Terpenoids. Part 40.[1] Oxidative Rearrangement of *ent*-17-Norkauran-16-one with Thallium(III) Nitrate and Synthesis of *ent*-9(8→15αH)*abeo*-Kaurane

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Treatment of *ent*-17-norkauran-16-one (1) with thallium trinitrate in acetic acid gave several oxidative rearrangement products [(4), (5a), (5b), and (6b)]. The diterpene skeleton of these rearrangement products, *ent*-9(8→15αH)*abeo*-kaurane (17), has been synthesised.

THALLIUM(III) salts are ' soft ' acids,[2] and can oxidize various ' soft ' bases.[2] Recently we described an allylic oxidation by thallium trinitrate (TTN).[3] There have been many reports concerning rearrangements of type A [4] (see Scheme), that is, 1,2-migration of an alkyl or aryl group bonded to a carbonyl carbon atom by thallium(III) salts. However only one example of a rearrangement of type B with the same reagents has been described.[4d]

We now report a novel rearrangement of type B.

McKillop, Taylor, *et al.*[4c] have reported that the reaction of cyclopentanone with TTN gave a complex mixture, whereas the corresponding reaction with cyclohexanone gave cyclopentanecarboxylic acid, the typical type A rearrangement product. The reaction of *ent*-17-norkauran-16-one (1) [5] with TTN seemed interesting, because the type A rearrangement product (2) would be

[1] Part 39, E. Fujita, M. Node, and H. Hori, *J.C.S. Perkin I*, 1977, 611.

[2] P. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533; T.-L. Ho, *Chem. Rev.*, 1975, **75**, 1.

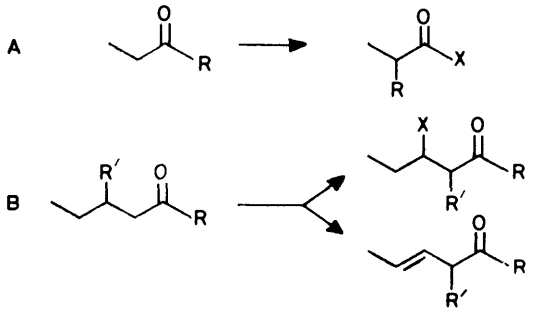
[3] M. Ochiai and E. Fujita, *J.C.S. Chem. Comm.*, 1975, 967.

[4] (*a*) K. B. Wiberg and W. Koch, *Tetrahedron Letters*, 1966, 1779; (*b*) A. McKillop, B. P. Swann, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1971, **93**, 4919; (*c*) A. McKillop, J. D. Hunt, and E. C. Taylor, *J. Org. Chem.*, 1972, **37**, 3381; (*d*) G. Ortar and A. Romeo, *J.C.S. Perkin I*, 1976, 111.

[5] C. Djerassi, M. Cais, and L. A. Mitscher, *J. Amer. Chem. Soc.*, 1959, **81**, 2386.

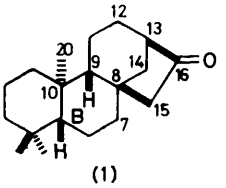
highly strained, and this type of rearrangement would thus be disfavoured.

The initial steps of this reaction must be the formation of a π-complex by electrophilic attack of TTN on the enol form of (1) from the less hindered α-side, and subsequent

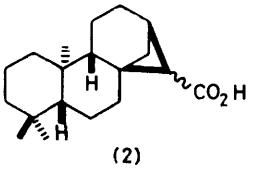


SCHEME X = nucleophile

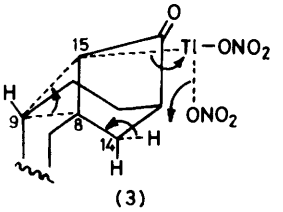
conversion into the 15α-thallio-compound. Since the 8,9-bond is antiperiplanar to the 15,Tl-bond, the next step would be expected to be migration of the 8,9-bond to the 15-position *via* a convenient concerted pathway, as shown in formula (3).



