Terpenoids. Part 41.[1] Reactions of *ent*-Kaurenes and 13β-Kaurenes with Thallium(III) Nitrate in 1,2-Dimethoxyethane and a Mutual Allylic Rearrangement of the Allylic Nitrate Products

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The reaction of *ent*-kaur-16-ene (1) or 13β-kaur-16-ene (4) with thallium(III) nitrate in glyme gave only allylic nitrate products, in high yield. The same reaction with *ent*-kaur-15-ene (16) gave the nitrates (2) and (3), an epoxide (22), and an allylic alcohol (5). Similar treatment of 13β-kaur-15-ene (21) afforded the allylic alcohols (9) and (10) and the ketones (23) and (24) : considerable amounts of starting material were recovered. The significance of the differences between these reactions is discussed. A mutual allylic rearrangement of the allylic nitrate products is reported.

IN a recent communication,[2] we reported the formation of the allylic nitrates (2) and (3) in the reaction of *ent*-kaur-16-ene (1) with thallium(III) nitrate (TTN) in 1,2-dimethoxyethane (glyme), and the mutual allylic rearrangement of these products. This paper gives a full account of this work and the reaction of 13β-kaurenes with TTN. Grant and his co-workers [3] have also reported the formation of allylic nitrates in the reactions of labdane-type diterpenes with TTN.

(I) *Reactions of* ent-*Kaur*-16-*ene* (1) *and* 13β-*Kaur*-16-*ene* (4) *with TTN.*—*ent*-Kaur-16-ene (1) was treated with TTN in glyme for 20 min to give *ent*-kaur-16-en-15β-yl nitrate (2) and *ent*-kaur-15-en-17-yl nitrate (3) in 48 and

30% yield, respectively, after rapid column chromatography on silica gel impregnated with silver nitrate.[†] Molecular formulae ($C_{20}H_{31}NO_3$) and i.r. and mass spectra were in accord with the nitrate structure. Reduction [4] of compound (2) by 80% hydrazine hydrate in the presence of 5% palladium–charcoal gave *ent*-kaur-16-en-15β-ol (5) [5] in good yield, which established the structure (2). Since proton signals similar to those of 17-H_2 and 15-H of *ent*-kaur-15-en-17-ol (6) [5] were observed in the n.m.r. spectrum of the minor product (3), it was assumed to be the nitrate of (6); indeed reduction of (3) gave the alcohol (6) in high yield.

Similarly, treatment of 13β-kaur-16-ene (4) with TTN gave the nitrates (7) and (8).[‡] Each compound on treat-

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† A crude mixture before the column separation was shown to consist of (2) and (3) in the ratio 22 : 15 by the n.m.r. spectrum. However adsorption of compound (2) on a silica gel column for 1 h brought about extensive rearrangement to (3) (see Experimental section).

‡ A mixture before chromatography was shown to consist of (7) and (8) in the ratio 3 : 2 by the n.m.r. spectrum. After chromatography, (7) and (8) were isolated in 33 and 50% yields, respectively, indicating partial isomerisation of the former into the latter.

[1] Part 40, E. Fujita, and M. Ochiai, *J.C.S. Perkin I*, 1977, 1182.
[2] M. Ochiai and E. Fujita, *J.C.S. Chem. Comm.*, 1975, 967.
[3] P. K. Grant, H. T. L. Liau, and K.-S. Low, *Austral. J. Chem.*, 1975, 28, 903.
[4] (*a*) R. Boshan, R. T. Merrow, and P. W. Van Dolah, *Chem. Rev.*, 1955, 55, 485; (*b*) L. P. Kuhn, *J. Amer. Chem. Soc.*, 1951, 73, 1510.
[5] M. F. Barnes and J. MacMillan, *J. Chem. Soc.* (*C*), 1967, 361.

ment with hydrazine hydrate and palladium–charcoal as above yielded the corresponding allylic alcohol, (9) [6] or (10).[7]
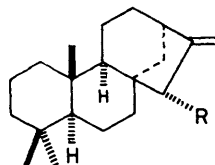
Since the reaction pathways for both ent-kaur-16-ene (1) and 13β-kaur-16-ene (4) are parallel, only the case of
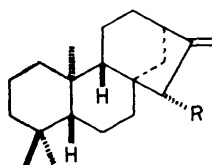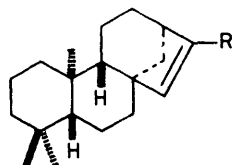
(1) R = H
(2) R = ONO₂
(5) R = OH

(4) R = H
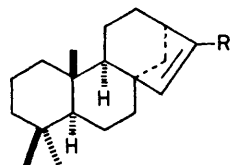(7) R = ONO₂
(9) R = OH

(3) R = CH₂·ONO₂
(6) R = CH₂·OH
(16) R = Me
(17) R = CHO
(18) R = CH₂·OMe

(8) R = CH₂·ONO₂
(10) R = CH₂·OH
(21) R = Me

compound (1) is shown in Scheme 1. The initial step is believed to be the rapid formation of a π-complex, and the following step the formation of an allylic organothallium compound (11).[8] A concerted pathway via a six-membered cyclic transition state (A) or a stepwise process via a carbocation (B) may be considered. Formation of (B) seems unlikely because of the nature of the solvent. In the transition state (A), C-15 changes from sp^3- to sp^2-hybridized, with removal of the non-bonded interactions between the 15β-H and the 11β-H in the starting material (1).* We therefore prefer the concerted pathway via (A).

