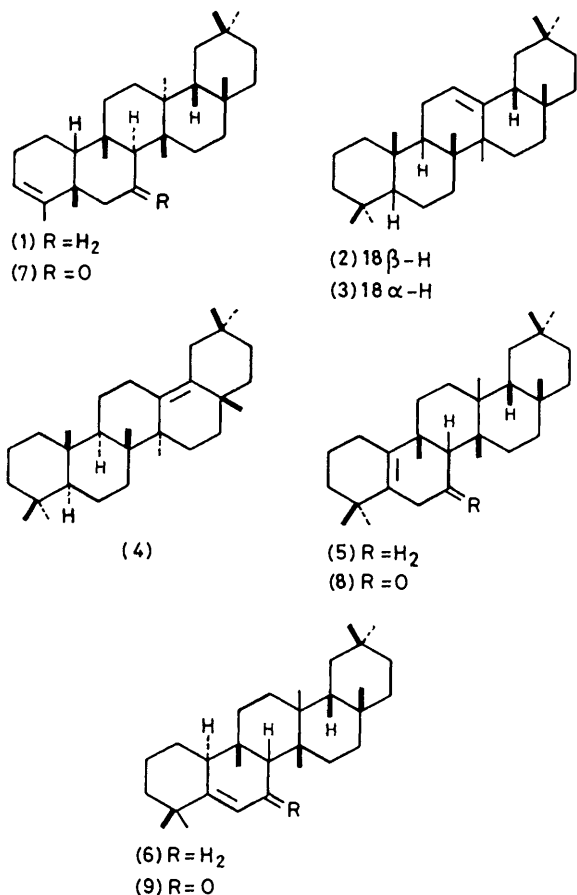


Terpenoids and Related Compounds. Part 24.¹ Molecular Rearrangements in Friedo-oleanenes

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D : A-Friedo-oleana-3,7-diene (10) underwent rearrangement on refluxing with hydrochloric acid in acetic acid to give the conjugated diene (12) [oleana-11,13(18)-diene]. Further, the action of phosphoryl chloride and pyridine on the 7-hydroxy-3-acetates (13) and (19) furnished the 7-ene-3-acetates (14) and (20), respectively. On the other hand the action of perchloric acid in acetic anhydride on (13) and (19) furnished the rearranged 14-ene-3-acetates (15) and (21), respectively. A part of this work constituted a correction of previously published work.

D : A-FRIEDO-OLEAN-3-ENE (1) undergoes acid-catalysed molecular rearrangement² to yield olean-12-ene (2), 18-*epi*-olean-12-ene (3), and olean-13(18)-ene (4). However under milder conditions (1) rearranges to glut-5(10)-ene (5),³ which on vigorous treatment with acids



yields an equilibrium mixture containing (2), (3), and (4). Spring and his co-workers⁴ however reported the isolation of a mixture of (2) and (4) only after acid-catalysed rearrangement of glut-5-ene (6).

¹ Part 23, P. Sengupta and S. K. Saha, *Indian J. Chem.*, in the press.

² E. J. Corey and J. J. Ursprung, *J. Amer. Chem. Soc.*, 1955, **77**, 3667; 1956, **78**, 5041; H. Dutler, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, 1955, **38**, 1268.

³ J. L. Courtney, R. M. Gascoigne, and A. Z. Szumer, *Chem. and Ind.*, 1956, 1479; V. V. Kane and R. Stevenson, *ibid.*, 1960, 1243; R. M. Coates, *Tetrahedron Letters*, 1967, 4143; H. W. Whitlock and M. C. Smith, *ibid.*, 1968, 821.

Further, it has been demonstrated^{4,5} that glut-5(10)-ene (5) and its derivatives are thermodynamically more stable than glut-5-ene (6) and its derivatives. It was concluded³ that the molecular rearrangement of (1) was not a single-step concerted process but a two-stage process, each step being an irreversible concerted process. The first step represents the conversion of (1) into (5) or (6) and the second consists of the conversion of (5) into a mixture of (2), (3), and (4).

