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TERPENOIDS AND RELATED COMPOUNDS—IX[1]

MOLECULAR REARRANGEMENTS INVOLVING GLUTENOLS

P. SENGUPTA[2] and S. GHOSH
Organic Chemistry Laboratory, University of Kalyani, Kalyani, Nadia, West Bengal, India

and

L. J. DURHAM
Department of Chemistry, Stanford University, Stanford, California

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Abstract—The molecular rearrangements of glutenols on treatment with phosphorus pentachloride and phosphorus oxychloride and pyridine as well as on solvolysis of the corresponding tosyl derivatives have been investigated. Glut-5-en-3β-ol (Ia) and glut-5(10)-en-3α-ol (IId) gave diene A (III). Glut-5-en-3α-ol (Id) gave diene B (VII) and glut-5(10)-en-3β-ol (IIa) gave diene C (XIII) by ring contraction.

THE molecular rearrangements in steroids[3] and triterpenoids[4] involving the hydroxyl group at C_3 or its derivatives offer a very interesting study. The rearrangements were effected by (a) treatment of the free alcohol with phosphorus pentachloride or phosphorus oxychloride in pyridine, (b) solvolysis of the corresponding tosyl or mesyl derivatives or (c) passage of mesyl or tosyl derivatives through a column of basic alumina. The systems studied so far are of the following types: (a) steroidal 5-en-3β-ol,[5–8] (b) steroidal 4,4-dimethyl 5-en-3β-ol,[9,10] (c) steroidal 4,4-dimethyl 5-en-3α-ol,[11]

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[2] To whom all enquiries about the paper should be made.
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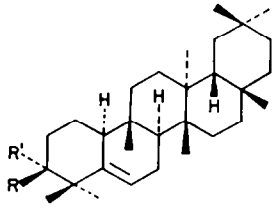
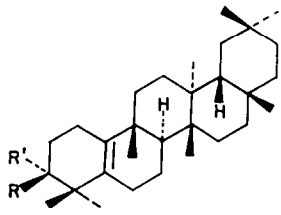
(d) steroidal 4,4-dimethyl 5-en-3β-ol and triterpenoid 3β-ol[4c,10,12–16] and (e) steroidal 4,4-dimethyl 3α-ol.[12a]

In a previous communication[17] we reported the isolation of glut-5-en 3β-ol (Ia) from the Indian plant *Euphorbia royleana*. This alcohol and its 3α-epimer (Id) form a new system in the fact that not only they lack the C_{10}-methyl group but the configuration at C_{10} bears an antipodal relationship to that of all the systems investigated earlier. So we took up a study of the molecular rearrangements of glut-5-en-3β-ol(Ia) and 3α-ol (Id) as well as of the other epimeric pair glut-5(10)-en-3β-ol (IIa) and 3α-ol (IId). Glut-5-en-3α-ol (Id) was prepared from glut-5-en-3β-ol (Ia) via



Ia R = OH, R′ = H
Ib R = OTs, R′ = H
Ic R = OAc, R′ = H
Id R = H, R′ = OH
Ie R = H, R′ = OTs
If R = H, R′ = OAc
Ig R, R′ = O



IIa R = OH, R′ = H
IIb R = OAc, R′ = H
IIc R = OTs, R′ = H
IId R = H, R′ = OH
IIe R = H, R′ = OAc
IIf R = H, R′ = OTs

glut-5-en-3-one[18] (Ig) following the method of Paton *et al.*[19] But for the preparation of glut-5(10)-en-3β-ol (IIa) we observed that mild proton catalysed isomerization of the acetate (Ic) to the isomeric acetate (IIb) followed by hydrolysis was more attractive than the literature method.[18] Similarly the epimeric alcohol (IId) was prepared by proton catalysed isomerization of glut-5-en-3α-yl acetate (If) followed by hydrolysis of the isomerized product.

