Reactions of *ent*-16- and *ent*-15-Kaurenes with Thallium(III) Trinitrate and a Sigmatropic Rearrangement between the Allylic Nitrate Products

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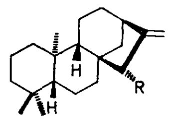
Summary The formation of the allylic nitrates, (**1b**) and (**2b**), in the reactions of both *ent*-16-kaurene (**1a**) and *ent*-15-kaurene (**2a**) with thallium(III) trinitrate, and a [3,3]-sigmatropic rearrangement between (**1b**) and (**2b**), are reported.

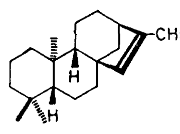
Recent reports by Cambie and his co-workers[1] on the reactions of phyllocladene and isophyllocladene with thallium(I) acetate–iodine have prompted us to publish our findings on the reactions of kaurenes with thallium(III) trinitrate (TTN).

The thallium(III) salts are 'soft acids', and they easily react with 'soft bases', for instance, olefins.[2] Treatment of *ent*-16-kaurene (**1a**) with TTN in glyme for 20 min gave a mixture of products, from which *ent*-16-kauren-15β-ol nitrate (**1b**) and *ent*-15-kauren-17-ol nitrate (**2b**) were isolated (by column chromatography on silica gel impregnated with silver nitrate) in 48 and 30% yields, respectively; {(**1b**), m.p. 75—76 °C, $C_{20}H_{31}NO_3$, ν_{max} ($CHCl_3$) 1626 and 1275 cm^{-1} (ONO_2), δ ($CDCl_3$) 5·42 br (1H, s) and 5·23 br (2H, s), *m/e* 333 (M^+), 287 ($M^+ - NO_2$), and 269 [$M^+ - (HONO_2 + H)$]; (**2b**), m.p. 98 °C, $C_{20}H_{31}NO_3$, ν_{max} ($CHCl_3$) 1622 and 1285 cm^{-1} (ONO_2), δ ($CDCl_3$) 5·58 (1H, s, 15-H) and 4·98 (2H, s, 17-H_2), *m/e* 333 (M^+), 287 ($M^+ - NO_2$), 271 ($M^+ - ONO_2$), and 269 [$M^+ - (HONO_2 + H)$]}. The following reactions also confirmed the structures of (**1b**) and (**2b**). Reduction of the nitrates (**1b**) and (**2b**) with 80% hydrazine hydrate in the presence of 5% palladium–charcoal in MeOH[3] gave the known allylic alcohols (**1c**) (77% yield) and (**2c**) (70% yield), respectively. The nitrate (**2b**) on hydrogenolysis with $LiAlH_4$ gave *ent*-15-kaurene (**2a**) in 89% yield, on treatment with MeONa in

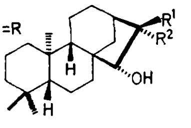
MeOH gave *ent*-17-methoxy-15-kaurene (**2d**),† m.p. 55—56 °C, $C_{21}H_{34}O$, δ ($CDCl_3$) 5·38 (1H, s, 15-H), 3·97 (2H, s, 17-H_2), and 3·37 (3H, s, OMe), in 69% yield, and on treatment with Bu^{t}OK in Bu^{t}OH afforded an αβ-unsaturated aldehyde (**2e**)[4] in 93% yield. Catalytic hydrogenation (PtO_2 in EtOH) of the nitrate (**1b**) gave the saturated alcohol isomers (**3**) and (**4**), in 41 and 28% yields, respectively. The fact that epimer (**3**) was obtained as the major product is probably due to steric hindrance of the α-side of ring D by the bulky nitrate.