(1)

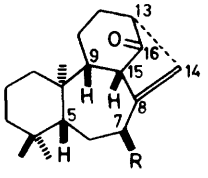


(2)

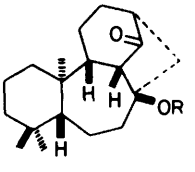


(3)

As expected, the reaction under the conditions indicated in the Experimental section gave compound (4) as the major product and (5a), (5b), and (6b) as minor products; some starting material (1) was recovered.

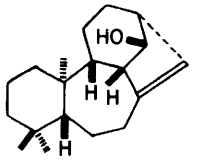


(4) R = H
(6a) R = OH
(6b) R = OAc

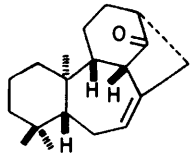


(5a) R = H
(5b) R = Ac

The structure and stereochemistry of compound (4), $C_{19}H_{28}O$, were deduced on the basis of i.r. and n.m.r. spectral data, which suggested the presence of a carbonyl group in a five-membered ring and a trisubstituted double bond, and the expected mechanism, and were supported by an n.m.r. study of the alcohol (7), derived from (4) by reduction with sodium borohydride, in the presence of the shift reagent $Eu(dpm)_3$. The largest paramagnetic shift was shown by the 16-H, and progressively smaller shifts by the 9-H, 15-H, and 13-H. A double-bond isomeric structure (8) was ruled out on the basis of the following evidence. Reduction of the epoxide (9) derived from (7) by treatment with lithium in ethylenediamine afforded a tertiary alcohol (10) and a secondary alcohol (11), identical with the product obtained by hydroboration of (4). (i) In the n.m.r. spectrum of compound (11), the 14α-H signal was observed as a doublet (*J* 4 Hz) at δ 3.77, showing coupling only to the 8-H because the torsion angle between the 14α-H and 13-H is 90°. (ii) In the i.r. spectrum of the diketone (12) derived from (11) by Jones oxidation, absorption bands characteristic of a cyclopentane-1,3-dione [6] were observed. (iii) The 16-oxo-group of the epoxide (13)



(7)



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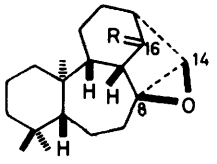
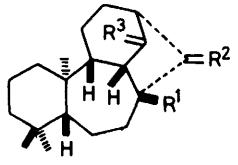


(9) R = α-H, β-OH
(13) R = O



(10) R^1 = OH, R^2 = H_2
R^3 = α-H, β-OH
(11) R^1 = H, R^2 = R^3 = α-H, β-OH
(12) R^1 = H, R^2 = R^3 = O

derived from (4) was not reduced by sodium borohydride. Attack of the reagent from the α-side is not possible because of steric hindrance by the epoxy-group. Attack from the β-side is also disfavoured because of a potential large non-bonded interaction between the putative hydroxy-group and the epoxy-group. Furthermore, compound (4) exhibited a big positive Cotton effect in its o.r.d. spectrum. Thus, the structure and absolute configuration of compound (4) were established.*

In the foregoing epoxide ring opening of compound (9), the alcohols (10) and (11) were obtained unexpectedly

* A recent *X*-ray crystallographic analysis [7] has confirmed the structure.

[6] M. Shiozaki, K. Mori, M. Matsui, and T. Hiraoka, *Tetrahedron Letters*, 1972, 657.

[7] T. Taga, T. Higashi, H. Iizuka, K. Osaki, M. Ochiai, and E. Fujita, *Acta Cryst.*, 1977, **B33**, 298.

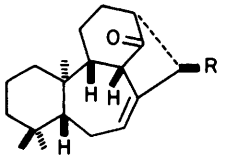
in the ratio 1 : 2.[8] This is probably due to the more effective release of non-bonded interaction between the 16α-H and the epoxide oxygen atom by elongation of the 8,O-bond than of the 14,O-bond. In fact, the 16α-H signal of compound (10) is observed at δ *ca.* 0.24, *i.e.* at lower field than that of compound (11).