Glut-5-en-3β-ol (Ia) on treatment with phosphorus pentachloride in pet. ether furnished a mixture, which on chromatography over alumina yielded a diene, $C_{30}H_{48}$, named diene A, m.p. 212–214°, $[\alpha]_D$ +114° as the major product. It showed maxima at 244 mμ (ε 19,900) in the UV indicating the presence of a *transoid* heteroannular diene system in the molecule and an IR band at 817 cm^{-1} (trisubstituted double bond). We suggest the structure (III) for diene A, on the basis of the above evidence supported by NMR data that show a multiplet centered around δ 5·66 (one vinyl H at C_6), a

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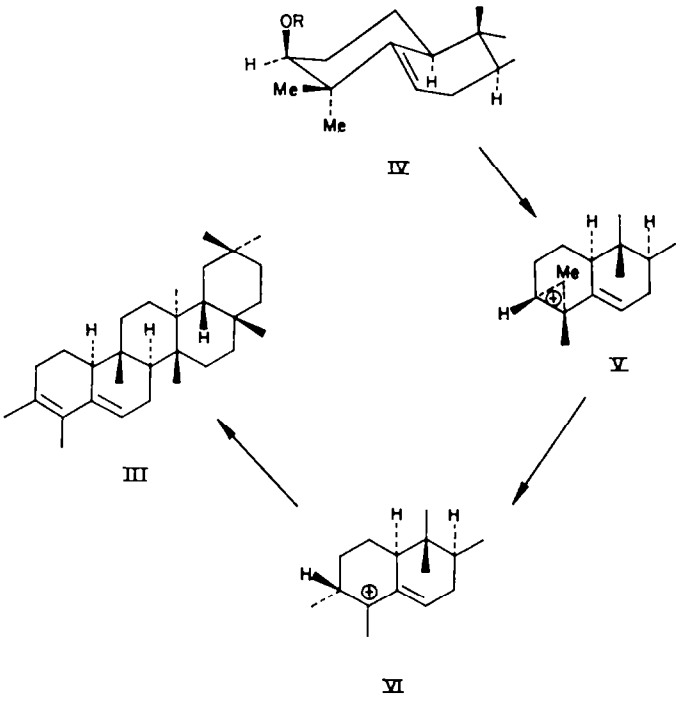
[19] A. C. Paton, F. S. Spring and R. Stevenson, *J. Chem. Soc.* 2640 (1958).

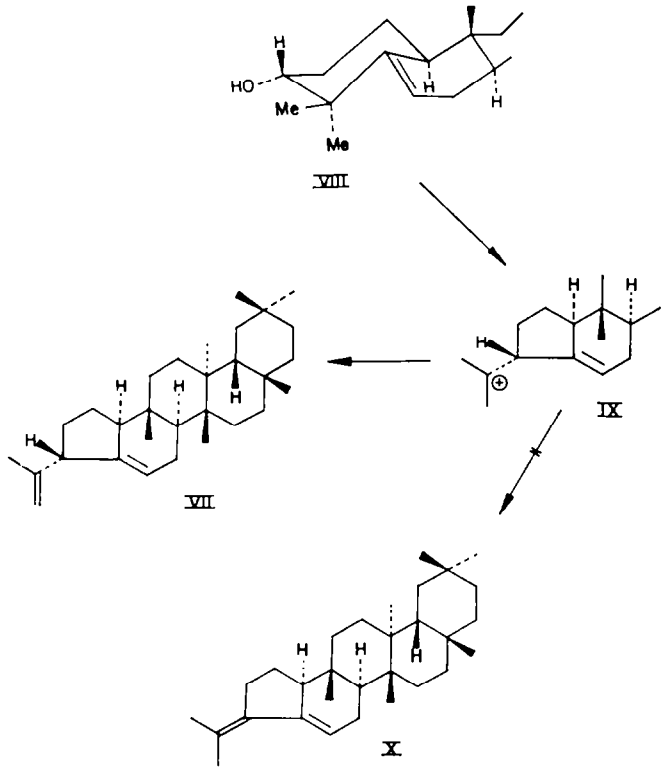
singlet at δ 1·74 (two C=C—CH_3 at C_3 and C_4) and signals at δ 0·79, 0·94, 0·98, 1·10 and 1·15 ppm (tertiary methyl groups).



Treatment of the glutenol (Ia) with phosphorus oxychloride and pyridine furnished a complex mixture, from which on chromatography we could isolate only diene A in very small amount, the rest being an intractable gum. However, it may be mentioned that glut-5-en-3β-yl toluene-*p*-sulfonate (Ib) remained unaffected for the most part on prolonged treatment with sodium acetate in aqueous acetone. Only a small amount of glut-5-en-3β-ol (Ia) with retention of configuration was obtained.

