ketone, is characteristic for each proton.[24] Δ is higher for H_3 than for H_4 and H_2 with isomers **1c** to **4c** and lower for H_2 than for H_3 and H_4 with isomers **1t** to **4t**. Values of Δ (in hertz) are given in Table V.

Likewise, for the determination of the configurations of dioxolanes we used the LIS effect of corresponding ketones. The configuration of dioxolanes **12t**, **12c**, **13t**, and **13c** was determined by the study of ketones **1t**, **1c**, **2t**, and **2c**. We assigned the configuration of dioxolanes **14c**, **14t**, **15c**, and **15t** by the evaluation of Δ for protons H_3 and H_4 in corresponding ketones (Table VI).

Acknowledgment. We wish to thank Dr. U. O. Cheriyan and Professor R. J. Taillefer of the University of Sherbrooke for their assistance in the English rewriting of this article.

Registry No.—Zinc, 7440-66-6.

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(20) Crude materials, from dihalocyclopropanation, are used as starting dioxolanes because they are easily decomposed into their corresponding ketones by distillation or chromatographic isolation. However, their assay by analytical chromatography showed a satisfactory purity.
(21) With exceptions for O and especially Q, which are fully reduced into the cyclopropane derivatives with boiling ethanol.
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Side-Chain Inversion of Steroidal Olefins Promoted by Hydrogen Chloride

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Received December 29,1977

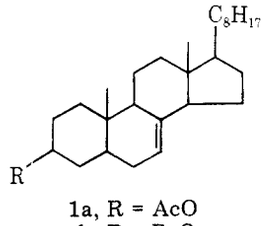
The reaction of hydrogen chloride on 7-, 8(14)-, and 14-ene steroids was investigated. A 14α-chloro compound is the product of kinetically controlled addition of the acid. A 14β-chloro compound with the side chain in the 17α configuration originates in diethyl ether at temperatures lower than −30 °C in the presence of hydrogen chloride, via a carbocation at C_{14}. There is evidence that the inversion occurs through two distinct rearrangements involving the intermediary formation of a 12,14α-cyclo-12,13-seco-5α-cholest-13(17)-ene.

In a previous communication[1] we reported that 3β-acetyloxy-5α-cholest-7-, -8(14)-, or -14-enes (**1a, 2a,** and **3a**) undergo inversion of the side chain by the action of hydrogen chloride in diethyl ether at −60 °C to yield 3β-acetyloxy-14-chloro-5α,14β,17β*H*-cholestane (**4a**), possibly through the intermediary formation of 3β-acetyloxy-12,14α-cyclo-12,13-seco-5α-cholest-13(17)-ene (**5a**). Caspi et al.[2] simultaneously described the isolation of 3β-acetyloxy-5α,17β*H*-cholest-14-ene (**6a**) by the action, on **2a,** of hydrogen chloride in chloroform at −78 °C and prolonged treatment with $NaHCO_3$. More recently it has been shown that the same rearrangement is also caused by hydrogen bromide.[3]

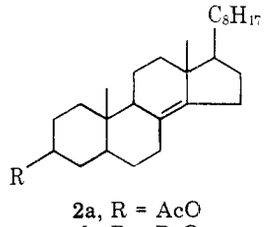
In order to clarify the mechanism of the side chain inversion, we decided to explore the processes involving the action of hydrogen chloride on 7-, 8(14)-, and 14-ene steroids.

Hydrogen chloride has long been considered to promote the direct isomerization of the 7 or 8(14) double bond of steroids to the 14 position.[4] In fact 14- and 8(14)-ene steroids in an approximately 1:1 ratio were isolated when the reaction was carried out at 0 °C in chloroform solution.[5] However Cornforth et al.,[6] operating at −30 °C on 3β-benzoyloxy-5α-cholest-8(14)-ene (**2b**), isolated a compound to which the structure of 3β-benzoyloxy-14α-chloro-5α-cholestane (**7a**) was attributed. When a chloroform solution containing this adduct was shaken with aqueous $NaHCO_3$, dehydrochlorination occurred and 3β-benzoyloxy-5α-cholest-14-ene (**3b**) was obtained.