Compound (5a) was identical with the hydroxy-ketone obtained by Jones oxidation of (10). It underwent dehydration with thionyl chloride in pyridine to give the olefin (4). The structure of (5b) was clarified by the formation of (10) from its reaction with lithium aluminium hydride.

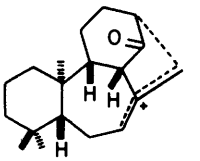
The n.m.r. spectrum of compound (6b) provided a reasonable assignment of the structure. Thus a doublet of doublets * (*J* 2 and 4 Hz) at δ 5.59 was assigned to the 7α-H, coupled to two protons on C-6, and a doublet (*J* 2.5 Hz) at δ 6.06 to the 14-H, coupled to the 13-H. The allylic coupling of the 14-H with the 7β-H observed in the n.m.r. spectrum of (4) had disappeared in that of (6b), and the 15-H signal showed a larger paramagnetic shift than that of the 14-H in the n.m.r. spectrum of (6a), the hydrolysis product of (6b), in the presence of Eu(dpm)$_3$. These facts support the β-configuration of the 7-acetoxy-group in (6b).

Compound (4) on treatment with TTN in acetic acid at room temperature for 6 days gave the acetate (6b) (15%); 56% of the starting material was recovered.[9] The formation of (6b) in this reaction probably proceeds by initial attack of TTN on the double bond from the less hindered β-side to form a π-complex, followed by conversion into the 14-thallio-7-ene (14), then finally formation of (6b) *via* the allylic cation (15). Attack of acetic acid at the 14-position would give compound (16). A stereomodel of (16) indicated that the 14α-H would not couple to the 13-H because the torsion angle between them is about 90°, and also that it would not show any long-range coupling. Thus, the 14α-H signal should appear as a doublet, owing to coupling to the 7-H. Furthermore, the 7-H would be coupled to the 14α-H and two protons on C-6, hence it would not give rise to a doublet. Thus, the foregoing n.m.r. data agree well with structure (6b) and exclude the possibility of structure (16). Compound (16) is also kinetically and thermodynamically much more disfavoured than compound (6b), because of a big non-bonded interaction between the 5β-H and the 15β-H. This is probably the reason for the predominant formation of (6b).

Migrations of the 12,13-bond to the 16-position have been reported. However migration of the 8,9-bond to the 15-position has been thought to be difficult because of ring strain in the transition state. Only one example has been described,[10] of a napelline derivative of the kaurane-type having a large strain in ring B due to the 7,20-bond. In our case, the organothallium intermediate is so active that it can overcome the unfavourable ring strain in the transition state and rearrange to the product (4) under very mild conditions. In the transition state (3), the decreasing non-bonded interaction between 10-Me and 14α-H may be a favourable factor.



(14) R = Tl(ONO$_2$)$_2$
(16) R = OAc



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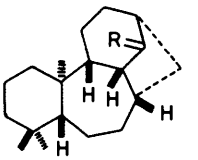

(17) R = α-H, β-Me
(18) R = O
(19) R = CH_2

Thus we have brought about rearrangement of the 8,9-bond to the 15-position of a kaurane derivative possessing no 7,20-bond. Our finding suggests the possibility of the natural occurrence of compounds having this new skeleton, and prompted us to synthesise the new hydrocarbon (17). Catalytic reduction of the double bond of compound (4) from the less hindered β-side accompanied by the reduction of 16-oxo-group from the α-side and subsequent Jones oxidation gave the ketone (18), which on Wittig reaction afforded the exocyclic methylene derivative (19). Catalytic reduction of (19) yielded *ent*-9(8 ⟶ 15αH)*abeo*-kaurane (17) as the sole product. The hydrogenation must have taken place at the less hindered α-side; hence the β-configuration was reasonably assigned to the 16-methyl group.

