min. Work-up in the usual way gave a solid which crystallised from hexane in needles, m.p. 114 °C (74%); $\lambda_{max.}$ 267 nm (ε 16 700); $\nu_{max.}$ ($CHCl_3$) 3 600 and 3 440 cm^{-1} (free and bonded OH); δ 1.05 (3 H, s), 5.15 (1 H, t, *J* 7 Hz, H-2), 5.86 (1 H, s, C=CH), 6.75 (2 H, m), and 7.54 (1 H, d, *J* 9 Hz); *m/e* 230 ($C_{15}H_{18}O_2$, M^+).

Reaction of the Benz[e]*inden*-2-*ol* (13) *with the Simmons–Smith–Conia*[10,11] *Reagent*.—Freshly distilled methylene iodide[26] (265 mg) in ether (1 cm^3) was added dropwise to a stirred slurry of zinc–silver couple[10] (from 70 mg of zinc) in ether (2 cm^3) containing 1,2-dimethoxyethane (90 mg) at room temperature and stirring was continued for 1 h. The alcohol (13) in ether (1 cm^3) was added, the mixture refluxed for 1½ h, and then cooled to 0 °C. Pyridine (1 cm^3) in ether (2 cm^3) was then added and after filtration the solution was diluted with ether, and washed first with dilute hydrochloric acid and then with water. Drying ($MgSO_4$) and evaporation gave a pale yellow oil which turned blue unless it was immediately chromatographed [p.l.c. in ether–petroleum (1 : 1)]. *Compound* (14) recovered from the faster moving of the two bands had $\lambda_{max.}$ 267 nm (ε 10 100), $\nu_{max.}$ (film) 1 608 and 1 569 cm^{-1}, δ 1.25 (3 H, s), 1.21 (3 H, t, *J* 7.5 Hz), 3.58 (2 H, q, *J* 7.5 Hz), 6.06 (1 H, d, *J* 3 Hz, C=CH), 6.68—7.04 (2 H, m), and 7.56 (1 H, m), *m/e* 258 ($C_{17}H_{22}O_2$, M^+).

6-Methoxy-1-methyl-2-tetralone (22) was prepared from 7-methoxy-4-methyl-1,2-dihydronaphthalene (17) by oxidation with perphthalic acid[13] (yield 16%) or with perbenzoic acid[12] (yield 55%) as well as by the following method Compound (17) (23 g) in diglyme (20 cm^3) was added to a solution of sodium borohydride (2.15 g) in diglyme (50 cm^3). Boron trifluoride–diethyl ether complex (10.7 g) was added to the stirred solution at such a rate as to keep the temperature between 20 and 25 °C. Two hours after the addition, water (15 cm^3) was added dropwise. Aqueous sodium hydroxide (15 cm^3; 3M) was added (in one portion) followed by 30% hydrogen peroxide (15 cm^3, dropwise), the temperature being kept at *ca.* 40 °C. After 1 h the mixture was extracted with ether. Work-up gave 6-*methoxy*-1-*methyl*-*tetralin*-2-*ol* (18), m.p. 60—61° (from hexane) (21 g); $\lambda_{max.}$ 277 nm (ε 1 450), $\nu_{max.}$ ($CHCl_3$), 3 350 cm^{-1}, δ 1.28 (3 H, d, *J* 7 Hz), 6.64 (2 H, m), and 7.10 (1 H, d, *J* 7 Hz); *m/e* 192 ($C_{12}H_{16}O_2$, M^+).

Oxidation of the Tetralol (18).—(a) *Pfitzner–Moffat*.[14] To compound (18) (0.77 g) in benzene (6 cm^3), dimethyl sulphoxide (6 cm^3), pyridine (0.32 cm^3), and trifluoroacetic acid (0.16 cm^3) was added dicyclohexylcarbodi-imide (2.48 g), and the mixture was stirred for 12 h at room temperature under nitrogen. It was then treated with ether (50 cm^3) followed by oxalic acid (1.08 g) in methanol. After stirring for 1 h, water (100 cm^3) was added and the precipitated dicyclohexylurea removed. The organic layer was washed sequentially with aqueous sodium hydrogen carbonate and water and then dried and evaporated. 6-*Methoxy*-1-*methyl*-2-*tetralone* (22) was obtained as sole product (80%), b.p. 122° at 0.25 mmHg, $\lambda_{max.}$ 276 nm (ε 1 600), $\nu_{max.}$ (film) 1 710 cm^{-1}, δ 1.39 (3 H, d, *J* 7 Hz), 3.39 (1 H, q, *J* 7 Hz), and 6.90 (3 H, m, ArH), *m/e* 190 ($C_{12}H_{14}O_2$, M^+).