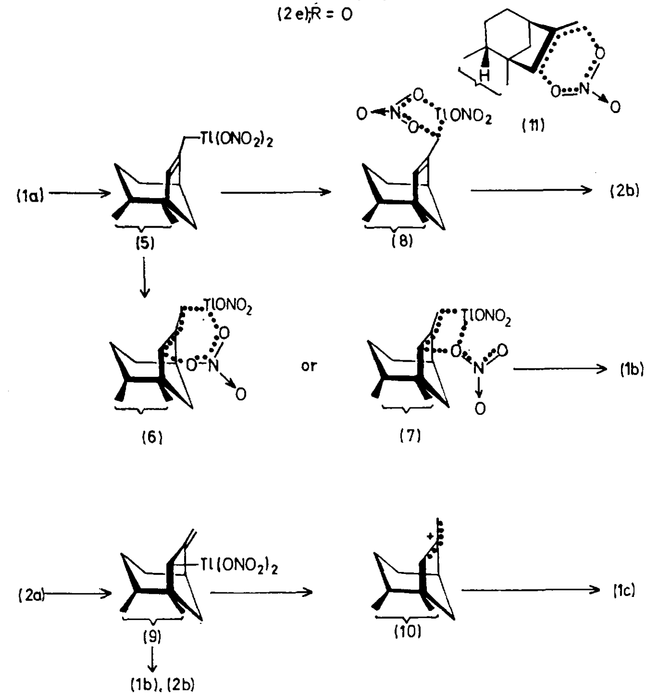
(1a);R=H
(1b);R =ONO_2
(1c);R =OH



(2a);R=H_2
(2b);R=$<^{H}_{ONO_2}$
(2c);R=$<^{H}_{OH}$
(2d);R=$<^{H}_{OMe}$
(2e);R = O



(3);R^1=H, R^2 = Me
(4);R^1=Me, R^2=H



Treatment of *ent*-15-kaurene (**2a**) with TTN in glyme for 3 h gave both nitrates (**1b**) and (**2b**) in 29% total yield and also *ent*-16-kauren-15β-ol (**1c**) in 24% yield.

The initial step in the oxidation of (**1a**) and (**2a**) with TTN must be the rapid formation of a π-complex, from which the allyl organothallium derivatives (**5**) and (**9**)[5] may be produced *via* a non classical carbonium ion by elimination of the 15- or 17-proton before attack of any nucleophile on the carbonium ions. The rate of formation of (**5**) is likely to be more rapid than that of (**9**), because the latter is more unstable than the former. The reaction with (**1a**) does in fact take a shorter time than that with (**2a**), as described previously.[6] The successive heterolysis of the C–Tl bond may occur rapidly, because of the low bond energy and the location of Tl on the allylic carbon atom, and its rate is probably more rapid in (**9**) than in (**5**). The more stable intermediate (**5**) only gives rise to nitrates (**1b**) and (**2b**) *via* intramolecular cyclic transition states[7] such as (**6**) [or (**7**)] and (**8**). On the other hand, the more unstable intermediate (**9**) may partially produce the allylic cation (**10**),[8] from which the alcohol (**1c**) can be formed by the nucleophilic addition[9] of the water of crystallization in TTN.

The nitrate (**1b**) on heating in benzene in a sealed tube at 100 °C for 25 h gave a mixture of the nitrates (**1b**) and (**2b**) in the ratio of 2:5. The nitrate (**2b**) on the same treatment also gave a mixture of (**1b**) and (**2b**) in the ratio of 1:2. These findings can be explained as a [3,3]sigmatropic rearrangement *via* an intramolecular cyclic transition state (**11**). It is reasonable that the thermodynamically more stable isomer (**2b**) is the major product.

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† This compound was also obtained in 83% yield by the reaction of (**2c**) with CH_2N_2 and BF_3-etherate.

[1] R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Chem. Comm.*, 1973, 359; *J.C.S. Perkin I*, 1974, 1120.

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

[3] R. Boshan, R. T. Merrow, and R. W. Van Dolah, *Chem. Rev.*, 1955, **55**, 485.

[4] M. F. Barnes and J. MacMillan, *J. Chem. Soc. (C)*, 1967, 361.

[5] J. B. Lee and M. J. Price, *Tetrahedron*, 1964, **20**, 1017; B. Cocton and A. C. De Paulet, *Bull. Soc. chim. France*, 1966, 2947; A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1973, **95**, 3635.

[6] *Cf.* A. G. Lee, in 'Organometallic Reactions,' ed. E. I. Becker and M. Tsutsui, Wiley, New York, 1975, Vol. 5, p. 1. It is described that the rate-determing step is probably in the formation of the C-Tl bond.

[7] A. McKillop, B. P. Swann, M. E. Ford, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1973, **95**, 3641.

[8] W. F. Erman, *J. Org. Chem.*, 1967, **32**, 765.

[9] A. McKillop, J. D. Hunt, R. D. Naylor, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1971, **93**, 4918.