181. 22-isoallo*Spirost*-8(14)-*en*-3β-*ol and* 3β-*Hydroxy*allo*pregn*-8(14)-*en*-20-*one*.*

By O. Mancera, D. H. R. Barton, G. Rosenkranz, and Carl Djerassi.

22-*isoallo*Spirost-8(14)-en-3β-yl acetate has been prepared by Raney-nickel-catalysed hydrogenation of the corresponding 5 : 7- and 7 : 9(11)-dienes and also by catalyst-hydrogen-induced double-bond rearrangement of the corresponding Δ^7-compound. The acetate has been characterised by various derivatives and has been converted, *via* the appropriate furosta-8(14) : 20(22)-diene derivative into 20-keto*allo*pregna-8(14) : 16-dien-3β-yl acetate. Hydrogenation of the latter gave 20-keto*allo*pregn-8(14)-en-3β-yl acetate, also prepared by double-bond rearrangement of the corresponding Δ^7-compound.

The 8(14)-olefinic linkages in these compounds are *not* rearranged to the 14(15)-positions by the action of hydrogen chloride.

The molecular rotation data are discussed briefly.

Investigations in the *trans*-A/B stenol series (I; R = alkyl; but with one nuclear double bond) have led to unambiguous characterisation of the possible double-bond positions by both chemical and optical methods (for an excellent summary see Fieser and Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., 1949). In compounds of this type R normally contains 8 or more carbon atoms. On the basis of our current theoretical concepts of the relation between chemical reactivity (or thermodynamic stability) and molecular structure it would be expected that changes in the nature of the side chain would not exert major chemical effects at isolated double-bond positions in the nucleus, for example, at positions 7(8), 8(9), or 8(14). So far as molecular rotation relations are concerned it is not possible to make such a precise estimate of the limiting interactions of substituent groups. However by analogy with the work of Barton and Cox (*J.*, 1948, 783) it would be expected that optical interaction of the nuclear double-bond positions with the side chain would not be significant provided (*a*) that the latter was not too unsaturated and (*b*) that it did not exert a distorting effect on the molecular framework. Clearly the definition of these two terms is not precise and their significance, in the absence of an adequate theory of optical activity, can only be assessed by empiricism. Recent advances in the steroidal sapogenin series have now made available substances with double bonds at various positions in the nucleus and having a sapogenin or acetyl side chain attached to ring D. It is with the properties of such compounds that the present communication is concerned.

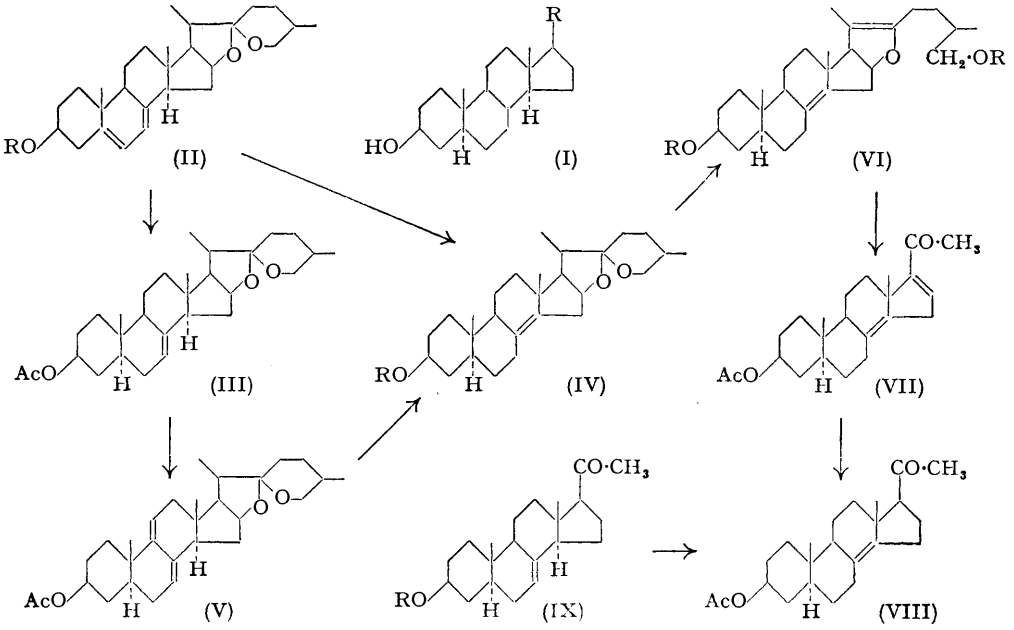
In a recent paper (Rosenkranz, Romo, and Berlin, *J. Org. Chem.*, 1951, **16**, 290) we reported the preparation of 22-*isoallo*spirosta-5 : 7-dien-3β-ol (II; R = H) and derivatives (cf. Chamberlain, Chemerda, Tishler, *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 2396). Hydrogenation of the acetate (II; R = Ac) at a platinum catalyst in ethyl acetate solution gave 22-*isoallo*spirost-7-en-3β-yl acetate (III) (Rosenkranz, Romo, Batres, and Djerassi, *J. Org. Chem.*, 1951, **16**, 298). We now find that hydrogenation of (II; R = Ac) at high pressure and high temperature in presence of Raney nickel (cf. Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 2402) affords 22-*isoallo*spirost-8(14)-en-3β-yl acetate (IV; R = Ac).† The same compound was also obtained by double-bond rearrangement of (III) (*a*) with a palladised charcoal catalyst in ethyl acetate–acetic acid solution and (*b*) under the same Raney nickel hydrogenating conditions. Similar Raney nickel hydrogenation of 22-*isoallo*spirosta-7 : 9(11)-dien-3β-yl acetate (V), prepared (Rosenkranz, Romo, Batres, and Djerassi, *loc. cit.*) by mercuric acetate dehydrogenation of (III), likewise afforded (IV;