EXPERIMENTAL

M.p.s were taken with a micro hot-stage apparatus. I.r. spectra were recorded with a Hitachi EPI-S2 spectrometer and n.m.r. spectra with a Varian T-60 spectrometer for solutions in [^{2}H]chloroform (tetramethylsilane as internal standard). Mass spectra were determined with a JEOL JMS-OISG double-focusing spectrometer. Optical rotations were measured with a JASCO DIP-180 automatic polarimeter or a JASCO J-20 spectropolarimeter. Extracts were dried over anhydrous Na_2SO_4. Unless otherwise stated, Mallinckrodt silicic acid and Kieselgel 0.05—0.2 mm (Merck) were used for column chromatography. T.l.c. plates were coated with silica gel G (Merck, nach Stahl).

Oxidative Rearrangement of ent-17-*Norkauran*-16-*one* (1).—TTN (700 mg, 1.58 mmol) was added to a solution of the ketone (1) (432 mg, 1.58 mmol) in acetic acid (15 ml). The mixture was stirred vigorously for 4 days at room temperature, precipitating white thallium(I) nitrate gradually. The inorganic salt was filtered off, and the filtrate was neutralised

* This signal is shifted to δ 4.53 in the spectrum of (6a).

[8] H. C. Brown, S. Ikegami, and J. H. Kawakami, *J. Org. Chem.*, 1970, **35**, 3243.

[9] *Cf.* B. Cocton and C. De Paulet, *Bull. Soc. chim. France*, 1966, **9**, 2947.

[10] M. Kodama, H. Kurihara, and S. Itô, *Tetrahedron Letters*, 1975, 1301.

with sodium hydrogen carbonate, and then extracted with ethyl acetate. The extracts were washed with water and dried. The solvent was evaporated off *in vacuo* to leave an oil, which was chromatographed on silica gel. Elution with methylene chloride–n-hexane (1 : 1) gave ent-17-*nor*-9-(8 ⟶ 15αH)abeo-*kaur*-8(14)-*en*-16-*one* (4) (173 mg, 40%) as needles, m.p. 104—105° (from methanol–water), $\nu_{max.}$ (KBr) 1 752 and 1 625 cm^{-1}, δ 0.83 (3 H, s), 0.92 (6 H, s), 3.00 (1 H, s, 15-H), and 5.70 (1 H, t, *J* 2 Hz, 14-H) (Found: C, 83.7; H, 10.3%; M^+, 272. $C_{19}H_{28}O$ requires C, 83.75; H, 10.35%; *M*, 272), o.r.d. (in $CHCl_3$) $[\phi]_{589}$ +33.1°, $[\phi]_{304}$ +2 828.8° (peak), $[\phi]_{289}$ 0°, and $[\phi]_{265}$ −2 339.2°; and subsequently starting material (1) (120 mg, 27.8%). Elution with methylene chloride gave a clear oil. Preparative t.l.c. [methanol–methylene chloride (1 : 99)] afforded ent-7α-*acetoxy*-17-*nor*-9(8 ⟶ 15αH)abeo-*kaur*-8(14)-*en*-16-*one* (6b) (16 mg, 3.1%) as needles, m.p. 165—166° (from cold methanol), $\nu_{max.}$ ($CHCl_3$) 1 758, 1 727, and 1 635 cm^{-1}, δ 0.83 (6 H, s), 0.93 (3 H, s), 2.03 (3 H, s), 3.22 (1 H, s, 15-H), 5.59 (1 H, dd, *J* 2 and 4 Hz, 7-H), and 6.06 (1 H, d, *J* 2.5 Hz, 14-H) (Found: C, 76.1; H, 9.25%; M^+, 330. $C_{21}H_{30}O_3$ requires C, 76.3; H, 9.15%; *M*, 330). Further elution with methylene chloride gave ent-8α-*acetoxy*-17-*nor*-9(8 ⟶ 15αH)abeo-*kauran*-16-*one* (5b) (25 mg, 4.8%) as plates, m.p. 148—157° (from acetone), $\nu_{max.}$ ($CHCl_3$) 1 737 and 1 723 cm^{-1}, δ 0.86, 0.92, 0.97, and 1.95 (each 3 H, s) (Found: M^+, 332.235. $C_{21}H_{32}O_3$ requires *M*, 332.235). Elution with methylene chloride–methanol (9 : 1) afforded ent-8α-*hydroxy*-17-*nor*-9(8 ⟶ 15αH)abeo-*kauran*-16-*one* (5a) (7 mg, 1.5%) as needles, m.p. 204—205° (from acetone), $\nu_{max.}$ (KBr) 3 390 and 1 730 cm^{-1}, δ 0.87, 0.92, and 0.97 (each 3 H, s) (Found: M^+, 290.229. $C_{19}H_{30}O_2$ requires *M*, 290.225).