The formation of diene A (III) from glut-5-en-3β-ol (Ia) having the 3β-hydroxyl and 4α-methyl groups in a *trans* 1,2-diaxial orientation (IV, R = H) requires that the intermediate chlorophosphate ester (IV, R = chlorophosphate) first forms the non-classical carbonium ion (V), which then passes through the classical carbonium ion (VI) to diene A by the final elimination of the proton from C_3.

Glut-5-en-3α-ol (Id) which has the hydroxyl group at C_3 in equatorial conformation was expected to behave like steroidal 4,4-dimethyl-5-en-3β-ols. When the free alcohol (Id) was treated with phosphorus pentachloride in pet. ether, a diene, $C_{30}H_{48}$, named diene B, m.p. 150–153°, $[\alpha]_D$ +47° was obtained as the major product. It showed no absorption maxima between 200–300 mμ in the UV indicating the absence of any conjugated diene system. The IR spectra showed bands at 1640 (ethylenic double bond), 890 (C=CH_2) and 825 cm^{-1} (trisubstituted double bond). The structure (VII) is suggested for diene B on the basis of the above physical properties and NMR data which show a multiplet around δ 5·33 (one vinyl H at C_6), a multiplet centered around δ 4·47 (2H, —C=CH_2), a singlet at δ 1·66 (3H, —C=C—CH_3), signals at δ 1·17,



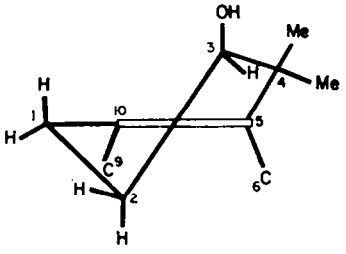
1·08, 1·03, 0·99, 0·95 and 0·72 (6 tertiary methyl groups) and a multiplet at 83 ppm (1H, doubly allylic H at C_3).

When the corresponding tosyl derivative (Ie) was treated with sodium acetate in aqueous acetone, the same diene B (VII), m.p. 150–153° was obtained as the major product.

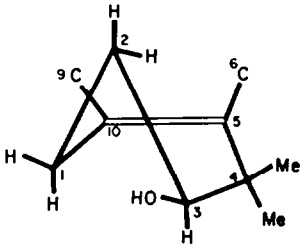
The ring contraction during pentachloride treatment of the alcohol (Id) or during solvolysis of its tosyl derivative (Ie) has been possible since the oxygen atom, C_3, C_4 and C_5 (VIII) lie in one plane. The intermediate cation (IX) after the Wagner–Meerwein shift could stabilize by the elimination of the proton from C_3 to produce the *cisoid* diene (X). However, the presence of this *cisoid* diene could not be detected in the reaction mixture. On the contrary, in the major product, the cation (IX) was stabilized by elimination of a proton from one of the two methyl groups to produce the non-conjugated diene B (VII). The corresponding steroidal 4,4-dimethyl-5-en-3β-ol systems are known to give mostly the conjugated dienes.[9,10] This difference in behavior may be due to the 1,3-diaxial interaction between the methyl groups at C_9 and C_{14} in (X), which interaction is absent in the steroidal 4,4-dimethyl-5-en systems. As a result of this interaction ring B is deformed thus overcrowding the vinyl hydrogen at C_6 and one of the two methyl groups at C_4 in (X), hence theoretically increasing the energy of the molecule. This extra strain is possibly released in (VII), where due to free rotation around the C_3—C_4 single bond, the methyl or methylene group at C_4 may attain a different plane to avoid overcrowding with the vinyl hydrogen atom at C_6.

An inspection of the Dreiding model for ring A of glut-5(10)-en-3β-ol (IIa)

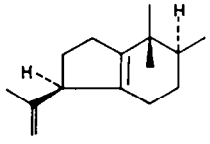
reveals that the hydroxyl group may have either an axial (XI) or an equatorial (XII) conformation.[19] Theoretically it may be predicted that if the hydroxyl group in this alcohol (IIa) is equatorial, ring contraction through retropinacoline transformation would take place during dehydration. Indeed as described below ring contraction was encountered and so it could be stated that in contrast to the glut-5-en system, glut-5(10)-en-3-ol system has the 3β-hydroxyl group in preferred equatorial conformation (XII) at least at the time of the reaction.