* This paper is Part XVII in the Syntex series on Steroidal Sapogenins; for Part XVI see Djerassi, Batres, Velesco, and Rosenkranz, *J. Amer. Chem. Soc.*, in the press. It is also to be regarded as Part XVIII in the series (by D. H. R. B.) on "The Application of the Method of Molecular Rotation Differences to Steroids"; for Part XVII see Barton and Rosenfelder, *J.*, 1951, 2381.

† The compound to which this constitution was previously assigned (Rosenkranz, Romo, Batres, and Djerassi, *loc. cit.*) has been shown to be a mixture of the 8(14)- and 7(8)-unsaturated isomers, rearrangement of the latter to the former having been incomplete owing to the use of too little acetic acid in the hydrogenation medium.

R = Ac). Alkaline hydrolysis of 22-*isoallo*spirost-8(14)-en-3β-yl acetate afforded the corresponding alcohol (IV; R = H) further characterised as the benzoate. The homogeneity of these compounds was carefully established by methods summarised in the Experimental section.

The assignment of the ethylenic linkage to the 8(14)-position in these compounds is based on the following evidence: first, analogy to reactions already well established in the stenol series (Fieser and Fieser, *op. cit.*); secondly, the molecular-rotation differences on acylation (see discussion below); thirdly, the ultra-violet spectra (see Experimental)



which indicate a tetrasubstituted double bond exocyclic to two rings rather than a tetrasubstituted double bond of the 8(9)-stenol type (see Bladon, Henbest, and Woods, *Chem. and Ind.*, 1951, 866; Halsall, *ibid.*, p. 867); fourthly, the acetate failed to react with osmium tetroxide in ethereal solution. Ergost-8(14)-en-3β-yl acetate is likewise unaffected by this reagent whereas the corresponding 8(9)-isomer reacts readily (see Barton and Cox, *J.*, 1949, 214).

On treatment with acetic anhydride at 200° 22-*isoallo*spirost-8(14)-en-3β-yl acetate (IV; R = Ac) was converted into *allo*furosta-8(14) : 20(22)-diene-3β : 26-diol diacetate (VI; R = Ac), characterised by alkaline hydrolysis to the corresponding diol (VI; R = H). Oxidation of (VI; R = Ac) with chromic acid followed by controlled hydrolysis (see Djerassi, Romo, and Rosenkranz, *J. Org. Chem.*, 1951, **16**, 754) afforded 20-keto*allo*pregna-8(14) : 16-dien-3β-yl acetate (VII), hydrogenation of which, at a palladised charcoal catalyst in ethyl acetate solution, gave 20-keto*allo*pregn-8(14)-en-3β-yl acetate (VIII). The acetate (VIII) was also prepared by double-bond rearrangement of 20-keto*allo*pregn-7-en-3β-yl acetate (IX; R = Ac) (Djerassi, Romo, and Rosenkranz, *loc. cit.*) at palladised charcoal in acetic acid. The assignment of the 8(14)-double bond position in the 20-keto-*allo*pregn-8(14)-en-3β-yl acetate is confirmed by its ultra-violet absorption spectrum (see Experimental).