Reduction of the Ketone (4) *with Sodium Borohydride*.—To an ice cooled solution of (4) (165 mg) in methanol (15 ml) was added sodium borohydride (165 mg), and the mixture was stirred for 30 min. Acetone (0.2 ml) was added and the solution was stirred for a few min then evaporated *in vacuo*. Water was added, and the mixture extracted with ethyl acetate. The extract was treated as usual to give an oil, which was chromatographed to yield ent-17-*nor*-9(8 ⟶ 15αH)abeo-*kaur*-8(14)-*en*-16α-*ol* (7) (150 mg, 90%) as an amorphous substance, $\nu_{max.}$ ($CHCl_3$) 3 580, 3 435, and 1 630 cm^{-1}, δ 0.85 (3 H, s), 0.92 (6H, s), 2.63 (1 H, d, *J* 6 Hz, 15-H), 4.08 (1 H, t, *J* 6 Hz, 16-H), and 5.40 (1 H, t, *J* 2 Hz, 14-H) (Found: M^+, 274.232. $C_{19}H_{30}O$ requires *M*, 274.230).

Epoxidation of the Alcohol (7).—The alcohol (7) (19 mg) was dissolved in methylene chloride (1 ml), and sodium hydrogen carbonate (10 mg) and *m*-chloroperbenzoic acid (19 mg) were added. The mixture was stirred for 1 h at room temperature, and then added to methylene chloride (50 ml). After washing with sodium carbonate and water and drying, the solution was evaporated to leave an oil, which was purified by chromatography on aluminium oxide [W 200 basic (Woelm)] to give ent-8α,14α-*epoxy*-17-*nor*-9(8 ⟶ 15αH)abeo-*kauran*-16α-ol (9) (17 mg, 85%) as plates, m.p. 195—196° (from acetonitrile), $\nu_{max.}$ ($CHCl_3$) 3 600 and 3 440 cm^{-1}, δ 0.83 (3 H, s), 0.93 (6 H, s), 3.13 (1 H, s, 14-H), and 4.06 (1 H, t, *J* 5 Hz, 16-H) (Found: C, 78.4; H, 10.25%; M^+, 290. $C_{19}H_{30}O_2$ requires C, 78.55; H, 10.4%; *M*, 290).

Reduction of the Epoxide (9) *with Lithium in Ethylenediamine*.—The epoxide (9) (76 mg) was dissolved in ethylenediamine (2 ml) under nitrogen, and lithium (15 mg) was added at room temperature. After stirring for 30 min, a blue-purple colour persisted. The mixture was cooled and water (1 ml) was added to destroy the excess of reagent. The mixture was extracted with tetrahydrofuran and treated as usual. Chromatography separated two products. The less polar product, ent-17-*nor*-9(8 ⟶ 15αH)abeo-*kaurane*-8α,16α-*diol* (10), was obtained as needles (17 mg, 22%), m.p. 188—196° (from acetone–water), $\nu_{max.}$ (KBr) 3 400 cm^{-1}, δ 0.90 (6 H, s), 0.93 (3 H, s), and 4.50 (1 H, t, *J* 5 Hz, 16-H) (Found: C, 77.85; H, 11.0%; M^+, 292. $C_{19}H_{32}O_2$ requires C, 78.05; H, 11.05%; *M*, 292). The more polar compound (the major product) was the 8α,14α-*diol* (11) (36 mg, 47%), obtained as needles, m.p. 180—181° (from methanol), $\nu_{max.}$ (KBr) 3 370 cm^{-1}, δ 0.83, 0.85, and 0.89 (each 3 H, s), 3.77 (1 H, d, *J* 4 Hz, 14-H), and 4.26 (1 H, t, *J* 5 Hz, 16-H) (Found: C, 78.15; H, 11.3%; M^+, 292. $C_{19}H_{32}O_2$ requires C, 78.05; H, 11.05%; *M*, 292).