In order to definitively prove that the 14-ene (**3b**) is never formed by the direct action of hydrogen chloride on 8(14)-ene



1a, R = AcO
b, R = BzO



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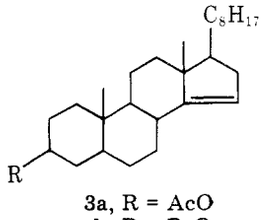
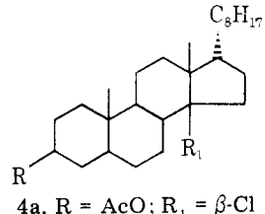
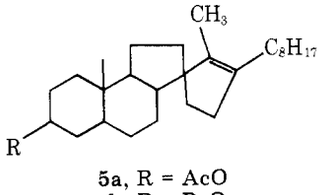
b, R = BzO



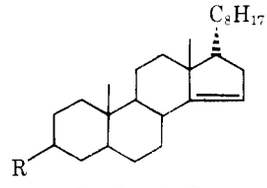
3a, R = AcO
b, R = BzO



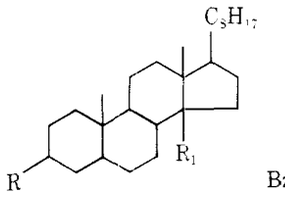
4a, R = AcO; R_1 = β-Cl
b, R = BzO; R_1 = β-Cl
c, R = AcO; R_1 = β-H



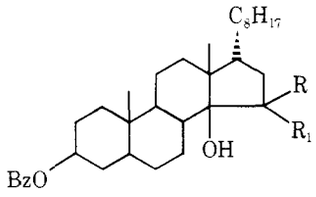
5a, R = AcO
b, R = BzO



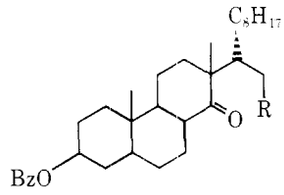
6a, R = AcO
b, R = BzO



7a, R = BzO; R_1 = α-Cl
b, R = BzO; R_1 = β-Cl
c, R = AcO; R_1 = β-H

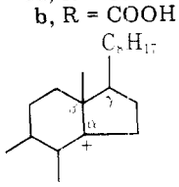


8a, R = 15β-OH; R_1 = H
b, R = R_1 = O



C_8H_{17} $C_8H_{17}CH{=}CHCHO$
10

9a, R = CHO
b, R = COOH



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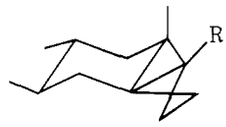

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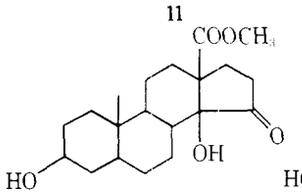
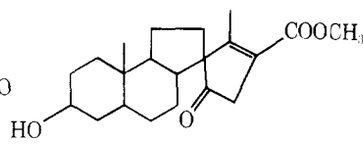


13



14

(**2b**), we submitted **3b** at −30 °C in chloroform to the action of hydrogen chloride. 7-Ene (**1b**) and 8(14)-ene (**2b**) were treated under the same conditions in separate experiments. In each case the ^1H NMR spectrum of the residue, obtained from the evaporation of the reaction mixture, did not show any signal attributable to olefinic protons. The only product isolated by crystallization was the chloro derivative, to which the structure **7a** is now assigned on the basis of ^1H NMR evidence. The mother liquors did not contain any 8(14) isomer. The ^1H NMR spectrum of **7a** shows a singlet for the C-18 protons at δ 0.92. The C-18 protons resonate at δ 1.18 in the 14β-chloro derivative **4b.** Since side-chain inversion from the 17α to the 17β configuration causes an upfield shift of 0.06 ppm as measured in 3β-acetyloxy-5α,14β-cholestane (**7c**)[7] and in 3β-acetyloxy-5α,14β,17β*H*-cholestane (**4c**),[2] a value of δ 1.12 is expected for the C-18 protons of the as yet unknown 3β-acetyloxy-14-chloro-5α,14β-cholestane (**7b**). Moreover the 0.27-ppm downfield shift for the C-18 protons of **7a,** with respect to the 14α-unsubstituted compound, compares well with the reported value of 0.25 ppm downfield shift for the C-19 protons of the 5α-chloro steroids.[8]