(b) *Wicha–Zarecki*.[16] Compound (18) (1 g) in chloroform (40 cm^3) containing pyridine (2 g) was treated with 0.82M-chlorine in carbon tetrachloride (10 cm^3). After 30 min air was blown through the solution, which was then washed with 5% hydrochloric acid (10 cm^3) and then water (10 cm^3). Work-up gave an oil which was chromatographed (3 : 7 ether–petroleum) on grade II neutral alumina. 5,7-*Dichloro*-6-*methoxy*-1-*methyltetralin*-2-*ol* (20) was obtained as an oil (870 mg), $\lambda_{max.}$ 276 nm (ε 1 425), $\nu_{max.}$ (film) 3 400 cm^{-1}, δ 1.25 (3 H, d, *J* 7 Hz), 2.81 (3 H, m, H-1 and 4-H_2), and 7.20 (1 H, s), *m/e* 260 ($C_{12}H_{14}O_2Cl_2$, M^+, 48%), 262 (32%), and 264 (6%). Thorough search of the chromatogram did not reveal any ketonic material.

(c) *Jones*.[27] To a stirred solution of compound (18) (2 g) in pure acetone (20 cm^3) at 0 °C was added chromic acid solution until an excess was detected (*ca.* 3 mol. equiv.). Work up gave 2-(2-*acetyl*-5-*methoxyphenyl*)*propionic acid* (21) (2.09 g), m.p. 108° (from hexane), $\lambda_{max.}$ 269 nm (ε 8 400), $\nu_{max.}$ ($CHCl_3$) 3 440br, 1 725, and 1 670 cm^{-1}, δ 2.54 (3 H, s), 2.67 (2 H, t, *J* 8 Hz), 3.20 (2 H, t, *J* 8 Hz), 3.82 (3 H, s), 6.90 (2 H, m), 7.89 (1 H, d, *J* 8 H), and 9.39br (1 H, s, CO_2H), *m/e* 222 ($C_{12}H_{14}O_4$, M^+).

Compound (18) when treated with *one* equiv. of chromic acid gave an 80% recovery of starting material.

6-*Methoxy*-1-*methyl*-1-(*prop*-2-*ynyl*)-2-*tetralone* (23).—To a stirred suspension of sodium hydride (0.76 g; freed from mineral oil by washing with petroleum) in diglyme (50 cm^3) at 45 °C under nitrogen was added dropwise during 30 min a solution of 3-bromopropyne (3.80 g) and 6-methoxy-1-methyl-2-tetralone (6.0 g) in diglyme (10 cm^3). The mixture was stirred for 15 h at 45 °C, cooled, treated with dilute hydrochloric acid, and then extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated. Chromatography (grade II neutral alumina; 5 : 95 ether–petroleum) followed by crystallisation from methanol gave *compound* (23) (4.07 g), m.p. 104—105°, $\lambda_{max.}$ 277 nm (ε 1 320), $\nu_{max.}$ ($CHCl_3$) 3 310 and 1 710 cm^{-1}, δ 1.40 (3 H, s), 1.79 (1 H, t, *J* 2 Hz, C≡CH), 2.62 (4 H, m, H-3 and side chain CH_2), 6.72 (2 H, m), and 7.27 (1 H, d, *J* 8 Hz), *m/e* 228 ($C_{15}H_{16}O_2$, M^+).

1-*Acetonyl*-6-*methoxy*-1-*methyl*-2-*tetralone* (24) was prepared from the acetylene (23) exactly as compound (11) was prepared[4] from compound (10) (yield 88%); m.p 70—71° (from methanol), $\lambda_{max.}$ 277 nm (ε 1 700), $\nu_{max.}$ ($CHCl_3$) 1 710 cm^{-1}, δ 1.29 (3 H, s), 1.82 (3 H, s), 2.55—3.45 (6 H, m, CH_2), and 6.60—7.06 (3 H, m), *m/e* 246 ($C_{15}H_{18}O_3$, M^+).