Hydroboration of the Enone (4).—To a solution of compound (4) (50 mg) in tetrahydrofuran (5 ml) was added at 0 °C 0.33M-diborane in tetrahydrofuran (5 ml). After stirring for 10 min at 0 °C, the mixture was allowed to warm to 25 °C and stirred for 12 h. The solution was hydrolysed with water (5 ml), and 3N-sodium hydroxide (3 ml) and 30% hydrogen peroxide (6 ml) were added. The mixture was stirred for 1 h. Extraction with ether, washing with water, drying, and evaporation afforded a viscous residue, which was chromatographed to yield the diol (11) (29 mg, 54%) as crystals, m.p. 179—180°, identical (i.r. and mixed m.p.) with the foregoing sample.

Jones Oxidation of the Alcohol (11).—To a solution of the alcohol (11) (33 mg) in acetone (1 ml) was added an excess of Jones reagent and the mixture was stirred for 10 min with cooling in ice. Isopropyl alcohol (0.3 ml) was added, and the mixture was poured onto water and extracted with ethyl acetate. The usual treatment of the extract gave a crystalline product, which was chromatographed to yield the 14,16-*dione* (12) (25 mg, 77%), as needles, m.p. 120—121° (from methanol), $\nu_{max.}$ (KBr) 1 765 and 1 730 cm^{-1}, δ 0.83, 0.88, and 0.93 (each 3 H, s) (Found: M^+, 288.204. $C_{19}H_{28}O_2$ requires *M*, 288.209).

Epoxidation of the Olefin (4).—The unsaturated ketone (4) (11 mg) was treated with *m*-chloroperbenzoic acid (14 mg) and sodium hydrogen carbonate (5 mg). Chromatography (aluminium oxide) gave ent-8α,14α-*epoxy*-17-*nor*-9(8 ⟶ 15αH)abeo-*kauran*-16-*one* (13) (10 mg, 86%) as plates, m.p. 164—165° (from methanol), $\nu_{max.}$ ($CHCl_3$) 1 760 cm^{-1}, δ 0.85, 0.93, and 0.98 (each 3 H, s), and 3.40 (1 H, s, 14-H) (Found: C, 78.8; H, 10.2%; M^+, 288. $C_{19}H_{28}O_2$ requires C, 79.1; H, 9.8%; *M*, 288).

Jones Oxidation of the Diol (10).—Compound (10) (6 mg) was oxidised with an excess of Jones reagent to yield the ketone (5a) (5 mg, 84%) as crystals, m.p. 204—205°, identical (i.r. and mixed m.p.) with the foregoing sample.

Dehydration of the Alcohol (5a) *with Thionyl Chloride*.—To a solution of (5a) (20 mg) in pyridine (1 ml) was added thionyl chloride (0.2 ml) at 0 °C. After stirring for 10 min, the mixture was added to water and extracted with ether. Washing with water, drying, and evaporation afforded a residue, which was purified by preparative t.l.c. (methylene chloride) to yield the unsaturated ketone (4) (10 mg, 53%) as crystals, m.p. 102—103°, identical (i.r. and mixed m.p.) with the foregoing sample.

Reduction of the Ketone (5b) *with Lithium Aluminium Hydride*.—To a solution of (5b) (118 mg) in tetrahydrofuran (5 ml) was added lithium aluminium hydride (120 mg) at 0 °C. After stirring for 1 h, the mixture was added to a large quantity of cold ethyl acetate. Evaporation, after

washing with water and drying, left the diol (10) (98 mg, 94.4%) as crystals, m.p. 187—194°, identical (i.r. and mixed m.p.) with the foregoing sample.