It was shown by us⁶ that the presence of a 7-oxo-function in the friedo-olean-3-ene skeleton seriously affected the course of molecular rearrangement. Thus with friedo-olean-3-en-7-one (7) the rearrangement was restricted to the first stage to yield a separable mixture of (8) and (9). Kitkuchi and his co-workers⁷ showed that a 16-oxo-function in the friedo-oleanene skeleton did not limit the rearrangement to the first stage, and oleanen-16-ones were obtained.

The present work deals with the effect of a Δ^7 -linkage on the molecular rearrangement of friedo-olean-3-ene. For this purpose D : A-friedo-oleana-3,7-diene (10) was prepared in good yield by dehydration of putranjivadiol (11)⁸ with phosphoryl chloride and pyridine. The ¹H n.m.r. spectrum showed singlets at δ 0.95 (3 H), 0.98 (3 H), 1.00 (6 H), 1.04 (3 H), 1.12 (3 H), and 1.21 (6 H) for the eight methyl groups. The signals for the olefinic protons at C-3 and C-7 merged into a broad multiplet (2 H) around δ 5.38. When the diene (10) was refluxed with aqueous hydrochloric acid and acetic acid for 14 h, the major component isolated was the conjugated diene (12), with physical data in complete agreement with those reported.⁹ The n.m.r. spectrum of (12) showed singlets at δ 0.73 (3 H), 0.75 (3 H), 0.82 (3 H), 0.87 (3 H), 0.88 (3 H), 0.98 (6 H), and 1.05 (3 H) for the eight tertiary methyl groups. The signal for the olefinic proton at C-11 appeared as a pair of doublets (1 H) at δ 6.33

⁴ J. M. Beaton, F. S. Spring, R. Stevenson, and J. L. Steward, *Tetrahedron*, 1958, **2**, 246; J. M. Beaton, F. S. Spring, and R. Stevenson, *J. Chem. Soc.*, 1955, 2616; F. S. Spring, J. M. Beaton, R. Stevenson, and J. L. Steward, *Chem. and Ind.*, 1956, 1054.

⁵ P. Sengupta, S. Ghosh, and L. J. Durham, *Tetrahedron*, 1966, **22**, 3469.

⁶ P. Sengupta, J. Mukherjee, and M. Sen, *Tetrahedron*, 1971, **27**, 2473.

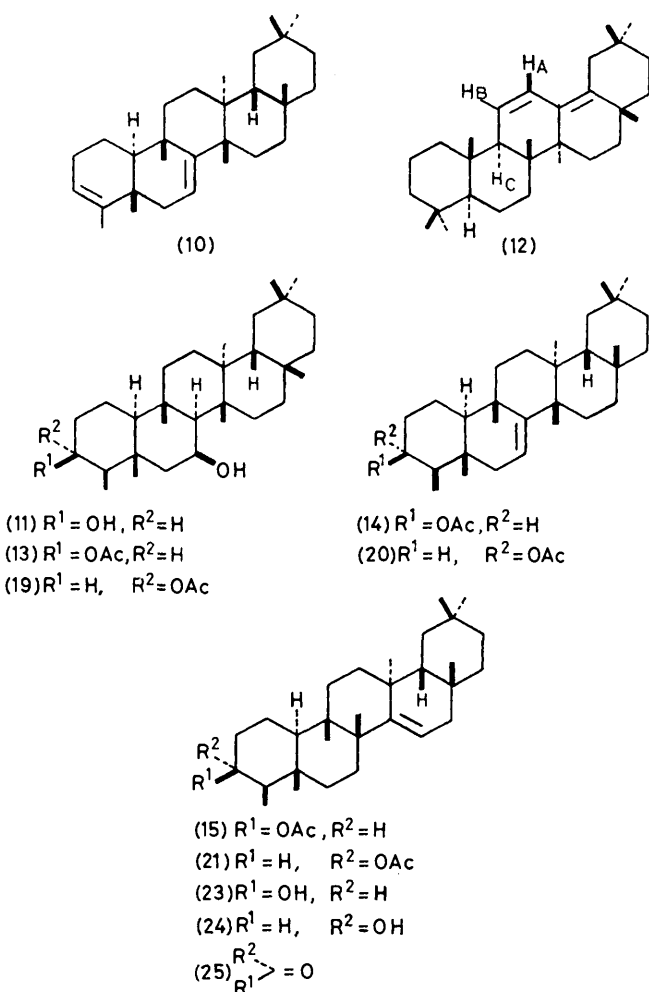
⁷ T. Kitkuchi, M. Takayama, T. Toyoda, M. Arimoto, and M. Niwa, *Chem. and Pharm. Bull. (Japan)*, 1973, **21**, 2243.