The subsequent heterolysis of the carbon–thallium bond of (11) is considered to proceed rapidly because of the low bond energy [9] and the location in an allylic position. The product (3) may be formed through a concerted S_Ni process [see (12)], and the product (2) through (13) or (14) by a concerted S_Ni' path. However an alternative pathway to (2) and (3) via an intimate ion pair (15) cannot be excluded.

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* In 13β-kaur-16-ene (4) an additional large non-bonded interaction between the 15β-H and the 20-Me is also removed.

[6] L. H. Briggs, R. C. Cambie, and P. S. Rutledge, J. Chem. Soc., 1963, 5374.

[7] R. Henderson and R. Hodges, Tetrahedron, 1960, 11, 226.

[8] B. Cocton and A. C. De Paulet, Bull. Soc. chim. France, 1966, 2947.

[9] A. McKillop and E. C. Taylor, Chem. in Brit., 1973, 9, 4.

Allylic nitrates are easily convertible into various types of useful compound.[4] Thus the nitrates (2) and (3) are convertible into allylic alcohols as described above; reduction of (3) with lithium aluminium hydride gave the hydrocarbon (16); [5] on treatment with potassium t-butoxide in t-butyl alcohol, (3) gave the αβ-unsaturated aldehyde (17); [5] on treatment with sodium methoxide, (3) gave the ether (18), which was identical with the compound derived from (6) by methylation with diazomethane and boron trifluoride–ether; compound (2) on catalytic reduction afforded the alcohols (19) and (20) in the ratio 4 : 3. Usually catalytic reduction of ent-kaur-16-ene takes place predominantly from the α-side.[10] Probably because of the large bulk of the 15α-nitrate group in (2), an unusual ratio of stereoisomers was obtained.

(II) Reactions of ent-Kaur-15-ene (16) and 13β-Kaur-15-ene (21) with TTN.—The reaction of ent-kaur-15-ene (16) with TTN took 3 h and afforded the allylic nitrates (2) and (3) (total yield 29%), ent-15β,16-epoxykaurane (22) [6] (12%), and the allylic alcohol (5) (24%). T.l.c. showed a spot whose R_F value was identical with that of (6), but no pure compound was isolated. The reaction of 13β-kaur-15-ene (21) with TTN was much slower: after 24 h 24% of the starting material was recovered. The products were the allylic alcohols (9) (8.8%) and (10) (7.6%), 13β,16β-kauran-15-one (23) (2.5%), and 12β-atisan-15-one (24) (5.7%). No allylic nitrates [(7) or (8)] were obtained. Compounds (23) and (24) were identical with authentic samples derived from the epoxide (25) by acid-catalysed rearrangement.[11]

In the reaction of (16) with TTN, an allylic organothallium intermediate (29) may be produced from the initially formed π-complex (26). Both a concerted pathway through (27) and a stepwise process via a carbocation (28) are possible. The rate-determining step is the formation of the organothallium compound.[12] The step (1) ⟶ (11) which removes non-bonded interactions proceeds rapidly, whereas the step (16) ⟶ (29) which changes the initially favoured sp^2-hybridized C-15 into the sterically more hindered sp^3-hybridized carbon atom took much longer.

The product (2) is assumed to be derived from (29) via a concerted S_Ni process similar to (12). The product (3) may be derived from (29) via a concerted S_Ni' process [cf. (13) and (14)]. An alternative pathway via an intimate ion pair (15) may also be possible. The allylic organothallium intermediate (29) has non-bonded interactions between the 11β-H and the 15β-H and amongst the 15α-Tl substituent, the 7α-H, and the 14β-H, and therefore is less stable than (11). Thus it may partially

[10] L. H. Briggs, B. F. Cain, R. C. Cambie, B. R. Davis, P. S. Rutledge, and J. K. Wilmshurst, J. Chem. Soc., 1963, 1345.