Solid **7a** was stable at room temperature for at least 1 year. It was rapidly transformed in chloroform solution at 25 °C (and more slowly at 0 °C) into **2b** and **3b** in a 1:4 ratio, both in the presence or absence of 0.5 M $NaHCO_3$, as determined by TLC on silica gel–$AgNO_3$.[9] **7a** was quantitatively transformed into **3b** by treatment with a 0.5 M methanolic solution of triethylamine. The high rate of solvolysis of **7a** is in good agreement with the postulated effect of strong steric strain in enhancing the rates of solvolysis of highly branched tertiary chlorides.[10-12] Formation of both **2b** and **3b** indicates that carbonium ion intermediates are involved in the reaction.

The electrophilic addition of hydrogen chloride to olefins has long been considered to involve intermediates with carbonium ion character.[13,14a] Moreover, there is evidence that the structure of the olefin plays a role in the reaction mechanism.[14b] The exclusive formation of a 14α-chloro derivative from 7-, 8(14)-, and 14-enes indicates that a common C-14 carbonium ion intermediate is involved in the reaction.

When the addition of hydrogen chloride was carried out in diethyl ether at −30, −60, or −78 °C for 3–7 h to 0.01-M solutions of **1b, 2b,** or **3b,** respectively, 3β-benzoyloxy-14-chloro-5α,14β-17βH-cholestane (**4b**) was quantitatively isolated.[15,16] **4b** was stable at 25 °C in chloroform or ether solution, as well as in the presence of 0.5 M $NaHCO_3$; it was quantitatively transformed into the epimerized 14-ene **6b** by triethylamine in methanol at 50 °C, and was solvolyzed in methanol at the same temperature to yield the compounds **6b** and **5b**[17] in 20:1 ratio as determined by GLC and TLC on silica gel–$AgNO_3$.

The epimerized 14-enes **6a** and **6b** were quantitatively reconverted into the 14β-chloro compounds **4a** and **4b** by addition, at −78 °C, of hydrogen chloride for few minutes, and transformed into the spiranic compounds **5a** and **5b** by treatment with 4-toluenesulfonic acid in boiling benzene.

The addition of hydrogen chloride to either **2b** or **3b** in diethyl ether at −78 °C for 20 min resulted in the quantitative formation of the 14α-chloride **7a,** which was quantitatively transformed into the epimerized 14β-chloro compound **4b** by further exposure to the hydrogen chloride.

These results prove that the epimerized 14-chloro compounds originate from the "natural" 14α-chloro compounds, the products of kinetically controlled addition of hydrogen chloride to an 8(14)- or a 14-ene steroid, and suggest that **7a** is transformed into **4b** via a discrete cationic intermediate.[14b] This was proven by submitting **7a** at −78 °C to hydrogen chloride enriched in ^3HCl. The labeled **4b** was dehydrochlorinated with triethylamine in methanol to give **6b,** showing a 25% loss of radioactivity associated to a hydrogen of the 15 position. The location of the residual radioactivity was ascertained as follows. The labeled **6b** was oxidized to the diol **8a** with OsO_4. The configuration of the 14β-OH (and by consequence of the 15β-OH) was assigned by measurement of the shift of the C-18 proton signal in the solvent pair deuteriochloroform–pyridine.[18] The observed value (0.16 ppm) was identical with that calculated for a dihedral angle of 60° between the C-18 methyl group and the 14β-hydroxy group. The labeled **8a** was oxidized with chromium trioxide to the hydroxy ketone **8b,** which contained 50% of the radioactivity of the labeled **4b,** thus proving that both the 15-hydrogens were labeled. The hydroxy ketone **8b** was oxidized with chromium trioxide to the keto acid **9b,** which contained 25% of the original radioactivity of **4b** after alkaline exchange at room temperature and rebenzoylation, thus indicating that 25% of the radioactivity of **4b** was associated with the 8-hydrogen. To locate the residual 25% of the radioactivity of **4b,** the compound **6b** was ozonized and the resulting keto aldehyde **9a** was pyrolyzed[6] to give the unsaturated aldehyde **10** (isolated as the semicarbazone) which contained 51% of the total radioactivity. The semicarbazone of the aldehyde **10** was degraded to the (*R*)(−)-2,6-dimethylheptanoic acid,[19] isolated as the amide,[20] which showed a complete loss of radioactivity. This fact indicated that the label in fragment **10** is located at the aldehydic hydrogen (25%) and at the 17-hydrogen (25%). Position 16 could be excluded, since at least part of the radioactivity in this position should be lost in the retro-Michael reaction on the keto aldehyde **9a.**