⁸ P. Sengupta, A. K. Chakravarty, L. J. Durham, A. Duffield, and C. Djerassi, *Tetrahedron*, 1968, **24**, 1205; P. Sengupta, *J. Indian Chem. Soc.*, 1974, **51**, 131.

⁹ J. L. Courtney, R. M. Gascoigne, and A. Z. Szumer, *J. Chem. Soc.*, 1958, 881.

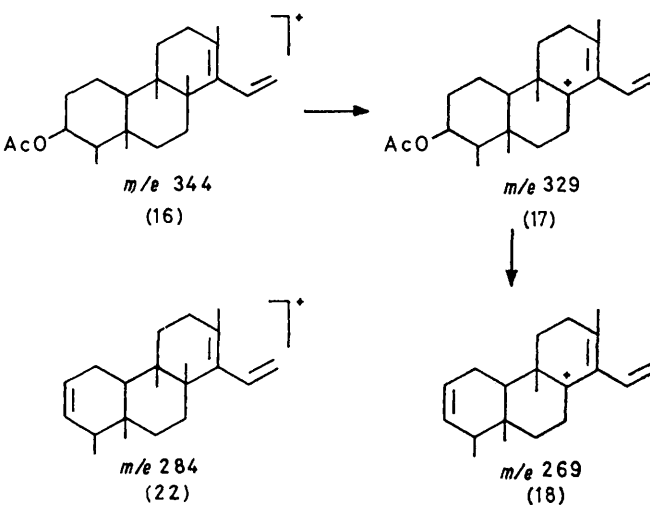
(J_{AB} 11, J_{BC} 3 Hz) and that for the olefinic proton at C-12 as a pair of doublets (1 H) at δ 5.32 (J_{AB} 11, J_{AC} 2 Hz).

We have previously¹⁰ reported the preparation of the ene-acetate (14), m.p. 152–156°, [α]_D –35.8°, by the action of a drop of perchloric acid on 3 β -acetoxyfriedo-olean-7 β -ol (13) in acetic anhydride. Since we needed the ene-acetate (14) for another purpose, we decided to prepare it by the action of phosphoryl chloride and pyridine on the hydroxy-acetate (13). To our surprise this method gave a different ene-acetate, m.p. 230–232°, [α]_D –23.7°. It is known that elimination of water in a highly basic medium like pyridine does not normally lead to any skeletal rearrangement. Hence the ene-acetate of m.p. 230–232° must have structure (14). The n.m.r. spectrum showed an ill-defined multiplet (1 H) at δ 4.9 for the proton at C-3 and a triplet (1 H) at δ 5.27 (J 4 Hz) for the olefinic proton at C-7.