[11] (a) P. A. Gunn, R. McCrindle, and R. G. Roy, J. Chem. Soc. (C), 1971, 1018; (b) K. M. Baker, L. H. Briggs, J. G. St. C. Buchanan, R. C. Cambie, B. R. Davis, R. C. Hayward, G. A. S. Long, and P. S. Lutledge, J.C.S. Perkin I, 1972, 190.
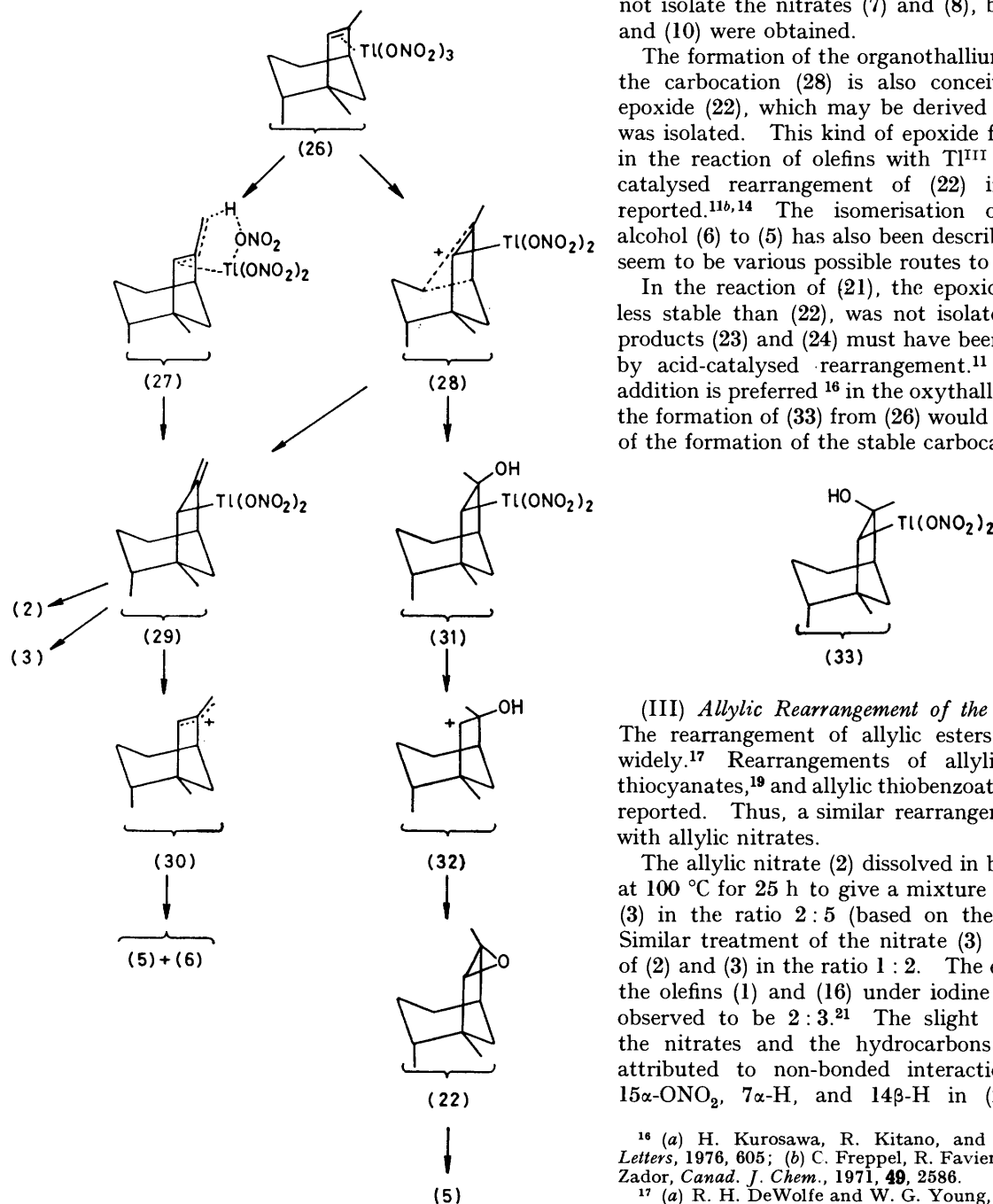
[12] (a) A. G. Lee, in 'Organometallic Reactions,' ed. E. I. Becker and M. Tsutsui, Wiley, New York, 1975, vol. 5, 1; (b) J. E. Byrd and J. Halpern, J. Amer. Chem. Soc., 1973, 95, 2586; (c) P. Abley, J. E. Byrd, and J. Halpern, ibid., p. 2591.