As has long been established, dry hydrogen chloride in chloroform isomerises the 8(14)-double bond in *trans*-A/B-stenols to an equilibrium (cf. Barton, Cox, and Holness, *J.*, 1949, 1771) mixture containing about 50% each of the 8(14)- and the 14(15)-isomer. We found that treatment of 22-*isoallo*spirost-8(14)-en-3β-yl benzoate or acetate (IV; R = Bz or Ac, respectively) under these conditions caused *no* detectable isomerisation of the double bond. A similar observation was made with 20-keto*allo*pregn-8(14)-en-3β-yl acetate (VIII). These

facts show that the nature of the side chain and of its attachment to ring D exerts an influence on the 8(14)- and 14(15)-positions, either in altering the relative stabilities of the two ethylenic linkages (thermodynamic explanation) or (as is less likely) in preventing carbonium-ion formation (kinetic explanation). In either case these observations are contrary to the simple chemical theory outlined in the introductory paragraph. Incidentally they make it probable that the anhydrocorticosterone acetate, m. p. 143°, $[\alpha]_D$ +98°, prepared by Shoppee and Reichstein (*Helv. Chim. Acta*, 1943, **26**, 1316) must have the isolated ethylenic linkage at the 8(14)- rather than at the 14(15)-position (cf. Fieser and Fieser, *op. cit.*, p. 409).

The molecular-rotation data for compounds of the sapogenin series possessing isolated double bonds in the nucleus appear worthy of brief comment. Tables 1 and 2 summarise the molecular rotations of compounds having isolated double bonds at position 5(6), 7(8), or 8(14). In each case (see Table 1) the shift in molecular rotation (Rule of Shift) observed

TABLE 1.

Compound	Molecular rotations: Alcohol	Acetate	Benzoate	Δ_1	Δ_2	Refs.
22-*isoallo*Spirost-5-en-3β-ol	−534°	−578°	−472°	−44°	+62°	(1)
Cholest-5-en-3β-ol	−154	−188	− 74	−34	+80	(2)
22-*isoallo*Spirost-7-en-3β-ol	−315	−306	−295	+ 9	+20	(3)
Ergost-7-en-3β-ol	− 8	− 18	+ 10	−10	+18	(2)
22-*isoallo*Spirost-8(14)-en-3β-ol...	− 99	−146	−140	−47	−41	(4)
Ergost-8(14)-en-3β-ol	+ 44	+ 4	± 0	−40	−44	(2)

Refs. (1) Rosenkranz, Romo, and Berlin, *J. Org. Chem.*, 1951, **16**, 290. (2) Barton and Cox, *J.*, 1948, 783. (3) Rosenkranz, Romo, Batres, and Djerassi, *J. Org. Chem.*, 1951, **16**, 298. (4) This paper.

on acetylation and benzoylation is in good agreement with standard values obtained in the stenol series. When, however, comparisons of the contributions of the ethylenic linkages to the molecular rotations are made (see Table 2) the position is different. Double bonds at 5(6) and at 7(8) in the 22-*isoallo*spirostan-3β-ol nucleus make contributions which are in

TABLE 2. *Contribution of the double bond to the molecular rotation.**

Compound	Sapogenin series, etc.	Stenol series (standard values)	References.
22-*isoallo*Spirost-5-en-3β-ol (diosgenin)	−230°	−253°	(1), (2)
22-*isoallo*Spirost-7-en-3β-ol	− 11	− 68	(3), (4)
22-*isoallo*Spirost-8(14)-en-3β-ol	+205	− 16	(4), (5)
20-Keto*allo*pregn-8(14)-en-3β-yl acetate	+ 45		(2), (5)

* With respect to the corresponding saturated 5-*allo*-compound. For the molecular rotation (−304°) of 22-*isoallo*spirostan-3β-ol (tigogenin) see Ref. (1) in Table 1.