7-*Methoxy*-9b-*methyl*-1,4,5,9b-*tetrahydrobenz*[e]*inden*-2-*one* (26).—Compound (24) (2 g) was cyclised by refluxing overnight in methanol (50 cm^3) containing potassium hydroxide (1 g) under nitrogen. Chromatography (grade II neutral alumina; 1 : 4 ether–petroleum) gave compound (26) as a pale yellow *oil* (1.38 g), $\lambda_{max.}$ 226 nm (ε 19 000), $\nu_{max.}$ (film) 1 690 cm^{-1}, δ 1.46 (3 H, s), 5.85 (1 H, s, C=CH), and 6.45—7.25 (3 H, m), *m/e* 228 ($C_{15}H_{16}O_2$, M^+).

7-*Methoxy*-9b-*methyl*-1,2,3,4,5,9b-*hexahydro*-2H-*benz*[e]-

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inden-2-*ol* (27).—A solution of aluminium hydride [18] in tetrahydrofuran (1.6 cm^2; 1.03M) was added in one portion to a stirred solution of compound (26) (0.54 g) in tetrahydrofuran (5 cm^3) at 0 °C. After 5 min water and then ether were added; the ethereal extract was washed (5% HCl), then dried and evaporated. The resulting *oil* (27) (one component on g.l.c.) was preparatively chromatographed (3 : 1 ether–petroleum); yield 305 mg, $\lambda_{max.}$ 279 nm (ε 1 900), $\nu_{max.}$ ($CHCl_3$) 3 595 (free OH) and 3 450 cm^{-1} (bonded OH), δ 1.27 (3 H, s), 5.07 (1 H, t, *J* 6 Hz, H-2), 5.51 (1 H, s, C=CH), 6.67 (1 H, d, *J* 2 Hz, H-6), 6.87 (1 H, dd, *J* 2 and 8 Hz, H-8), and 7.16 (1 H, d, *J* 8 Hz, H-9), *m/e* 230 ($C_{15}H_{18}O_2$, M^+).

7-*Methoxy*-9bα-*methyl*-1,3,3a,4,5,9b-*hexahydro*-3β,3aβ-*methanobenz*[e]*inden*-2β-*ol* (28).—Freshly prepared methylene iodide [26] (400 mg) in ether (1 cm^3) was added dropwise to a stirred slurry of a zinc–silver couple [from zinc (110 mg) in ether (2 cm^3)] at room temperature. After 1 h compound (27) (300 mg) in ether (2 cm^3) containing 1,2-dimethoxyethane (135 mg) was added in one portion. The mixture was refluxed for 1 h., then cooled to 0 °C and pyridine (2 cm^3) was added. The precipitated zinc salts were filtered off and washed with ether. The filtrate and washings were combined and treated with dilute hydrochloric acid and with water before being dried and evaporated. The oil thus produced was chromatographically homogeneous; p.l.c. furnished *compound* (28) (162 mg), $\lambda_{max.}$ 279 nm (ε 2 050), $\nu_{max.}$ ($CHCl_3$) 3 595 (free OH), 3 430 (bonded OH), and 1 608 cm^{-1}, δ 0.11 (1 H, dd, *J* 5 and 7 Hz), 0.71 (1 H, m), 1.22 (3 H, s, 9b-Me and 2 H, m), 4.70 (1 H, m, H-2), 6.68 (2 H, s, H-6 and -8), and 6.90 (1 H, d, *J* 9 Hz), *m/e* 244 ($C_{16}H_{20}O_2$, M^+).

7-*Methoxy*-trans-3a,9b-*dimethyl*-1,3,3a,4,5,9b-*hexahydrobenz*[e]*inden*-2-*one* (30).—Compound (28) (265 mg) was oxidised with chromic acid in acetone [27] and the product purified by p.l.c. (2 : 3 ether–petroleum). 7-*Methoxy*-9bα-*methyl*-1,3,3a,4,5,9b-*hexahydro*-3β,3aβ-*methanobenz*[e]*inden*-2-*one* (29) was obtained as prisms (165 mg), m.p. 104—105° (from ethanol), $\lambda_{max.}$ 279 nm (ε 1 600), $\nu_{max.}$ ($CHCl_3$) 1 722 cm^{-1}, δ 0.80—1.14 (2 H, m), 1.36 (1 H, m, H-3), and 6.56—6.88 (3 H, m), *m/e* 242 ($C_{16}H_{18}O_2$, M^+).