Scheme 1

(19) R¹=H, R²=Me
(20) R¹=Me, R²=H
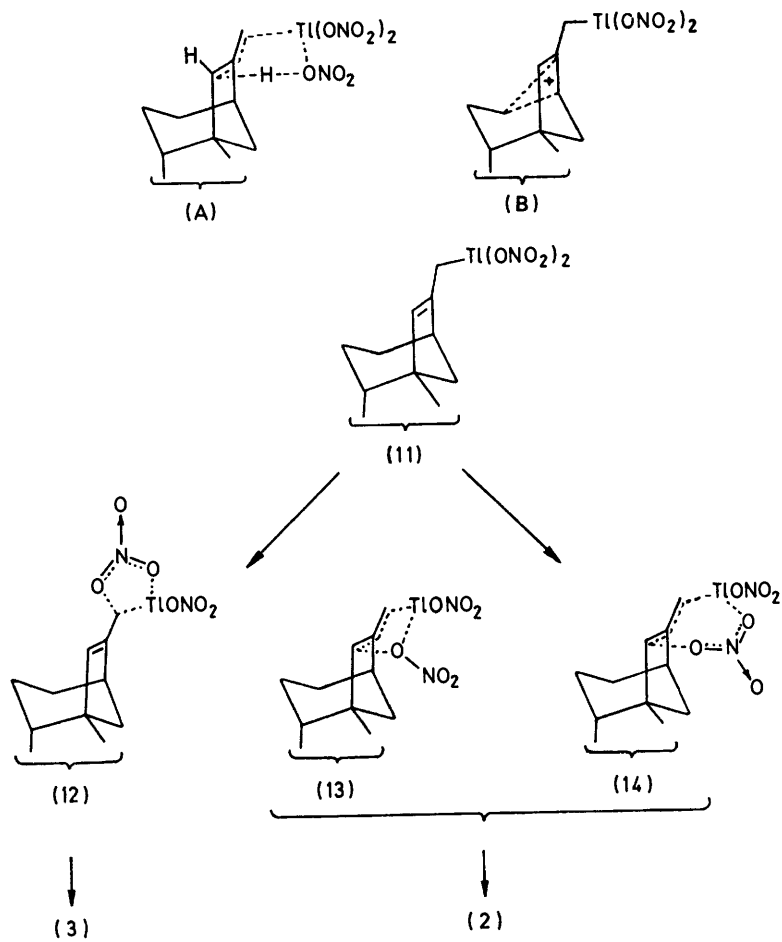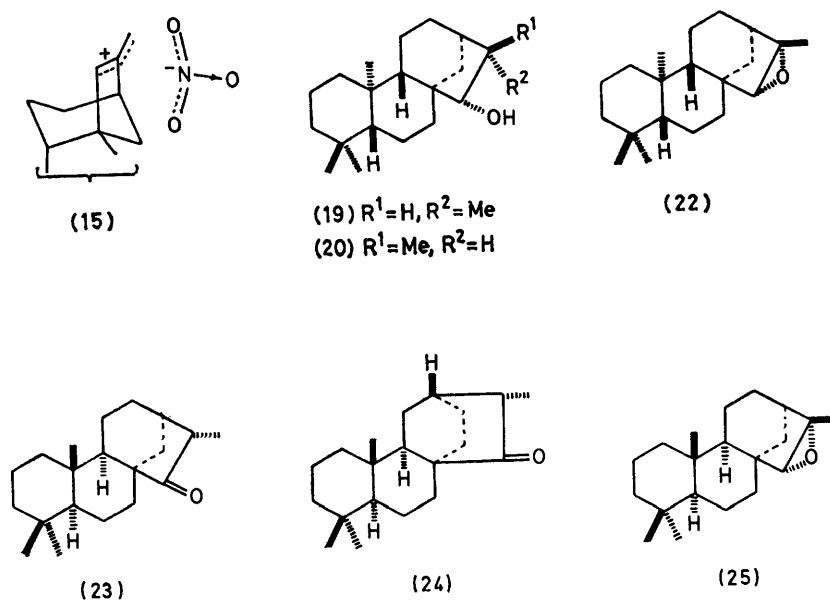
decompose to allylic cation (30), nucleophilic attack on which by water of crystallisation in the TTN would result in the alcohols (5) and (6).

SCHEME 2

In the reaction of (21) with TTN, non-bonded interaction between the 20-Me and the 15β-H in the allylic

organothallium intermediate corresponding to (29) is so large that the intermediate may decompose entirely to the allylic cation corresponding to (30). Thus we did not isolate the nitrates (7) and (8), but the alcohols (9) and (10) were obtained.

The formation of the organothallium alcohol (31) from the carbocation (28) is also conceivable; in fact an epoxide (22), which may be derived from (31) *via* (32), was isolated. This kind of epoxide formation is known in the reaction of olefins with Tl^{III} salts.[13] The acid-catalysed rearrangement of (22) into (5) has been reported.[11b,14] The isomerisation of another allylic alcohol (6) to (5) has also been described.[15] Thus, there seem to be various possible routes to (5).