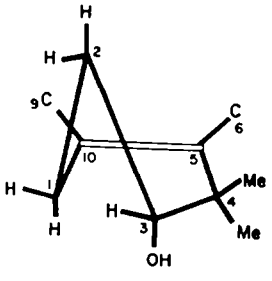
XI



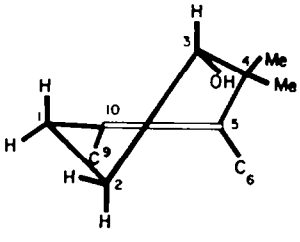
XII



XIII



XIV



XV

When the alcohol (IIa) was treated with phosphorus pentachloride in pet. ether a diene, $C_{30}H_{48}$, m.p. 195–198°, $[\alpha]_D$ −70°, named diene C was obtained as the major product. It showed no absorption maxima in the region from 200 to 300 mμ in the UV. The IR absorption spectra showed a peak at 885 cm^{-1} (C=CH_2). The absence of any band at around 820 cm^{-1} indicated the absence of any trisubstituted double bond. The structure (XIII) is suggested for diene C on the basis of the above physical evidence along with the NMR data that show a multiplet centered around δ 4·65 (2H, C=CH_2), a singlet at δ 1·58 (3H, C=C—H_3) and a multiplet at δ 3·1 ppm (1H; doubly allylic H at C_3). It may be mentioned that Rangaswami and Sambamurthy[20] obtained a diene, m.p. 195–197°, $[\alpha]_D$ −53° from the reaction of phosphorus oxychloride and pyridine on the alcohol (IIa) and assigned the structure (XIII) to it, since it gave formaldehyde on ozonolysis In all probability this diene is identical with our diene C.

[20] S. Rangaswami and K.Sambamurthy, *Proc. Indian Acad. Sci.* **54A**, 132 (1961).

When the corresponding tosyl derivative (IIc) was refluxed with aqueous acetone containing sodium acetate, the same diene C, m.p. 195–198° was obtained as the major product.

An inspection of the Dreiding model of ring A of the 3α-ol (IId) reveals that here also the hydroxyl group may attain either an axial (XIV) or an equatorial (XV) conformation. As shown below, in the case of this epimer (IId), instead of ring contraction, migration of a methyl group from C_4 to C_3 occurred. Hence the preferred orientation of the hydroxyl group at C_3 in this epimer (IId) is axial at least at the time of the reaction.

The alcohol (IId) on treatment with phosphorus pentachloride in pet. ether gave diene A, m.p. 212–215°, $[\alpha]_D$ +112° as the major product, evidently by migration of methyl group accompanied by isomerization of the 5(10) double bond to 5(6) position. Attempted solvolysis of the corresponding tosyl derivative (IIf) yielded a crystalline derivative, m.p. 170–172°, $[\alpha]_D$ +49° whose UV absorption spectra revealed that it was a mixture containing 10% of a conjugated diene, and also glut-5(10)-en-3α-ol (IId) with retention of configuration.

EXPERIMENTAL

All m.ps are uncorrected. The pet. ether used had b.p. 60–80°. UV absorption spectra were measured in n-hexane.

Glut-5-en-3β-ol (Ia), m.p. 206–208°, $[\alpha]_D$ +62° ($CHCl_3$) was obtained from *Euphorbia royleana*.[17] I.R. Peaks at 3420 (hydroxyl), 1378 and 1362 (gem-dimethyl) and 820 cm^{-1} (trisubstituted double bond).