Refs. (1) See Ref. (1), Table 1. (2) See Ref. (2), Table 1. (3) See Ref. (3), Table 1. (4) Barton and Klyne, *Chem. and Ind.*, 1948, 755. (5) This paper.

fair agreement with the standard values of the stenol series. The 22-*isoallo*spirost-8(14)-en-3β-ol described in the present paper is an outstanding exception and demonstrates a strong vicinal effect of the sapogenin side chain, presumably produced by the mutual distorting interactions of the latter with the 8(14)-double bond. This effect is parallel to the anomalous chemical behaviour mentioned above. However 20-keto*allo*pregn-8(14)-en-3β-yl acetate, which shows similar anomalous chemical behaviour, has a molecular rotation contribution for its ethylenic linkage which is in fair agreement with the standard value.

EXPERIMENTAL

M. p.s are uncorrected. All rotations were taken in chloroform solution; the values recorded have been approximated to the nearest degree. Ultra-violet absorption spectra were determined in absolute ethanol solution, with a Unicam Spectrophotometer, Model SP 500. They have not been corrected for instrument error in the 195—220-mμ range (see Bladon, Henbest, and Wood, *loc. cit.*). Infra-red spectra were determined by Srta. Paquita Revaque and her staff for carbon disulphide solutions, with a Perkin–Elmer single-beam model 12-C spectrometer (sodium chloride prism).

Light petroleum refers throughout to the fraction of b. p. 40—60°.

Microanalyses are by Srta. Amparo Barba of the Syntex Microanalytical Dept.

Savory and Moore's alumina for chromatography was used unless stated to the contrary.

22-isoallo*Spirost*-8(14)-*en*-3β-*yl Acetate*.—(a) *By Raney nickel hydrogenation of* 22-iso*spirosta*-5 : 7-*dien*-3β-*yl acetate*. A mixture of spectroscopically pure 22-*iso*spirosta-5 : 7-dien-3β-yl acetate (5·0 g.) (Rosenkranz, Romo, and Berlin, *J. Org. Chem.*, 1951, **16**, 290), W-4 Raney nickel catalyst (3·0 g.) (Pavlic and Adkins, *J. Amer. Chem. Soc.*, 1946, **68**, 1471), and 95% ethanol (200 ml.) was shaken for 8 hours in an autoclave with hydrogen at 1000—1200 lb./sq. in. and 150°. The catalyst was filtered off and extracted well with chloroform, and the combined extract and filtrate were evaporated to dryness. The greenish residue was taken up in chloroform, washed well with dilute acid and water, dried, and evaporated. Recrystallisation from chloroform–methanol yielded 2·9 g. (58%) of colourless crystals with m. p. 200—204°, $[\alpha]_D$ −31·5° (*c*, 0·67), which gave a yellow colour with tetranitromethane, but showed no selective absorption in the ultra-violet above 220 mμ.

Although further crystallisation did not alter the physical properties reported above, a further purification was effected by chromatography. The acetate (3·0 g.) was carefully chromatographed (10 fractions) over alumina. Elution with 1 : 1-benzene–light petroleum afforded pure 22-isoallo*spirost*-8(14)-*en*-3β-*yl acetate* which, recrystallised from chloroform–methanol, had m. p. 210—212°, $[\alpha]_D$ −32° (*c*, 8·11), $[M]_D$ −146°, $\lambda_{max.}$ 203 mμ, $\varepsilon_{max.}$ 7700, ε_{215} 4050 (*c*, 0·0050) (Found: C, 75·9; H, 9·6. $C_{29}H_{44}O_4$ requires C, 76·25; H, 9·7%). The constants were unchanged on repeated recrystallisation.

Under the same conditions of catalytic hydrogenation 22-*iso*spirost-5-en-3β-yl acetate (diosgenin acetate) gave 22-*isoallo*spirostan-3β-yl acetate in 90% yield.