In the reaction of (21), the epoxide (25), apparently less stable than (22), was not isolated, but the ketone products (23) and (24) must have been derived from (25) by acid-catalysed rearrangement.[11] Generally, *trans*-addition is preferred[16] in the oxythalliation reaction, but the formation of (33) from (26) would be difficult because of the formation of the stable carbocation (28).
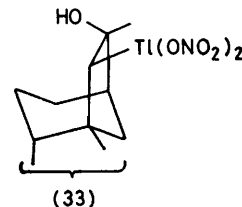
(III) *Allylic Rearrangement of the Allylic Nitrates.*—The rearrangement of allylic esters has been studied widely.[17] Rearrangements of allylic azides,[18] allylic thiocyanates,[19] and allylic thiobenzoates[20] have also been reported. Thus, a similar rearrangement was expected with allylic nitrates.

The allylic nitrate (2) dissolved in benzene was heated at 100 °C for 25 h to give a mixture of nitrates (2) and (3) in the ratio 2 : 5 (based on the n.m.r. spectrum). Similar treatment of the nitrate (3) afforded a mixture of (2) and (3) in the ratio 1 : 2. The equilibrium ratio of the olefins (1) and (16) under iodine catalysis has been observed to be 2 : 3.[21] The slight difference between the nitrates and the hydrocarbons may partially be attributed to non-bonded interactions involving the 15α-ONO$_2$, 7α-H, and 14β-H in (2). When heated

[16] (a) H. Kurosawa, R. Kitano, and R. Okawara, *Chem. Letters*, 1976, 605; (b) C. Freppel, R. Favier, J.-C. Richer, and M. Zador, *Canad. J. Chem.*, 1971, **49**, 2586.

[17] (a) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, 1956, **66**, 753; (b) C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, New York, 1956, p. 586; (c) E. S. Lewis and J. T. Hill, *J. Amer. Chem. Soc.*, 1969, **91**, 7458.

[18] A. Gagneux, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, 1969, **91**, 7458.

[19] (a) A. Iliceto, A. Fava, and U. Mazzucato, *Tetrahedron Letters*, 1960, 27; (b) P. A. S. Smith and D. W. Emerson, *J. Amer. Chem. Soc.*, 1960, **82**, 3076.

[20] S. G. Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 4285.

[21] A. Yoshikoshi, M. Kitadani, and Y. Kitahara, *Tetrahedron*, 1967, **23**, 1175.

[13] W. Kruse and T. M. Bednarski, *J. Org. Chem.*, 1971, **36**, 1154.

[14] F. Piozzi, P. Venturella, A. Bellino, and M. L. Marino, *J.C.S. Perkin I*, 1973, 1164.

[15] J. MacMillan and E. R. H. Walker, *J.C.S. Perkin I*, 1972, 981.

under reflux in benzene for 7 h, the allylic nitrate (7) was entirely converted into (8), which on similar treatment was unchanged. This great difference from the ent-kaurene series is probably attributable to a non-bonded interaction between the 20-Me and 15β-H in (7). The foregoing fact agrees with the iodine-catalysed isomerisation of (4) into (21).[15]

The allylic rearrangements (2) ⟶ (3) and (7) ⟶ (8) were also observed in chromatography on silica gel column (see above).

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 (solutions in [²H]chloroform; tetramethylsilane as internal standard). The mass spectra were determined with a JEOL JMS-OISG double-focusing mass spectrometer. Extracts were dried over anhydrous Na_2SO_4. Mallinckrodt silicic acid and Kieselgel (0.05—0.2 mm; Merck) were used for column chromatography. T.l.c. plates were coated with Silicagel G nach Stahl (Merck).

Reaction of ent-*Kaur-16-ene* (1) *with TTN.*—TTN (400 mg, 0.9 mmol) was added to a solution of ent-kaur-16-ene (1) (200 mg, 0.74 mmol) in 1,2-dimethoxyethane (glyme) (10 ml). The mixture was stirred for 20 min at room temperature. Precipitated thallium(I) nitrate was filtered off, and the filtrate was added to chloroform (50 ml). The solution was washed with water and dried. The solvent was evaporated off *in vacuo* to leave an oil, which was chromatographed on silica gel impregnated with silver nitrate (10%) to give two products. The product with larger R_F value, the 15β-*nitrate* (2), was obtained as prisms (118 mg, 48%), m.p. 75—76° (from acetone-methanol), $v_{max.}$ (CHCl₃) 1 626, 1 275, and 855 cm⁻¹, δ 0.83, 0.87, and 1.05 (each 3 H, s), and 5.23 and 5.42 (2 H, s, and 1 H, s, 15-H, 17-H₂), m/e 333 (M^+), 318 ($M^+ - CH_3$), 287 ($M^+ - NO_2$), and 269 [$M^+ - (HNO_3 + H)$] (Found: C, 72.25; H, 9.45; N, 3.9%; M^+, 333.226. $C_{20}H_{31}NO_3$ requires C, 72.05; H, 9.35; N, 4.2%; *M*, 333.230). The product with smaller R_F value, the 17-*nitrate* (3), was obtained as prisms (73 mg, 30%), m.p. 98° (from acetone), $v_{max.}$ (CHCl₃) 1 622, 1 285, and 854 cm⁻¹, δ 0.80, 0.87, and 1.03 (each 3 H, s), 4.98 (2 H, s, 17-H₂), and 5.58 (1 H, s, 15-H), m/e 333 (M^+), 318 ($M^+ - CH_3$), 287 ($M^+ - NO_2$), 271 ($M^+ - ONO_2$), and 269 [$M^+ - (HNO_3 + H)$] (Found: C, 72.0; H, 9.45; N, 3.9%; M^+, 333.228).