Glut-5-en-3α-ol (Id), m.p. 200–203°, $[\alpha]_D$ +63° ($CHCl_3$) was prepared from glut-5-en-3-one (Ig) according to the method of Paton *et al.*[18]

Glut-5(10)-en-3β-yl acetate (IIb). Glut-5-en-3β-yl acetate (Ic; 0·2 g), m.p. 188–192° was refluxed for 2 hr with glacial AcOH (40 ml) and conc. HCl (6 ml). The reaction mixture was cooled and the precipitated crystalline solid was filtered. On crystallization from $CHCl_3$–acetone, it furnished IIb, m.p. 291–295°, $[\alpha]_D$ −18° ($CHCl_3$) (lit.[19] m.p. 297–299°, [α] −23°). (Found: C, 82·24; H, 11·21. Calc. for $C_{32}H_{52}O_2$: C, 81·99; H, 11·18%.) NMR: Multiplet centered around δ 4·70 ppm (1H, α-hydrogen at C_3); singlet at δ 2·04 ppm (3H, —CO·CH_3); signals at δ 0·93, 1·00, 1·18 and 1·37 ppm (tertiary methyl groups); no signal for olefinic proton at δ 5·00 to δ 6·00 ppm.

Glut-5(10)-en-3β-ol (IIa). Compound IIb (0·7 g) was refluxed for 8 hr on a steam bath with benzene (20 ml) and 5% methanolic KOH (25 ml). The reaction product was cooled, diluted with cold water and the precipitated solid was taken up in ether. The ether solution was washed with water, dried (Na_2SO_4) and evaporated and the residue (0·69 g) was chromatographed over alumina (70 g). Elution with benzene furnished a crystalline solid (0·67 g), which was then crystallized from $CHCl_3$–MeOH to furnish pure IIa, m.p. 242–244°, $[\alpha]_D$ −40° ($CHCl_3$) (lit.[19] m.p. 244–245°, $[\alpha]_D$ −42·5°).

Glut-5(10)-en-3α-ol (IId). Dry HCl was passed through a solution of glut-5-en-3α-yl acetate (If; 1·1 g) in $CHCl_3$ (150 ml) at 0° for 1 hr. After allowing to stand for 24 hr at room temp the solution was again cooled to 0°, dry HCl was passed through it for 1 hr and allowed to stand for 24 hr at room temp. This operation was repeated for 3 more days. Then the HCl was neutralized by the cautious addition of Na_2CO_3 and the $CHCl_3$ solution was washed with water and dried (Na_2SO_4). The gummy solid residue (1·04 g), obtained on removal of solvent, was hydrolysed by refluxing for 5 hr with 5% methanolic KOH (50 ml) in benzene (50 ml) and the crude product (1 g) was chromatographed over activated alumina (100 g). Elution with pet. ether–benzene (1:9) furnished a crystalline solid (0·32 g), m.p. 236–248°, which on crystallization from $CHCl_3$–MeOH yielded pure IId, m.p. 256–259°, $[\alpha]_D$ −38° ($CHCl_3$) (lit.[19] m.p. 258–259°, $[\alpha]_D$ −42°).

Treatment of Ia *with* PCl_5. Compound Ia (0·4 g), m.p. 206–208° was added to a suspension of PCl_5 (0·26 g) in dry pet. ether (25 ml) and the mixture was shaken for 35 min, when the solution became clear. The reaction mixture was again shaken for 5 min after the addition of hot water (5 ml) to decompose the excess PCl_5. The pet. ether solution, after dilution with ether, was washed with

water, dried (Na_2SO_4) and the residue (0·3 g), obtained after the removal of the solvent, was chromatographed over activated alumina (20 g). Elution with pet. ether furnished a solid (0·26 g), m.p. 140–152°, which on repeated crystallizations from $CHCl_3$–MeOH gave pure diene A (III), m.p. 212–214°, $[\alpha]_D$ +114° ($CHCl_3$). (Found: C, 88·21; H, 11·62. $C_{30}H_{48}$ requires: C, 88·16; H, 11·84%.) UV: λ_{max} 244 mμ (ε 19,900). IR: a peak at 817 cm^{-1} (trisubstituted double bond) but no hydroxyl peak. NMR: multiplet centered around δ 5·66 ppm (one vinyl H at C_6); singlet at δ 1·74 ppm (6H, two C=C—CH_3); signals at δ 0·79, 0·94, 0·98, 1·10 and 1·15 ppm (tertiary methyl).