(b) *By Raney nickel hydrogenation of* 22-isoallo*spirosta*-7 : 9(11)-*dien*-3β-*yl acetate*. Similar hydrogenation of 22-*isoallo*spirosta-7 : 9(11)-dien-3β-yl acetate (1·5 g.) (Rosenkranz, Romo, Batres, and Djerassi, *J. Org. Chem.*, 1951, **16**, 298) at W-4 Raney nickel (2·0 g.) in 95% ethanol (80 ml.), afforded the same 22-*isoallo*spirost-8(14)-en-3β-yl acetate (0·31 g.), the identity being confirmed by the infra-red absorption spectrum.

(c) *By rearrangement of* 22-isoallo*spirost*-7-*en*-3β-*yl acetate*. A mixture of 10% palladized charcoal (200 mg.; American Platinum Works, Newark, N.J.), acetic acid (20 ml.), and ethyl acetate (30 ml.) was shaken with hydrogen to pre-reduce the catalyst and then there was added a solution of pure 22-*isoallo*spirost-7-en-3β-yl acetate (2·0 g.) (Rosenkranz, Romo, Batres, and Djerassi, *loc. cit.*) in acetic acid (30 ml.) and ethyl acetate (250 ml.), and shaking under hydrogen was continued for 18 hours (no gas uptake was observed). After working up in the usual way, recrystallisation from chloroform–methanol afforded 22-*isoallo*spirost-8(14)-en-3β-yl acetate (1·72 g.), m. p. 203—206°, $[\alpha]_D$ −35° (*c*, 0·67). The identity was confirmed by the infra-red absorption spectrum.

A similar rearrangement was effected by using W-4 Raney nickel. 22-*isoallo*Spirost-7-en-3β-yl acetate (3 g.) in admixture with the catalyst (3·0 g.) and ethanol (100 ml.) was treated with hydrogen as in the preparation of 22-*isoallo*spirost-8(14)-en-3β-yl acetate reported above. After being worked up in the usual way, the once recrystallised reaction product [1·7 g.; m. p. 197—200, $[\alpha]_D$ −42° (*c*, 0·67)] was chromatographed over 50 g. of alumina (Aluminium Company of America, Alosco grade F-20, minus 80 mesh) and the infra-red spectra of the crystalline eluates were determined. In this way it was shown that 22-*isoallo*spirost-8(14)-3β-yl acetate was eluted first (benzene–hexane = 1 : 4) whilst unchanged starting material was eluted subsequently (benzene–hexane = 2 : 3). Recrystallisation from chloroform–methanol gave 22-*isoallo*spirost-8(14)-en-3β-yl acetate (1·1 g.), m. p. 203—206°, $[\alpha]_D$ −35° (*c*, 0·67), and slightly impure 22-*isoallo*spirost-7-en-3β-yl acetate, m. p. 216—220°, $[\alpha]_D$ −65° (*c*, 0·67), respectively.

22-*isoallo*Spirost-8(14)-en-3β-yl acetate was recovered (75%) unchanged after being shaken with mercuric acetate in chloroform–acetic acid (cf. Rosenkranz, Romo, Batres, and Djerassi, *J. Org. Chem.*, 1951, **16**, 298). It was likewise recovered (78%) when treated with osmium tetroxide in ethereal solution containing a few drops of pyridine for 12 days at room temperature.

Treatment of 22-isoallo*Spirost*-8(4)-*en*-3β-*yl Acetate with Hydrogen Chloride*.—The acetate (800 mg.), prepared by route (a) above, was dissolved in 25 ml. of chloroform and treated with a vigorous stream of hydrogen chloride gas at room temperature for ½ hour. The chloroform was removed *in vacuo* and the residue recrystallised three times from chloroform–methanol, to give pure 22-*isoallo*spirost-8(14)-en-3β-yl acetate, m. p. 210—213°, $[\alpha]_D$ −32° (*c*, 2·95), undepressed in m. p. on admixture with pure acetate [see under (a) above]. Clearly the hydrogen chloride treatment leads to a purification of the acetate, which cannot be effected (see above) by crystallisation alone.

