was hydrolysed by steam distillation.[9] After 2 h, TLC showed the hydrolysis to be complete. Charcoal (1 g) was added, and the solution neutralised with barium hydroxide and barium carbonate. The precipitated barium sulfate was filtered off and washed with hot water. The solution and washings were combined and evaporated to a syrup which was dissolved in hot glacial acetic acid (25 ml). The solution was cooled, nucleated with a few crystals of D-mannose, and kept for 2 days with occasional stirring, and then for one day in a refrigerator. The crystalline D-mannose was filtered off, washed with cold ethanol, then ether and dried, yield 13 g; m.p. 130 – 131 °C, $[\alpha]_D^{20}$ + 14° (equil., water) {lit.[3] $[\alpha]_D^{20}$ + 14.2° (equil., water)}.

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Triterpenes. *p*-Toluenesulfonic Acid Catalysed Rearrangement of 18α,19α and 18β,19β Isomers of 3β,28-Diacetoxy-epoxylupane

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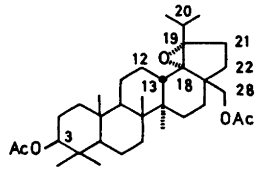
In a previous communication [1] we reported the BF_3-catalysed rearrangement of the 18α,19α- and 18β,19β-epoxylupane derivatives *1* and *2*. This paper deals with the rearrangement of the same epoxides *1* and *2* catalysed by the protic acid *p*-toluenesulfonic acid (TosOH). The reaction of either epoxide with $BF_3.Et_2O$ or TosOH afforded the same E-ring opened rearrangement product, *i.e.* the baccharane derivative *3*, the other products consisting of a number of dienes. In general, TosOH yields more dehydration products and less skeletally rearranged compound *3* than the BF_3-etherate.



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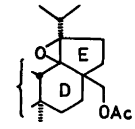

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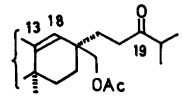

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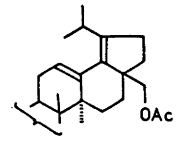

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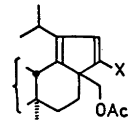

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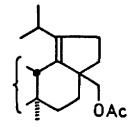
7 X = Br



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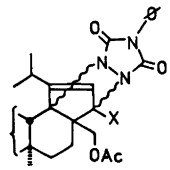
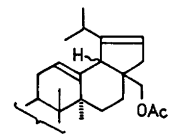


8 X = H
9 X = Br



10

The 18β,19β-epoxylupane derivative *2*, when treated with TosOH in benzene, gave in *ca.* 30 % yield the baccharane derivative *3* as compared to the *ca.* 90 % obtained with BF_3-etherate. The main products in the TosOH reaction were two conjugated dienes, together *ca.* 70 %. The less polar diene on $AgNO_3$ impregnated silica plate was identical with the compound *4* obtained in a 10 % yield from the BF_3-catalysed reaction of the β-epoxide *2*. The more polar diene had the structure *5*. Prolonged reaction time increased the proportional amount of diene *4*. Isomerisation of diene *5* to diene *4* was confirmed by a separate experiment under the same conditions. For comparison, the diene *5* was prepared from *6 via* a low-temperature bromination-dehydrobromination. This reaction at room temperature gave a mixture of products, among them the bromodiene *7*, which was also obtained from *6 via* a NBS/dehydrobromination sequence. Both the diene *5* and bromodiene *7* form a Diels-Alder adduct *8* and *9* with 4-phenyl-1,2,4-triazoline-3,5-dione. The ^1H NMR spectra of the adducts show the known [2] low field δ value (6.20 and 6.25) for the C-21 proton.

Reaction of the 18α,19α-epoxy derivative *1* with TosOH affords *ca.* 85 % of the baccharane derivative *3*, while BF_3-etherate yields this compound quantitatively. The TosOH catalysed reaction gives, in addition, *ca.* 15 % of the unconjugated diene *10*.

Experimental. For general experimental information see Ref. 1.