Treatment of Ia *with* $POCl_3$ *and pyridine.* A mixture of Ia (0·4 g), m.p. 206–208°, pyridine (40 ml) and $POCl_3$ (3·2 ml) was heated on a steam bath for 2 hr when the solution became dark red. It was then heated to boiling for a short time, cooled to 0° and poured into crushed ice. The precipitated semi-solid mass was taken up in ether and the ether solution was washed with water, dried (Na_2SO_4) and evaporated. The residue (0·38 g) was then chromatographed over a column of activated alumina (50 g). Elution with pet. ether gave a solid (0·3 g), which on crystallization from $CHCl_3$–MeOH gave a diene (0·04 g), m.p. 212–214°; $[\alpha]_D$ +114° identical (mixed m.p. and IR) with diene A (III) mentioned above.

Glut 5-*en*-3β-yl *toluene*-p-*sulfonate* (Ib). Compound Ia (0·8 g), m.p. 206–208° was added portionwise to a mixture of toluene-*p*-sulfonyl chloride (2 g) and pyridine (20 ml) at 0° and the reaction mixture, after allowing to stand at room temp for 72 hr, was poured into ice. After working up as usual, the crude tosyl derivative was crystallized from acetone to furnish pure Ib, m.p. 119° dec. (Found: C, 76·63; H, 9·51. $C_{37}H_{56}O_3S$ requires: C, 76·55; H, 9·65%.)

Attempted Solvolysis of Ib. A mixture of compound Ib (0·75 g), m.p. 119° dec, acetone (200 ml), water (4·6 ml) and anhydrous AcONa (0·84 g) was refluxed for 100 hr. The residue after distilling off the acetone was treated with water and taken up in ether. The ether layer was washed with water, dried (Na_2SO_4) and evaporated. The residue (0·7 g) was digested with pet. ether (150 ml). The pet. ether insoluble part (0·55 g) was found to be unreacted tosyl derivative (Ib). The pet. ether soluble part (0·15 g) was chromatographed over activated alumina (20 g). Elution with pet. ether did not furnish any hydrocarbon, but elution with benzene gave a solid (145 mg), m.p. 199–207°, which on crystallization from MeOH furnished Ia, m.p. 205–208°, identical (mixed m.p.) with an authentic specimen.

Treatment of Id *with* PCl_5. Compound Id (0·8 g), m.p. 200–203° was added to a suspension of PCl_5 (0·5 g) in dry pet. ether (45 ml) and the mixture was shaken for 35 min when a clear solution resulted. The reaction mixture was again shaken for 5 min after the addition of hot water (5 ml) to decompose the excess PCl_5. After working up as above, the residue (0·6 g) was chromatographed over alumina (70 g) and elution with pet. ether furnished a crystalline solid (0·54 g), m.p. 128–143°, which on repeated crystallizations from $CHCl_3$–acetone yielded diene B (VII), m.p. 150–153°, $[\alpha]_D$ +47°. (Found: C, 88·13; H, 11·93. $C_{30}H_{48}$ requires: C, 88·16; H, 11·84%.) UV: no absorption maxima in the region 200 mμ to 300 mμ. IR: peaks at 1640 (ethylenic double bond), 890 (C=CH_2) and 825 cm^{-1} (trisubstituted double bond). NMR: multiplet centered around δ 5·33 ppm (one vinyl H at C_6); multiplet centered around δ 4·74 ppm (2H, C=CH_2); singlet at δ 1·66 ppm (3H, C=C—CH_3); signals at δ 1·17, 1·08, 1·03, 0·99, 0·95 and 0·72 ppm (six tertiary methyl groups) and a multiplet at δ 3 ppm (1H, doubly allylic H at C_3).

Solvolysis of glut-5-*en*-3α-*yl toluene*-p-*sulfonate* (Ie). Compound Id (0·75 g), m.p. 200–203° was added to a mixture of toluene-*p*-sulfonyl chloride (0·87 g) and pyridine (20 ml) at 0° and the mixture was allowed to stand at room temp for 72 hr. After working up as usual, the crude tosyl derivative (Ie) was subjected to solvolysis.

A mixture of the above crude tosyl derivative (Ie; 0·7 g), anhydrous AcONa (0·34 g), acetone (16·6 ml) and water (1·6 ml) was refluxed for 60 hr. After working up as usual, the crude product (0·28 g) was chromatographed over a column of activated alumina (20 g). Elution with pet. ether furnished a solid (0·24 g), m.p. 128–145°, which on several crystallizations from $CHCl_3$–MeOH yielded pure diene B (VII), m.p. 150–153°, identical (mixed m.p. and IR) with diene B described above.