Lithium (50 mg) was dissolved in dry stirred liquid ammonia (40 cm^3). The ketone (29) (120 mg) in ether (1 cm^3) was added and the mixture allowed to reflux for 1 h. It was then treated with an excess of dry ammonium chloride and the ammonia was evaporated off. Addition of water was followed by extraction with ether. The material from the ether layer was gently oxidised with chromic acid.[27] The sole product was the trans-*ketone* (30); after p.l.c. (2 : 3 ether–petroleum) it was an oil (63 mg), $\lambda_{max.}$ 277 nm (ε 2 000), $\nu_{max.}$ ($CHCl_3$) 1 738 cm^{-1}, *m/e* 244 ($C_{16}H_{20}O_2$, M^+). The n.m.r. spectrum is given in the following paper.

2-(2-*Chloroallyl*)-6-*methoxy*-2-*methyl*-1-*tetralone* (3).—A solution of 6-methoxy-2-methyl-1-tetralone (9) (5 g) and 2,3-dichloropropene (5.2 g) in diglyme (10 cm^3) was added dropwise to a stirred slurry of sodium hydride (0.72 g; washed with petroleum) in diglyme (25 cm^3) at 40 °C under nitrogen. After a further 18 h stirring, water was added and the mixture extracted with ether. Work-up of the extract gave an oil which was chromatographed on grade II neutral alumina (5 : 95 ether–petroleum) to furnish [3] *compound* (3) (5.32 g), $\lambda_{max.}$ 275 nm (ε 12 100), $\nu_{max.}$ (film) 1 670 cm^{-1}, δ 1.21 (3 H, s), 5.14 (1 H, s) and 5.25 (1 H, s) ($CCl=CH_2$), 6.65 (1 H, d, *J* 2.7 Hz, H-5), 6.78 (1 H , dd, *J* 2.7 and 8 Hz, H-7), and 7.98 (1 H, d, *J* 8 Hz, H-8), *m/e* 264 ($C_{15}H_{17}ClO_2$, M^+).

2-(2-*Chloroallyl*)-6-*methoxy*-2-*methyl*-1-*methylenetetralin* (34).—Compound (3) (4 g) in ether (10 cm^3) was added dropwise to a stirred solution of methylmagnesium iodide [from magnesium (1.1 g), methyl iodide (7 g), and ether (50 cm^3)]. After 4 h saturated aqueous ammonium chloride (30 cm^3) was added, the ether layer separated, and the aqueous phase extracted with ether. The combined ethereal extracts were washed and dried. Evaporation yielded a yellow oil (single component by g.l.c.). Chromatography (grade II neutral alumina; petroleum) yielded *compound* (34) (3.04 g) as an oil, $\lambda_{max.}$ 262 nm (ε 11 200), $\nu_{max.}$ (film) 1 620 cm^{-1}, δ 1.36 (3 H, s), 5.01 (2 H, s, $C=CH_2$), 5.28 (1 H, s) and 5.41 (1 H, s) ($CCl=CH_2$), 6.72 (2 H, m, H-5 and -7), and 7.54 (1 H, d, *J* 8 Hz, H-8), *m/e* 262 ($C_{16}H_{19}ClO$, M^+).

7-*Methoxy*-cis-3a,9b-*dimethyl*-1,3,3a,4,5,9b-*hexahydrobenz*[e]*inden*-2-*one* (40).—Compound (34) (1.31 g) in ether (2 cm^3) was added to 98% formic acid (70 cm^3) and the light green solution was then refluxed for 1 h, during which time it gradually became orange. The solution was cooled, and poured into iced water (750 cm^3), and after 5 min extracted with ether. The extract was thoroughly washed with sodium hydrogen carbonate solution, then water, dried ($MgSO_4$), and evaporated. G.l.c. showed the absence of starting material and the presence in approximately equal amounts of three products. P.l.c. (2 : 3 ether–petroleum) gave, as the more polar of two fractions the cis-*dimethylhexahydrobenzindenone* (40) (400 mg), $\lambda_{max.}$ 277 nm (ε 1 400), $\nu_{max.}$ ($CHCl_3$) 1 738 and 945 cm^{-1}, *m/e* 244 ($C_{16}H_{20}O_2$, M^+). The n.m.r. spectrum is given in the following paper.