22-isoallo*Spirost*-8(14)-*en*-3β-*yl Benzoate*.—Pure 22-*isoallo*spirosten-3β-yl acetate (750 mg.) (see above) was hydrolysed by 10% potassium hydroxide in boiling 1 : 1 dioxan–methanol (50 ml.) during 2 hours. After being worked up in the usual way, the alcohol was benzoylated (pyridine–benzoyl chloride overnight at room temperature). The *benzoate*, recrystallised twice from chloroform–methanol, had m. p. 179°, $[\alpha]_D$ −27° (*c*, 9·32), −27° (*c*, 8·13), $[M]_D$ −140°, unchanged on further recrystallisation (Found : C, 79·0; H, 9·05. $C_{34}H_{46}O_4$ requires C, 78·7; H, 8·95%).

The benzoate (800 mg.) was treated with dry hydrogen chloride as for the corresponding acetate (see above). One recrystallisation of the product from chloroform–methanol furnished 700 mg. of pure benzoate, $[\alpha]_D$ −27° (*c*, 8·33), m. p. 179°, undepressed on admixture with starting material.

22-isoallo*Spirost*-8(14)-*en*-3β-*ol*.—Pure 22-*isoallo*spirost-8(14)-en-3β-yl benzoate (400 mg.) was hydrolysed with potassium hydroxide in dioxan–methanol as for the hydrolysis of the acetate (see above). The 22-isoallo*spirost*-8(14)-3β-*ol* thus obtained was recrystallised from methanol, and had m. p. 178—179°, $[\alpha]_D$ −24° (*c*, 5·75), $[M]_D$ −99°, giving a marked depression in m. p. on admixture with the starting benzoate (Found : C, 78·05; H, 10·4. $C_{27}H_{42}O_3$ requires C, 78·2; H, 10·2%).

Acetylation (pyridine–acetic anhydride overnight at room temperature) gave back pure 22-*isoallo*spirost-8(14)-3β-yl acetate, thus confirming its homogeneity.

allo*Furosta*-8(14) : 20(22)-*diene*-3β : 26-*diol*.—22-*isoallo*Spirost-8(14)-en-3β-yl acetate (1·0 g.) in acetic anhydride (4 ml.) was heated in a sealed tube at 200° for 10 hours. After the mixture had been poured into water and extracted with ether, the oily furostadienediol diacetate was hydrolysed with 5% methanolic potassium hydroxide (30 minutes' refluxing) and purified by chromatography on 30 g. of ethyl-acetate-washed Alumina (same Alorco grade as above, but left under ethyl acetate for 2 days, filtered, washed with hexane, and reactivated at 100° for 2 days. This type of alumina is neutral and not too active and we have used it for polyhydroxy-adrenal steroids, 17-hydroxy-20-ketones which undergo the D-homo-rearrangement under alkaline conditions, or furosten derivatives). The material eluted with ether was recrystallised twice from hexane–acetone, to give allo*furosta*-8(14) : 20(22)-*diene*-3β : 26-*diol* as rectangular plates, m. p. 167—168°, $[\alpha]_D^{20}$ +54° (*c*, 0·67) (Found : C, 78·1; H, 10·1. $C_{27}H_{42}O_3$ requires C, 78·2; H, 10·2%).

20-*Keto*allo*pregna*-8(14) : 16-*dien*-3β-*yl Acetate*.—22-*isoallo*Spirost-8(14)-en-3β-yl acetate (3·0 g.) was converted into the corresponding furostadiene diacetate as indicated above, and the oily diacetate was oxidised with chromium trioxide and hydrolyzed exactly as described for the corresponding Δ^7-isomer (Djerassi, Romo, and Rosenkranz, *J. Org. Chem.*, 1951, **16**, 754). Recrystallisation from chloroform–methanol yielded 0·85 g. (36%) of colourless 20-*keto*allo*pregna*-8(14) : 16-*diene*-3β-*yl acetate* (Found : C, 77·75; H, 9·05. $C_{23}H_{32}O_3$ requires C, 77·5; H, 9·05%), with the following constants : m. p. 189—190°, $[\alpha]_D$ +90° (*c*, 0·67), infra-red bands at 1760 cm.$^{-1}$ (Δ^{16}-20-ketone), and at 1736 and 1239 cm.$^{-1}$ (acetate bands), in excellent agreement with the values reported by Jones *et al.* (*J. Amer. Chem. Soc.*, 1950, **72**, 956). The ultra-violet maximum at 230 mμ (log ε 4·07) is abnormally low for a Δ^{16}-20-ketone as far as the position of the maximum is concerned, but this has been confirmed a number of times with different batches. Careful chromatography and spectrophotometric analysis of the individual fractions did not give any material with a maximum above 230 mμ. Apparently, this hypsochromic shift is due to the 8(14)-double bond. The only other Δ^{16}-20-ketone with a maximum around 230 mμ is one described by Wagner, Moore, and Folker (*ibid.*, p. 1856).