Treatment of IIa *with* PCl_5. Compound IIa (0·75 g), m.p. 242–244°, was added to a suspension of PCl_5 (0·5 g) in dry pet. ether (45 ml) and the mixture was shaken for 35 min, when the solution became clear. After working up as above, the residue (0·5 g) was chromatographed over a column of activated alumina (70 g). Elution with pet. ether gave a crystalline solid (0·47 g), m.p. 148–186°, which on repeated crystallizations from $CHCl_3$–MeOH furnished pure diene C (XIII), m.p. 195–198°,

$[\alpha]_D$ −70°. (Found: C, 88·03; H, 11·98. $C_{30}H_{48}$ requires: C, 88·16; H, 11·76%.) UV: no absorption maxima in the region 200 mμ to 300 mμ. IR: peaks at 885 cm^{-1} (C=CH_2), but none at around 820 cm^{-1} (absence of trisubstituted double bond). NMR: multiplet centered around δ 4·65 ppm (2H, C=CH_2); singlet at δ 1·58 ppm (3H, C=C—CH_3) and a multiplet at δ 3·1 ppm (1H, doubly allylic H at C_3).

Solvolysis of glut-5(10)-en-3β-yl toluene-p-sulfonate (IIc). To a mixture of toluene-*p*-sulfonyl chloride (2 g) and pyridine (20 ml) cooled to 0° was added IIa (0·75 g), m.p. 195–198°, and the reaction mixture was allowed to stand at room temp for 72 hr, when the solution became clear. After working up as usual, the crude tosyl derivative (IIc) was directly subjected to solvolysis.

A mixture of IIc, acetone (50 ml), water (4·6 ml) and anhydrous AcONa (0·84 g) was refluxed for 60 hr. The residue (0·5 g), obtained after working up as usual was chromatographed over a column of activated alumina (70 g). Elution with pet. ether gave a solid (0·45 g), m.p. 166–188°, which on repeated crystallizations from $CHCl_3$–MeOH furnished pure diene C, m.p. 195–198° identical (mixed m.p. and IR) with diene C (XIII) described above.

Treatment of IId *with* PCl_5. Compound IId (0·22 g), m.p. 256–259° was added to a mixture of PCl_5 (0·15 g) in dry pet. ether (14 ml) and the mixture was shaken for 35 min when a clear solution resulted. The residue (0·21 g) obtained after working up as usual, was chromatographed over a column of activated alumina (20 g). Elution with pet. ether gave a solid (0·19 g), m.p. 124–160°, which on repeated crystallizations from $CHCl_3$–MeOH gave pure diene A (III), m.p. 212–214°, $[\alpha]_D$ +116° ($CHCl_3$) identical (mixed m.p. and IR) with diene A described before.

Solvolysis of glut-5(10) en-3α-yl toluene-p-sulfonate (IIf). A mixture of IId (0·32 g), m.p. 256–259°, toluene-*p*-sulfonyl chloride (0·9 g) and pyridine (15 ml) was allowed to stand at room temp for 72 hr. After working up as usual, the crude tosyl derivative (IIf) was directly subjected to solvolysis.

A mixture of IIf (0·3 g), anhydrous AcONa (0·35 g), acetone (25 ml) and water (2 ml) was refluxed for 60 hr. After working up as usual, the crude residue (0·3 g) was chromatographed over a column of activated alumina (30 g). Elution with pet. ether gave a solid (90 mg), m.p. 145–160°, which on repeated crystallizations from $CHCl_3$–MeOH yielded a crystalline solid, m.p. 170–172°, $[\alpha]_D$ +49°. (Found: C, 88·04; H, 11·72. $C_{30}H_{48}$ requires: C, 88·16; H, 11·76%.) However, its UV absorption spectra showed λ_{max} 248 mμ (ε 1,980), which indicated that it was a mixture containing only 10% of a *transoid* diene. This material could not be purified further.

Elution with pet. ether and benzene (1:4) in the above chromatogram furnished a solid (0·2 g), m.p. 232–250°, which on repeated crystallizations from $CHCl_3$–MeOH yielded IId, m.p. 256–259° identical (mixed m.p.) with an authentic specimen.

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