The less polar fraction (510 mg) was injected into a Wilkins Aerograph Autoprep preparative vapour phase chromatograph equipped with a spiral steel column (20 ft × ⅜ in) packed with 30% SE 30 on 30—60 mesh Chromosorb W. Two pure compounds were obtained. 2-*Chloro*-7-*methoxy*-cis-3a,9b-*dimethyl*-3a,4,5,9b-*tetrahydro*-1H-*benz*[e]*indene* (43), an oil, had $\nu_{max.}$ ($CHCl_3$) 3 060 and 2 925 cm^{-1}, δ 1.06 (3 H, s), 1.32 (3 H, s), 1.64 (2 H, m, 4-H_2), 2.68 (4 H, m, 1- and 5-H_2), 5.54 (1 H, s, H-3), 6.54 (1 H, d, *J* 2.5 Hz, H-6), 6.75 (1 H, dd, *J* 2.5 and 8 Hz, H-8), and 7.20 (1 H, d, *J* 8 Hz, H-9), *m/e* 262 ($C_{16}H_{19}ClO$, M^+; 100%).

The Δ^1-*isomer* (44), also an oil, had $\nu_{max.}$ ($CHCl_3$) 2 963 and 2 935 cm^{-1}, δ 1.14 (3 H, s), 1.28 (3 H, s), 1.60 (2 H, m, 4-H_2), 2.44 (2 H, m, 3-H_2), 2.70 (2 H, m, 5-H_2), 5.67 (1 H, s, H-1), 6.60 (1 H, d, *J* 3 Hz, H-6), 6.78 (1 H, dd, *J* 3 and 8 Hz, H-8), and 7.20 (1 H, d, *J* 8 Hz, H-9), *m/e* 262 ($C_{16}H_{19}ClO$, M^+; 22%). The constitutions of compounds (43) and (44) are based on the δ values for C=CH (H-3 and H-1, respectively).

A mixture of compounds (43) and (44) (500 mg) was added to stirred concentrated sulphuric acid (25 cm^3) kept at 0 °C. After 30 min the solution was poured on to ice and extracted with ether. By p.l.c. the pure *cis*-ketone (40) (315 mg) was obtained; no other product was detected.

Conversion of 7-*Methoxy*-cis- *and* trans-3a,9b-*dimethyl*-1,3,3a,4,5,9b-*hexahydrobenz*[e]*inden*-2-*ones* [(40) *and* (30)] into 7-*Methoxy*-cis- *and* trans-3a,9b-*dimethyl*-2,3,3a,4,5,9b-*hexahydro*-1H-*benz*[e]*indenes* [(42) *and* (32)].—The benzindenone (40) (60 mg) in freshly distilled ethane-1,2-dithiol (1 cm^3) was treated with boron trifluoride–diethyl ether complex (20 mg) and the orange solution was then stirred at room temperature for 16 h. Ether (20 cm^3) was added and the solution washed with water (2 × 10 cm^3). The ether

layer was dried ($MgSO_4$) and evaporated. T.l.c. (1 : 4 ether–petroleum) showed the presence of only one compound. P.l.c. gave the *ethylene dithioacetal* (41) (56 mg) as an oil, $\nu_{max.}$ ($CHCl_3$) 990, 960, 948, 940, and 919 cm^{-1}, δ 1.05 (3 H, s) and 1.27 (3 H, s) (2 Me), 3.21 (4 H, s, SCH_2CH_2S), 6.56 (1 H, d, *J* 3 Hz, H-6), 6.72 (1 H, dd, *J* 3 and 9 Hz, H-8), and 7.20 (1 H, d, *J* 9 Hz, H-9). Raney nickel [28] (1 g) was added to compound (41) (50 mg) in pure ethanol (2 cm^3) and the mixture was then refluxed for 12 h, and extracted (Soxhlet) for 12 h with ethanol. Evaporation followed by p.l.c. gave the *benzindene* (42) (32 mg), δ 0.97 (3 H, s) and 1.19 (3 H, s) (2 Me), 6.59 (1 H, d, *J* 3 Hz, H-6), 6.74 (1 H, dd, *J* 3 and 9 Hz, H-8), and 7.29 (1 H, d, *J* 9 Hz, H-9), *m/e* 230 ($C_{16}H_{22}O$, M^+).