Reduction of the Allylic Nitrate (2).—A solution of the allylic nitrate (2) (33 mg) in methanol (2 ml) and tetrahydrofuran (0.8 ml) was added dropwise to 5% palladium-charcoal (30 mg) under nitrogen. 80% Hydrazine hydrate (35 mg) in methanol (75 mg) was then added and the mixture was stirred for 4 h under nitrogen. The catalyst was filtered off and the solution evaporated *in vacuo* to leave an oil, which was chromatographed. Elution with methylene chloride-hexane (1 : 1) gave ent-kaur-16-en-15β-ol (5) (22 mg, 77%), as needles, m.p. 92—93°, identical (i.r., n.m.r., and mass spectra, and mixed m.p.) with an authentic sample.[22]

Reduction of the Allylic Nitrate (3).—The allylic nitrate (3) (33 mg) was treated with 5% palladium-charcoal (30 mg) and 80% hydrazine hydrate (35 mg) as above. Chromatography gave ent-kaur-15-en-17-ol (6) (20 mg, 70%) as

needles, m.p. 138—139°, identical (i.r., n.m.r., and mass spectra, and mixed m.p.) with an authentic sample derived from ent-kaur-16-ene (1).[5]

Reaction of 13β-Kaur-16-ene (4) *with TTN.*—TTN (200 mg, 0.45 mmol) was added to a solution of 13β-kaur-16-ene (4) (100 mg, 0.37 mmol) in glyme (5.3 ml). The mixture was stirred for 30 min at room temperature. Thallium(I) nitrate was filtered off, and the filtrate was added to hexane (150 ml). Work-up in the usual way afforded an oil, which was chromatographed on silica gel impregnated with silver nitrate (10%) to give two products. The product with larger R_F value, the 15β-*nitrate* (7), was obtained as needles (40 mg, 33%), m.p. 122—123° (from acetone), $v_{max.}$ (KBr) 1 620, 1 275, and 850 cm⁻¹, δ 0.82, 0.85, and 1.03 (each 3 H, s), 5.18 (1 H, s, 17-H), 5.27 (1 H, s, 17-H), and 6.0 (1 H, s, 15-H), m/e 333 (M^+), 318 ($M^+ - CH_3$), 287 ($M^+ - NO_2$), and 269 [$M^+ - (HONO_2 + H)$] (Found: C, 72.0; H, 9.3; N, 4.05%; M^+, 333.230. $C_{20}H_{31}NO_3$ requires C, 72.05; H, 9.35; N, 4.2%; *M*, 333.230). The product with smaller R_F value, the 17-*nitrate* (8), was obtained as plates (61 mg, 50%), m.p. 72—73° (from acetone-methanol), $v_{max.}$ (KBr) 1 637, 1 282, and 875 cm⁻¹, δ 0.73, 0.82, and 0.85 (each 3 H, s), 4.98 (2 H, s, 17-H₂), and 5.88 (1 H, s, 15-H), m/e 333 (M^+), 318 ($M^+ - CH_3$), 287 ($M^+ - NO_2$), and 272 (Found: C, 72.15; H, 9.7; N, 4.25%).

Reduction of the Allylic Nitrate (7).—The allylic nitrate (7) (11 mg) was treated with 5% palladium-charcoal (15 mg) and 80% hydrazine hydrate (25 mg) under nitrogen. Chromatography gave 13β-kaur-16-en-15α-ol (9) (6 mg, 63%) as needles, m.p. 112—113°, identical (i.r. and mass spectra, and mixed m.p.) with an authentic sample (9) prepared from 13β-kaur-15-ene (21).[6]

Reduction of the Allylic Nitrate (8).—The allylic nitrate (8) (44 mg) was treated with 5% palladium-charcoal (80 mg) and 80% hydrazine hydrate (90 mg) under nitrogen as above. Chromatography gave 13β-kaur-15-en-17-ol (10) (25 mg, 66%) as needles, m.p. 125.5—126° (lit.,[7] 125.5—126.5°), $v_{max.}$ (KBr) 3 370, 1 630, and 836 cm⁻¹, δ 0.72, 0.82, and 0.85 (each 3 H, s), 4.17br (2 H, s, 17-H₂), and 5.63br (1 H, s, 15-H), m/e 288 (M^+).