Thus the structure of the ene-acetate¹⁰ of m.p. 152–156° had to be revised. It was established as the rearranged product (15) from physical data. The n.m.r. spectrum showed a multiplet (1 H) at δ 4.9 due to the proton at C-3 and the signal for the olefinic proton at

C-15 appeared as a pair of doublets (1 H) at δ 5.74 (J 5 and 7 Hz). The mass spectrum of this ene-acetate (15) was more diagnostic. The retro-Diels–Alder (RDA)



fragment (16) at m/e 344 was the base peak, and led to the fragments at m/e 329 (17) and 269 (18). The RDA fragment from the ene-acetate (14) was not significant, consistent with the spectra of related triterpenoids.¹¹ The unusual stability of the Δ^{14} -bond was due to the *cis*-BC ring junction. The ene-acetate (14), m.p. 230–232° could be rearranged to the ene-acetate (15), m.p. 152–156° on treatment with perchloric acid in acetic anhydride.

Similarly 3 α -acetoxyfriedo-olean-7 β -ol (19) on treatment with phosphoryl chloride and pyridine yielded the ene-acetate (20), m.p. 257–260°, [α]_D –52°, which was different from the ene-acetate,¹⁰ m.p. 147–148°, [α]_D –86°, obtained by the treatment of (19) with perchloric acid in acetic anhydride. The latter acetate must have structure (21). The mass spectrum of (21) showed the RDA fragment (16) at m/e 344 (75%) and the base peak at m/e 284 corresponding to the ion (22). The ene-acetate (20) could be rearranged to the ene-acetate (21) on treatment with perchloric acid in acetic anhydride. Hence the corresponding alcohols, m.p. 162–165°, [α]_D –51°, and m.p. 176–180°, [α]_D –74°, reported in ref. 10 had structures (23) and (24), respectively, and the corresponding ketone, m.p. 140–141°, [α]_D –87.8°, structure (25).

These results cast doubt on the structure published⁸ for the product of the treatment of 7 β -hydroxyfriedelane with acetic anhydride and perchloric acid. Work on this problem is in progress.

EXPERIMENTAL

U.v. spectra were taken for solutions in 95% ethanol and rotations for solutions in chloroform. N.m.r. spectra were taken at 60 MHz for solutions in deuteriochloroform

¹⁰ P. Sengupta and J. Mukherjee, *Tetrahedron*, 1968, **24**, 6259.

¹¹ H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 3688.

with tetramethylsilane as internal standard. Light petroleum used had b.p. 60–80 °C. I.r. spectra were taken for Nujol mulls.

D: *A-Friedo-oleana-3,7-diene* (10).—Phosphoryl chloride (10 ml) was slowly added to a solution of putranjivadiol⁸ (11) (0.5 g) in pyridine (62 ml). The solution was left overnight at room temperature, then refluxed for 5 min, cooled, and poured into crushed ice. After the usual work-up, the residue (0.49 g) was chromatographed over alumina (50 g). Elution with light petroleum furnished a solid (0.48 g), m.p. 198–205°, which on crystallisation from chloroform–acetone gave the *diene* (10), m.p. 212–215°, $[\alpha]_D + 49^\circ$ (Found: C, 88.15; H, 11.8. $C_{30}H_{48}$ requires C, 88.15; H, 11.85%), ν_{\max} 815 cm^{-1} (trisubstituted double bond); for n.m.r. data see main text; *m/e* 408 (M^+ , 12%), 393 (22), 218 (100), 205 (14), 203 (22), 189 (32), and 133 (22).

Rearrangement of D: *A-Friedo-oleana-3,7-diene* (10): *Oleane-11,13(18)-diene* (12).—The *diene* (10) (0.3 g) was refluxed with conc. hydrochloric acid (150 ml) and glacial acetic acid (240 ml) for 14 h. The solution was cooled and diluted with water to yield a solid (0.29 g), which was chromatographed over a column of silver-nitrate-impregnated silica gel (10 g). Elution with light petroleum furnished a solid (0.27 g), m.p. 188–195°, which on crystallisation from chloroform–acetone yielded pure *diene* (12),⁹ m.p. 215–220°, $[\alpha]_D - 60^\circ$ (Found: C, 88.2; H, 11.8. Calc. for $C_{30}H_{48}$: C, 88.15; H, 11.85%); for n.m.r. data see main text; λ_{\max} 242 (ϵ 31 450), 251 (35 800), and 260 nm (23 000).