The benzindenone (30) (90 mg) was treated with ethanedithiol as for the *cis*-compound. The *dithioacetal* (31) was obtained as an oil (78 mg), $\nu_{max.}$ ($CHCl_3$) 982, 953, and 915 cm^{-1}, δ 0.84 (3 H, s) and 1.11 (3 H, s) (2 Me), 3.28—3.69 (4 H, m, SCH_2CH_2S), and 6.77—7.07 (3 H, m, H-6, -8, and -9). The above dithioacetal (60 mg) was desulphurised exactly as for the *trans*-isomer and yielded the *benzindene* (32) (34 mg), δ 0.69 (3 H, s) and 1.06 (3 H, s) (2 Me), 6.65br (2 H, H-6 and -8), and 6.96 (1 H, d, *J* 9 Hz, H-9), *m/e* 230 ($C_{16}H_{22}O$, M^+).

7-*Methoxy*-cis-3a,9b-*dimethyl*-2,3,3a,4,5,9b-*hexahydro*-1H-*benz*[e]*indene* (48) *from* (−)-7-*Methoxy*-cis-3a,9b-*dimethyl*-1,2,3a,4,5,9b-*hexahydrobenz*[e]*indene*-3-*one* (46).—Compound (46) (8 mg; kindly provided by Dr. W. Graf, ETH) was treated with ethanedithiol exactly as in the preparations above. The *ethylene dithioacetal* (47) thus obtained (9 mg) was an oil, δ 1.19 (3 H, s) and 1.40 (3 H, s) (2 Me), 3.20 (4 H, apparent t, *J* 4 Hz, SCH_2CH_2S, A_2B_2),[29] 6.58br (1 H, H-6), 6.80 (1 H, dd, *J* 2.5 and 8 Hz, H-8), and 7.28 (1 H, d, *J* 8 Hz, H-9).

This compound (8 mg) was desulphurised as for the previous thioacetals. The product (48) (5 g) [*m/e* 230 (M^+)] gave an n.m.r. spectrum identical with that of the racemic compound (42).

6-*Methoxy*-1-*methylene*-2-*methyl*-2-(*prop*-2-*ynyl*)*tetralin* (36).—6-Methoxy-2-methyl-2-(prop-2-ynyl)-1-tetralone (10) (5.7 g) in ether (10 cm^3) was added slowly at room temperature to a stirred solution of methylmagnesium iodide [from magnesium (1.5 g), methyl iodide (10 g), and ether (50 cm^3)]. After 1 h saturated aqueous ammonium chloride (50 cm^3) was added and the mixture was extracted with ether. Work-up gave *compound* (36) (4.53 g), a pale yellow oil (after chromatography on neutral grade II alumina with petroleum); $\lambda_{max.}$ 260 nm (ε 9 200), $\nu_{max.}$ (film) 1 189 and 1 166 cm^{-1}, δ 1.36 (3 H, s, 2-Me), 5.04 (1 H, s) and 5.41 (1 H, s) (=CH_2), 6.63 (2 H, m, H-5 and -7), and 7.50 (1 H, d, *J* 8 Hz, H-8), *m/e* 226 ($C_{16}H_{18}O$, M^+)

Compound (36) (300 mg) in ether (1 cm^3) was added to 98% formic acid (20 cm^3) and the green solution was heated under reflux for 1 h, cooled, treated with iced water, and then extracted with ether. The major product, a diastereoisomeric mixture of 6-methoxy-1,2-dimethyl-2-(prop-2-ynyl)tetralins (38) (186 mg) was obtained by p.l.c. (3 : 17 ether–petroleum). The oil had $\lambda_{max.}$ 277 nm (ε 2 000), $\nu_{max.}$ (film) 3 310 and 2 120 cm^{-1}, δ 1.05 and 1.19 (both s, 2-Me) and 1.08 and 1.22 (both d, *J* Hz, 1-Me) (total intensity 6 H), 6.70 (2 H, m, H-5 and -7), and 7.08 (1 H, d, *J* 8 Hz H-8), *m/e* 228 (M^+, $C_{16}H_{20}O$).