Hydrogenolysis of the Allylic Nitrate (3) *with Lithium Aluminium Hydride.*—To a stirred solution of (3) (11 mg) in tetrahydrofuran (1 ml) was added lithium aluminium hydride (10 mg). After stirring at room temperature for 2 h, the mixture was added to cold ethyl acetate (50 ml). Evaporation, after washing with water and drying, left an oil, which was chromatographed and eluted with hexane to give ent-kaur-15-ene (16) (8 mg, 89%) as needles, m.p. 65—66°, identical (i.r., n.m.r., and mass spectra, and mixed m.p.) with an authentic sample prepared from ent-kaur-16-ene by iodine-catalysed isomerisation.[5]

Reaction of the Allylic Nitrate (3) *with Potassium t-Butoxide.*—The allylic nitrate (3) (20 mg) was dissolved in t-butyl alcohol (2 ml) with warming, and potassium t-butoxide (20 mg) was added at room temperature. The mixture was stirred for 1 h and then extracted with ethyl acetate (50 ml). Evaporation, after washing with water and drying, left an oil, which was chromatographed to yield the αβ-unsaturated aldehyde (17)[5] (16 mg, 93%), m.p. 118—119°, identical with an authentic sample derived from (6) by oxidation.

Reaction of the Allylic Nitrate (3) *with Sodium Methoxide.*—Sodium (20 mg) was dissolved in absolute methanol (2 ml). After cooling to room temperature, the allylic nitrate (3)

²² T. Fujita, I. Masuda, S. Takao, and E. Fujita, *J.C.S. Perkin I*, 1976, 2098.

(40 mg) was added. After stirring for 3 days, the solution was neutralised with 5% hydrochloric acid. Almost all the methanol was evaporated off *in vacuo*, and the residue was extracted with ethyl acetate. After the usual work-up, the residue was chromatographed and eluted with methylene chloride–hexane (3 : 7) to give the *allylic methyl ether* (18) (25 mg, 69%) as needles, m.p. 55—56° (from methanol), $\nu_{max.}$ (CHCl$_3$) 1 641 cm^{-1}, δ 0.82, 0.87, and 1.03 (each 3 H, s), 3.37 (3 H, s, OCH$_3$), 3.97 (2 H, d, J 1.5 Hz, 17-H$_2$), and 5.38 (1 H, m, 15-H), m/e 302 (M^+), 287 ($M^+ - $ CH$_3$), 270 ($M^+ - $ CH$_3$OH), and 255 [$M^+ - $ (CH$_3 + $ CH$_3$OH)] (Found: M^+, 302.262. C$_{21}$H$_{34}$O requires M, 302.261). Elution with methylene chloride–hexane (1 : 1) gave the $\alpha\beta$-unsaturated aldehyde (17) (4 mg, 12%), identical with an authentic sample.

Methylation of the Allylic Alcohol (6).—To a solution of the allylic alcohol (6) (16 mg) in absolute ether (2 ml) was added an excess of diazomethane in ether dried over sodium hydroxide. The solution was cooled to below -10 °C and boron trifluoride–ether solution (0.15 ml) was added with stirring. The yellow colour disappeared immediately. Ether (50 ml) was added, and then the solution was neutralised with sodium hydrogen carbonate, washed with water, and dried. Evaporation *in vacuo* left an oil, which was chromatographed to yield the ether (18) (14 mg, 83%) as needles, m.p. 55—56°, identical with a sample obtained from the allylic nitrate (3).

Catalytic Reduction of the Allylic Nitrate (2).—Platinum oxide (25 mg) was added to a solution of the allylic nitrate (2) (50 mg) in ethanol (5 ml), and hydrogenation was carried out for 40 min. Evaporation *in vacuo* left a residue which was chromatographed to isolate two compounds. The product with larger R_F value was *ent*-16α-kauran-15β-ol (19) (18 mg, 41%), needles, m.p. 76—77°, identical (i.r., n.m.r., and mass spectra) with an authentic sample prepared from (5) by catalytic hydrogenation.[23] The product with smaller R_F value was *ent*-kauran-15β-ol (20) (12 mg, 28%), needles, m.p. 139—141°, identical (i.r., n.m.r., and mass spectra) with an authentic sample.