20-*Keto*allo*pregn*-8(14)-*en*-3β-*yl Acetate*.—(a) *By hydrogenation of* 20-*keto*allo*pregn*-8(14) : 16-*dien*-3β-*yl acetate*. A solution of this acetate (0·5 g.) in ethyl acetate (40 ml.) was shaken with prereduced 10% palladised charcoal (80 mg.) in hydrogen at room temperature and atmospheric pressure. The gas uptake ceased after 20 minutes, 1·1 mols. having been consumed. Recrystallisation from methanol yielded 0·36 g. of 20-*keto*allo*pregn*-8(14)-*en*-3β-*yl acetate* as large prisms, m. p. 154—156°. This material was further purified by chromatography over alumina. The first two fractions eluted with benzene were recrystallised from light petroleum to give the pure acetate, m. p. 156—157°, $[\alpha]_D$ +90° (*c*, 3·41), $[M]_D$ +322°, $\lambda_{max.}$ 205 mμ [$\varepsilon_{max.}$ 10 500, ε_{215} 6700 (*c*, 0·0052)] and 282 mμ (ε 60), infra-red bands at 1706 cm.$^{-1}$ (unconjugated 20-keto-steroid, Jones *et al.*, *loc. cit.*) and at 1736 and 1239 cm.$^{-1}$ (acetate bands) (Found : C, 76·95; H, 9·6. $C_{23}H_{34}O_3$ requires C, 77·05; H, 9·55%).

(b) *By rearrangement of* 20-*keto*allo*pregn*-7-*en*-3β-*yl acetate*. To a prehydrogenated mixture of 10% palladised charcoal (100 mg.), glacial acetic acid (5 ml.), and ethyl acetate (15 ml.) there was added a solution of 20-keto*allo*pregn-7-en-3β-yl acetate (700 mg.) (Djerassi, Romo, and Rosen-

kranz, *loc. cit.*) in ethyl acetate (10 ml.); the mixture was shaken overnight in hydrogen (no gas uptake). After being worked up in the usual way the reaction product was triturated with hexane. Filtration afforded 580 mg. of a colourless solid, m. p. 152—155°, $[\alpha]_D$ +92° (*c*, 0·67). Two recrystallisations from methanol gave pure 20-keto*allo*pregn-8(14)-en-3β-yl acetate, m. p. 155—156°, $[\alpha]_D$ +95° (*c*, 0·67) (Found: C, 76·9; H, 9·5%). The infra-red spectrum was identical with that of a specimen prepared according to (a) above.

Action of Hydrogen Chloride on 20-*Keto*allo*pregn*-8(14)-*en*-3β-*yl Acetate*.—The acetate (200 mg.) in chloroform (10 ml.) was treated with dry hydrogen chloride as detailed above for the 8(14)-sapogenin benzoate. After removal of the chloroform by evaporation *in vacuo*, the product was chromatographed over alumina. Four fractions were collected, each being eluted with benzene (50 ml.) The m. p.s were, respectively, (1) 130—145°, (2) 152—155°, (3) 152—155°, and (4) 140—150°. Recrystallisation of fractions (2) and (3) combined from methanol afforded pure starting material, m. p. 156—157°, $[\alpha]_D$ +89° (*c*, 4·20). Fraction (1), recrystallised, had m. p. 150—152°, fraction (4), m. p. 152—154°. All fractions were undepressed in m. p. on admixture with pure 20-keto*allo*pregn-8(14)-en-3β-yl acetate.

SYNTEX RESEARCH LABORATORIES,
MEXICO CITY, D.F., MEXICO.
BIRKBECK COLLEGE, LONDON, W.C.1.

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