1-(2-*Chloroallyl*)-6-*methoxy*-1-*methyl*-2-*tetralone* (25).—A solution of 2,3-dichloropropene (1.93 g) and 6-methoxy-1-methyl-2-tetralone (22) (3 g) in diglyme (5 cm^3) was added during 10 min to a stirred slurry of sodium hydride (0.42 g; washed with petroleum) in diglyme (15 cm^3) under nitrogen at 15 °C, after which the temperature was raised to 45 °C and kept there for 18 h. Water (200 cm^3) was then added and the mixture thoroughly extracted with ether (3 × 80 cm^3). The combined extracts were washed with water to remove most of the diglyme and then dried and evaporated. Column chromatography (1 : 20 ether–petroleum) on grade II neutral alumina (100 g) furnished the pure *tetralone* (25) (2.91 g) as an oil, $\lambda_{max.}$ 277 nm (ε 1 850), $\nu_{max.}$ (film) 1 715 cm^{-1}, δ 1.41 (3 H, s, 1-Me), 4.80 (1 H, s) and 4.97 (1 H, s) ($CCl=CH_2$), 6.77 (2 H, m, H-5 and -7), and 7.18 (1 H, d, *J* 8 Hz, H-8), *m/e* 189 ($C_{15}H_{17}ClO_2$, $M^+ - C_3H_4Cl$).

1-(2-*Chloroallyl*)-6-*methoxy*-2,3-*dimethylnaphthalene* (54).—The above tetralone (2.4 g) in ether (5 cm^3) was added dropwise to a solution of methylmagnesium iodide [from magnesium (0.4 g), methyl iodide (2.8 g), and ether (50 cm^3)]. Work-up in the usual way gave a yellow oil which was chromatographed on a column of neutral grade II alumina (50 g) with petroleum. Elution with ether–petroleum (5 : 95) yielded unchanged tetralone (0.69 g); further elution (up to 20% ether) gave (as one stereoisomer) 1-(2-*chloroallyl*)-6-*methoxy*-1,2-*dimethyl*-2-*tetralol* (39) (1.10 g) as an oil, $\lambda_{max.}$ 277 nm (ε 1 900), $\nu_{max.}$ (film) 3 400 cm^{-1}, δ 1.17 (3 H, s) and 1.43 (3 H, s) (1- and 2-Me), 6.66 (2 H, m, H-5 and -7), and 7.16 (1 H, d, *J* 8 Hz, H-8). A solution of this compound (500 mg) in 98% formic acid (30 cm^3) was refluxed for 1 h, then poured onto ice, and the mixture was then extracted with ether. The extract was washed sequentially with aqueous sodium hydrogen carbonate and water, dried, and evaporated. The oil thus produced showed no i.r. carbonyl absorption; g.l.c. showed the presence (40%) of one compound and that compounds (40), (43), and (44) were absent. Preparative g.l.c. (SE 30 on Chromosorb W; 5 m × 6 mm) gave pure 1-(2-*chloroallyl*)-6-*methoxy*-2,3-*dimethylnaphthalene* (54) (102 mg) as a pale yellow oil which solidified, $\lambda_{max.}$ 233 nm (ε 45 000), $\nu_{max.}$ ($CHCl_3$) 1 624 and 1 606 cm^{-1}, δ 2.42 (3 H, s) and 2.54 (3 H, s) (2-Me and 3-Me), 3.88 (3 H, s, OMe), 3.95 (2 H, s, CH_2–CCl=), 4.93 (1 H, s) and 5.23 (1 H, s) ($CCl=CH_2$), 6.12 (3 H, m, H-4, -5, and -7), and 7.92 (1 H, d, *J* 10 Hz, H-8), *m/e* 260 ($C_{16}H_{17}ClO$, M^+) and 225 ($M^+ - Cl$).

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