Reaction of ent-*Kaur-15-ene* (16) *with TTN.*—TTN (200 mg, 0.45 mmol) was added to a solution of *ent*-kaur-15-ene (16) (100 mg, 0.37 mmol) in glyme (5 ml). The mixture was stirred for 3 h at room temperature, and thallium(I) nitrate was filtered off. The filtrate was added to chloroform (50 ml). The solution, after washing with water and drying, was evaporated *in vacuo* to leave an oil, which was chromatographed. Elution with hexane gave a mixture (35 mg, 29%) of nitrates (2) and (3), in the ratio 8 : 9 (by the n.m.r. signals of 16-H and 17-H$_2$). Elution with hexane–methylene chloride (1 : 1) gave a crystalline mass. Recrystallisation from ethanol furnished the *ent*-15β,16-epoxykaurane (22) (12.7 mg, 12%) as plates, m.p. 122—124°, identical (i.r., n.m.r., and mass spectra, and mixed m.p.) with an authentic sample prepared from *ent*-kaur-15-ene (16) by epoxidation.[6] The *ent*-kaur-15-en-17-ol (6) was detected in the mother liquor by t.l.c., but was not isolated. Further elution with the same solvents gave the *ent*-kaur-16-en-15β-ol (5) (25 mg, 24%) as needles, m.p. 90—91°, identical (i.r., n.m.r., and mass spectra, and mixed m.p.) with an authentic sample.[22]

Reaction of 13β-*Kaur-15-ene* (21) *with TTN.*—TTN (330

mg) was added to a solution of 13β-kaur-15-ene (21) (150 mg) in glyme (8 ml). The mixture was stirred for 24 h at room temperature. The precipitated inorganic salt was filtered off, and the filtrate was added to ethyl acetate (100 ml). Work-up in the usual way gave an oil, which was chromatographed. Elution with hexane gave starting material (21) (36 mg, 24%). Elution with hexane–methylene chloride (7 : 3) furnished a crystal (6 mg) of 13β,16β-kauran-15-one (23) (4 mg, 2.5%), m.p. 126—127° (from methanol), identical with an authentic sample prepared by the reaction [11b] of 15α,16-epoxy-13β-kaurane (25) with boron trifluoride. Elution with hexane–methylene chloride (1 : 1) gave an oil (51 mg). Preparative t.l.c. [hexane–methylene chloride (4 : 6)] yielded three products. The compound with highest R_F value was 12β-atisan-15-one (24) (9 mg, 5.7%), m.p. 134—135°, identical (i.r., n.m.r., and mass spectra, and mixed m.p.) with a freshly prepared sample.[11] The compound of intermediate R_F value was 13β-kaur-16-en-15α-ol (9) (14 mg, 8.8%), m.p. 111.5—112°, identical (i.r., n.m.r., and mass spectra, and mixed m.p.) with an authentic sample. The compound with lowest R_F value was 13β-kaur-15-en-17-ol (10) (12 mg, 7.6%), m.p. 125.5—126°, identical with an authentic sample.

Allylic Rearrangement by Heating.—(a) *The allylic nitrate* (2). The nitrate (2) (10 mg), dissolved in benzene (1 ml), was heated at 100 °C (oil-bath temp.) in a sealed tube for 25 h. The mixture was purified by chromatography (short column) to give a mixture (8 mg) of (2) and (3) in the ratio 2 : 5 (by n.m.r. signals of 15-H and 17-H$_2$).

(b) *The allylic nitrate* (3). The nitrate (3) (20 mg), dissolved in benzene (2 ml), similarly gave a mixture (19 mg) of (2) and (3) in the ratio 1 : 2 (by n.m.r.).

(c) *The allylic nitrate* (7). The nitrate (7) (9 mg), dissolved in benzene (2 ml), was refluxed for 7 h, after which it had disappeared completely (t.l.c.). Removal of the solvent afforded the allylic nitrate (8) (7.5 mg, 83%) as plates, m.p. 70—71°, identical with an authentic sample.

(d) *The allylic nitrate* (8). A solution of the nitrate (8) (10 mg) in benzene (2 ml) was refluxed for 7 h. Removal of the solvent left only the starting material (8 mg, 80%).

Treatment of the Nitrate (2) *with TTN, Thallium*(I) *Nitrate, and Nitric Acid.*—A solution of TTN (61 mg) and (2) (46 mg) in glyme (2.3 ml) was stirred for 3 h; no change was observed (t.l.c.). After addition of thallium(I) nitrate (37 mg) and stirring for 1 h, nitric acid (d 1.42; 0.04 ml) was added, and stirring was continued for 3 h; no change was again observed (t.l.c.).

Treatment of the Nitrate (2) *with Silica Gel.*—The nitrate (2) (14 mg) was adsorbed on silica gel (1 g). After 1 h elution with methylene chloride–hexane (1 : 9) gave a mixture (12 mg) of (2) and (3) (1 : 1).

[23] J. MacMillan and E. R. H. Walder, *J.C.S. Perkin I*, 1972, 986.