Reaction of Compound (4) *with TTN*.—The unsaturated ketone (4) (27 mg) was oxidised with TTN (49 mg) for 6 days, and the mixture was treated as above. Chromatography separated two compounds. The less polar was starting material (4) (15 mg, 56%). The more polar compound was the unsaturated acetate (6b) (5 mg, 15%), obtained as crystals, m.p. 164—165°, identical (i.r. and mixed m.p.) with the foregoing sample.

Hydrolysis of the Unsaturated Acetate (6b).—To a solution of (6b) (76 mg) in methanol (4 ml) was added a solution of potassium carbonate (48 mg) in water (2 ml), and the mixture was stirred for 15 h. Neutralisation with acetic acid, evaporation *in vacuo*, extraction of the residue with ethyl acetate, and the usual work-up gave a crystalline product, which was purified by chromatography to yield the *allylic alcohol* (6a) (37 mg, 56%) as plates, m.p. 184—186° (from ether), $\nu_{max.}$ (KBr) 3 474, 1 740, and 1 633 cm^{-1}, δ 0.83 (3 H, s), 0.92 (6 H, s), 3.22 (1 H, s, 15-H), 4.53 (1 H, dd, *J* 2 and 4 Hz, 7-H), and 5.87 (1 H, d, *J* 2.5 Hz, 14-H) (Found: C, 79.4; H, 9.9. $C_{19}H_{28}O_2$ requires C, 79.1; H, 9.8%).

Catalytic Reduction followed by Jones Oxidation of the Enone (4).—5% Palladium–charcoal (120 mg) was added to a solution of compound (4) (200 mg) in acetic acid (20 ml), and hydrogenation was continued for 2 h at 70 °C (oil-bath temperature). Evaporation after filtration left a residue (205 mg), which was oxidised with an excess of Jones reagent. Chromatography gave ent-17-*nor*-9(8 ⟶ 15αH)-abeo-*kauran*-16-*one* (18) (134 mg, 67%) as plates, m.p. 94—95° (from methanol), $\nu_{max.}$ (KBr) 1 740 cm^{-1}, δ 0.88 (6 H, s) and 0.98 (3 H, s) (Found: C, 83.0; H, 10.9%; M^+, 274. $C_{19}H_{30}O$ requires C, 83.15; H, 11.0%; *M*, 274).

Wittig Reaction with the Ketone (18).—To a suspension of methyltriphenylphosphonium iodide (560 mg) in ether (8 ml) under nitrogen was added a 1M-potassium t-butoxide in t-butyl alcohol (1.12 ml), and the mixture was stirred for 0.5 h at room temperature. A solution of the ketone (18) (76 mg) in benzene (2 ml) was added, and the mixture was stirred at room temperature for 2 h. Ice–water (1 ml) was added and the mixture was neutralised with dilute hydrochloric acid with cooling in ice. Extraction with n-hexane, drying, and evaporation afforded a viscous residue, which was chromatographed to yield ent-9(8 ⟶ 15αH)abeo-*kaur*-16-*ene* (19) (57 mg, 76%) as plates, m.p. 69° (from acetone and n-hexane), $\nu_{max.}$ (KBr) 1 666 and 886 cm^{-1}, δ 0.87 (6 H, s), 0.93 (3 H, s), and 4.52 (2 H, m, 17-H_2) (Found: C, 88.05; H, 11.65%; M^+, 272. $C_{20}H_{32}$ requires C, 88.15; H, 11.85%; *M*, 272).

Catalytic Hydrogenation of the Olefin (19).—The olefin (19) (38 mg), dissolved in methanol (5 ml) and ethyl acetate (5 ml), was hydrogenated over platinum oxide (5 mg) for 2 h. Evaporation, after filtration, gave a residue, which was chromatographed to yield ent-9(8 ⟶ 15αH)abeo-*kaurane* (17) (35 mg, 91%) as plates, m.p. 57—58° (from acetone), $[\alpha]_D^{20}$ +14° (*c* 0.14 in $CHCl_3$), δ 0.85 (6 H, s), 0.89 (3 H, s), and 1.02 (3 H, d, *J* 6 Hz, 17-H_3) (Found: M^+, 274.266. $C_{20}H_{34}$ requires *M*, 274.266). Purity was confirmed by g.l.c.

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