Reaction of 3β,28-diacetoxy-18β,19β-epoxylupane (2) with TosOH. 3β,28-Diacetoxy-18β,19β-epoxylupane [1] (*2*) (0.5 g) in dry benzene (20 ml), $TosOH.H_2O$ (0.1 g), and Ac_2O (0.15 g) was refluxed for 5 h. The mixture was washed with $NaHCO_3$ solution, dried, the solvent evaporated and the residue chromatographed on silica plates. The more polar of the two main fractions was 3β,28-diacetoxy-18,19-secolup-13(18)-en-19-one (*3*) crystallised from EtOH (0.1 g) m.p. 113 °C, $[\alpha]_D$ −35° (*c* 1.0). (Ref. 1, m.p. 115 °C, $[\alpha]_D$ −34.8°.) The less polar fraction was chromatographed on a 10 % $AgNO_3$ impregnated silica plate to give two compounds. The less polar compound was identified as 3β,28-diacetoxy-lupa-12,18-diene [1] (*4*) crystallised from EtOH (0.15 g) m.p. 140 °C, $[\alpha]_D$ +241° (*c.* 1.1). (Ref. 3, m.p. 140−143 °C, $[\alpha]_D$ +219°). The more polar 3β,28-diacetoxy-lupa-18,21-diene (*5*) crystallised from EtOH (0.1 g) had m.p. 217 °C, $[\alpha]_D$ −118° (*c* 1.0); λ_{max} (abs. EtOH) 253 nm (ε 3500); *m/e* (% rel. int.) 524 (13, M^+), 464 (18), 451 (35), 361 (13), 274 (12), 261 (13), 249 (7), 214 (21), 201 (100), 200 (45), 199 (23), 189 (44), 187 (52), 173 (82); δ (CCl_4) 6.30 (2 H, s, C-21 and C-22 protons; Eu(DPM)$_3$ addition splits the singlet to AB quartet *J* 5.3 Hz), 4.40 (1 H, m, 3αH), 4.40 and 3.35 (à 1 H, d, *J* 11 Hz, C-28 protons), 3.3−2.2 (2 H, m, C-13 and C-20 protons), 1.95 (6 H, s, acetyl protons), 1.25−0.75 (group of 7 methyls). Anal. $C_{34}H_{52}O_4$: C, H.

Isomerisation of 3β,28-diacetoxy-lupa-18,21-diene (5). 3β,28-Diacetoxy-lupa-18,21-diene (*5*) (0.2 g) in dry benzene (10 ml), $TosOH.H_2O$ (0.1 g), and Ac_2O (0.1 g) was refluxed for 2 h. The mixture was worked up as above and chromatographed on a 10 % $AgNO_3$ impregnated silica plate. The least polar main fraction (20 mg) was identical with 3β,28-diacetoxy-lupa-12,18-diene (*4*) obtained above.

Bromination of 3β,28-diacetoxy-lup-18-ene (6). To the solution of 3β,28-diacetoxy-lup-18-ene (*6*) (0.52 g) in $CHCl_3$ (10 ml) was added bromine (0.16 g) in CCl_4 (1 ml) at −40 °C. After 2 h the reaction mixture was washed with water, $NaHCO_3$ solution, dried and chromatographed on 10 % $AgNO_3$ impregnated silica plates. The main product was identical with 3β,28-diacetoxy-lupa-18,21-diene (5) obtained above. The reaction mixture contained, in addition, small amounts of starting material *6* and bromodiene *7*, characterised below.

At room temperature a similar reaction gave a complex mixture with increased amount of bromodiene *7*.

Reaction of 3β,28-diacetoxy-lup-18-ene (6) with NBS. 3β,28-Diacetoxy-lup-18-ene (*6*) (0.5 g), *N*-bromosuccinimide (0.7 g), and dibenzoylperoxide (0.2 g) in CCl_4 (30 ml) were refluxed for 15 min. Succinimide was filtered off, the mixture washed with $NaHCO_3$ solution, dried and evaporated. Chromatography on 10 % $AgNO_3$ impregnated silica plates gave 22-bromo-3β,28-diacetoxy-lupa-18,21-diene (*7*), crystallised from EtOH (0.3 g) m.p. 179 °C, $[\alpha]_D$ −116° (*c* 0.95); λ_{max} (abs. EtOH) 269 nm (ε 6100): ν 1730, 1615, 1550, 1225, 1215, δ (CCl_4) 6.45 (1 H, s, C-21 proton), 4.50 (1 H, m, 3αH), 4.47 and 3.95 (à 1 H, 2 d, *J* 11 Hz, C-28 protons), 3.15 (1 H, sept. *J* 6.5 Hz, C-20 proton), 2.7 (1 H, m, C-13 proton), 2.05 and 1.92 (à 3 H, s, acetyl protons), 1.2−0.75 (group of 7 methyls); *m/e* 604, 602. Anal. $C_{34}H_{51}BrO_4$: C, H.

Diels-Alder adducts 8 *and* 9. 3β,28-Diacetoxy-lupa-18,21-diene (*4*) (0.1 g) and 4-phenyl-1,2,4-triazoline-3,5-dione (0.05 g) in dry benzene (5 ml) were allowed to stand overnight. The solvent was evaporated and the residue chromatographed on a silica plate. Crystallisation from EtOH gave adduct *8* (0.05 g) m.p. 213 °C (decomp.), $[\alpha]_D$ −11° (*c* 1.0): δ ($CDCl_3$) 7.38 (5 H, phenyl), 6.20 (1 H, d, *J* 3 Hz, C-21 proton), 4.83 (1 H, d, *J* 3 Hz, C-22 proton), 4.8−4.1 (3 H, m, 3αH and C-28 protons), 2.10 and 2.05 (à 3 H, s, acetyl protons), 1.2−0.85 (group of 7 methyls).