3 β -Acetoxyl-friedo-olean-7-ene (14).—Phosphoryl chloride (5 ml) was slowly added to a solution of *3 β -acetoxyl-friedo-olean-7 β -ol* (13) (0.25 g) in pyridine (30 ml). The mixture was treated as above to yield a residue (0.24 g) which was chromatographed over a column of silver-nitrate-impregnated silica gel (25 g). Elution with light petroleum–benzene (9 : 1) furnished a solid (0.24 g), m.p. 224–228°, which on crystallisation from chloroform–acetone yielded pure *ene-acetate* (14), m.p. 230–232°, $[\alpha]_D - 23.7^\circ$ (Found: C, 81.9; H, 10.95. $C_{32}H_{52}O_2$ requires C, 82.0; H, 11.2%), ν_{\max} 1 740 and 1 240 (acetate) and 890 cm^{-1} (trisubstituted double bond); for n.m.r. data see main text; *m/e* 468 (M^+ , 6%), 453 (3), 408 (2), 393 (3), 218 (100), 205 (13), 203 (21), 189 (22), and 133 (26).

The Ene-acetate (15).—This was prepared from the

hydroxy-acetate (13) by the action of a drop of perchloric acid in acetic anhydride according to the published procedure;¹⁰ ν_{\max} 1 740 and 1 250 (acetate) and 825 cm^{-1} (trisubstituted double bond); for n.m.r. data see main text; *m/e* 468 (M^+ , 4%), 453 (4), 409 (3), 393 (3), 344 (100), 329 (26), 284 (47), 269 (29), and 203 (9).

Treatment of the Ene-acetate (14) with Acetic Anhydride and Perchloric Acid.—A drop of perchloric acid was added to an ice-cold suspension of the *ene-acetate* (14) (0.1 g) in acetic anhydride (5 ml). The mixture was stirred for 10–15 min then poured into cold saturated aqueous $NaHCO_3$. After the usual work-up the residue (0.1 g) was chromatographed over a column of silver-nitrate-impregnated silica gel (10 g). Elution with light petroleum furnished a solid (0.03 g), m.p. 145–152°, which on crystallisation from chloroform–methanol yielded pure (15), identical with that already obtained, m.p. 152–156°.

The Ene-acetate (20).—This was prepared from the hydroxy-acetate (19) by treatment with phosphoryl chloride–pyridine according to the above procedure. The resulting *ene-acetate* (20), m.p. 257–260°, $[\alpha]_D - 52^\circ$, showed δ 2.05 (3 H, s, OAc), 4.65 (1 H, m, H-3), and 5.33 (1 H, m, H-7), besides methyl signals; *m/e* 468 (M^+ , 10%), 453 (5), 408 (8), 393 (10), 218 (100), 205 (14), 203 (22), 189 (20), and 133 (38) (Found: C, 82.0; H, 11.0. $C_{32}H_{52}O_2$ requires C, 82.0; H, 11.2%).

The Ene-acetate (21).—This was prepared according to the published procedure;¹⁰ m.p. 147–148°, $[\alpha]_D - 86^\circ$, δ 2.00 (3 H, s, OAc), 4.7 (1 H, m, H-3), and 5.76 (1 H, dd, *J* 4 and 8 Hz, H-15), besides the methyl signals; *m/e* 468 (M^+ , 6%), 453 (4), 408 (4), 393 (5), 344 (75), 329 (7), 284 (100), 269 (75), and 203 (36).

Treatment of the Ene-acetate (20) with Acetic Anhydride and Perchloric Acid.—The *ene-acetate* (20) on treatment with perchloric acid and acetic anhydride as above furnished the *ene-acetate* (21), identical with that described above, m.p. 147–148°.

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