Similar treatment of 22-bromo-3β,28-diacetoxy-lupa-18,21-diene (*7*) gave adduct *9*, m.p. 172 °C (decomp.), $[\alpha]_D$ +35° (*c* 1.0); δ ($CDCl_3$) 7.37 (5 H, phenyl), 6.25 (1 H, s, C-21 proton), 3.5 (3 H, m, 3αH and C-28 protons), 2.12 and 2.02 (à 3 H, s, acetyl protons), 1.15−0.8 (group of 7 methyls).

Reaction of 3b,28-diacetoxy-18α,19α-epoxylupane (1) with TosOH. 3β,28-Diacetoxy-18α,19α-epoxylupane [1] (*1*) (1.0 g), TosOH.H_2O (0.15 g) and Ac_2O (0.2 g) in dry benzene (25 ml) were refluxed for 35 min and worked up. Chromatography on silica plates gave 3β,28-diacetoxy-18,19-secolup-13(18)-en-19-one (*3*) (0.8 g) identical with the compound above, and 3β,28-diacetoxy-lupa-12,19(21)-diene (*10*), crystallised from EtOH (0.11 g), m.p. 124 °C, $[\alpha]_D$ −6° (*c* 1.0); *m/e* (% rel. int.) 524 (7, M^+), 464 (12), 451 (21), 404 (5), 391 (6), 274 (11), 261 (24), 225 (5), 215 (11), 214 (15), 213 (7), 203 (11), 202 (25), 201 (100), 200 (11), 199 (18), 190 (16), 189 (25), 187 (21), 185 (17), 171 (21); δ (CCl_4) 5.4 (1 H, m, C-21 proton), 5.2 (1 H, m, C-12 proton), 4.35 (1 H, m, 3αH), 3.92 (2 H, AB quart. *J* 11 Hz, C-28 protons), 2.9 (1 H, br. s, C-18 proton), 1.95 (6 H, s, acetyl protons), 1.1 − 0.8 (group of 7 methyls). Anal. $C_{34}H_{52}O_4$: C, H.

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Derivatives and Reactions of Glutacondialdehyde. VI. Isoxazoline Formation from the Glutacondialdehyde Anion

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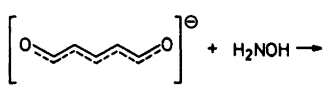
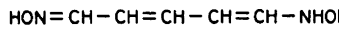
The formation of pyridines [1] and pyrylium salts [2] as well as 3-formyl-2(1*H*)-pyridinethiones [3] from the glutacondialdehyde anion (*1*) is well-known, while the formation of other heterocyclic systems from *1* has not been reported.

Baumgarten reported [4] the reaction of *1* and hydroxylamine to give the dioxime of glutacondialdehyde to which he assigned the structures *2a* or *2b*:

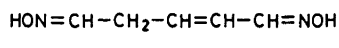


1



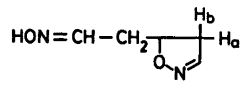
2a

or



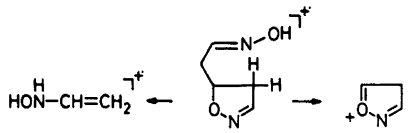
2b

As a part of our interest in the chemistry of *1* we have reinvestigated this reaction, and found that the anion *1* reacts with hydroxylamine in a more interesting manner than could be anticipated.[4] In this contribution we wish to report that the correct structure of the reaction products is *3*, thus giving a new synthesis of the Δ^2-isoxazoline system:



3

The UV spectrum of the product showed bands at $\lambda_{max} = 215$ nm (log $\varepsilon = 3.44$) indicating the absence of a highly conjugated system as in the simple glutacondialdehyde derivatives.[6] The mass spectrum of the compound is in accordance with structure *3*. The molecular ion peak is seen at *m/e* = 128, while dominant fragment ion peaks are seen at *m/e* = 59 and 70. The fragmentation of *3* can be rationalized in the following way:



m/e = 59(66%) *m/e* = 128(6.4%) *m/e* = 70(100%)

The ^1H NMR spectrum of *3* shows in the cases of H(4a) and H(4b) the usual pattern of non-equivalent ring protons. The chemical shift and coupling constants are given in Table 1. The values of the coupling constants and chemical shift are in close agreement with values in similar compounds as reported by several authors.[5] The ^{13}C NMR spectrum of *3* consists of five lines as stated in Table 1. The assignment of the lines has been done by recording the gated decoupled spectrum.