It can be concluded that, in the rearrangement of **7a** to **4b,** the discrete cation **11** should be formed. Moreover a hydrogen is lost from the 17α position and a hydrogen added at the 17β position.

Transformation of the cation **11** into the 14β-chloro compound **4b** requires inversion at the γ carbon to the charge. Intermediary formation of the very strained pentacyclic

compound **12** appears very unlikely, as both junctions of the cyclopropane ring are trans. A more reasonable hypothesis appears to be consistent with intermediary formation of the spiranic olefin **5b**. Some facts are in agreement with this assumption: (a) methyl 3β,14β-dihydroxy-15-oxo-5β,14β-androstane-17β-carboxylate (**13**) was transposed by thionyl chloride in pyridine into the spiranic compound **14**;[21] (b) the acetate **3a** was transformed in part into the spiro compound **5a** by boron trifluoride in benzene;[22] (c) spiro compounds such as **5** are formed by treatment of 7-, 8(14)-, and 14-ene steroids with 4-toluenesulfonic acid in refluxing benzene.[17] However, it seems unlikely that transposition is promoted by a classical, planar carbocation **11**, since there is no conformation of the molecule in which the C_{12}–C_{13} bond is aligned with the vacant p orbital at C_{14}, as it appears from molecular models. This assumption is supported by the evidence that the transposition of the 10β-methyl group of 5α-cholestane-4α,5α-diol 4α-acetate occurs owing to the alignment of the C_{10}–C_{19} bond with the vacant p orbital at C_5.[23] Moreover the presence of the label at the 8 and 15 position of **4b** proves that 8(14)- and 14-enes are reversibly formed during the transposition, which could occur by addition of hydrogen chloride to the Δ^{14} double bond by way of an Ad_E3 mechanism[14c] involving a transition state in which the chlorine atom of acid interacts with the β side of the carbocation. The interaction allows alignment of the C_{12}–C_{13} bond and promotes ring *C* contraction and formation of the spiro compound, with the loss of the 17α-hydrogen.

Final evidence of intermediary formation of the spiro compounds requires that the action of hydrogen chloride on these products should afford epimerized 14β-chloro compounds. In fact **5b** was instantaneously transformed into **4b** when dissolved at −78 °C in hydrogen chloride saturated ether. It can be inferred that a proton attacks **5b** at the 17β position, promoting ring C enlargement with final introduction of a chloride ion at the 14β position.

Experimental Section

All melting points are uncorrected. Infrared spectra were taken as Nujol mulls and absorptions are reported as reciprocal centimeters, NMR spectra were taken on a Varian HA-100 as chloroform-d_1 solutions and are reported as δ units relative to Me_4Si, and optical rotations were taken as chloroform solutions. Gas–liquid chromatography (GC) was done on 1 or 3% SE 30 columns (2 m × 2.5 mm). The mass spectra were determined on an LKB 9000 spectrometer either by GC (on 3% SE 30 column, 2 m × 2.5 mm) or by direct inlet (di). Radioactivity determinations were carried out as reported previously.[24] Molar radioactivity (MR) was expressed in nCi/nmol.

3β-Benzoyloxy-14-chloro-5α,14α-cholestane (7a). The benzoates **1b, 2b,** and **3b** in $CHCl_3$ were treated with HCl under the same conditions described by Cornforth[6] for **2b.** In each case the obtained solid white residue did not show any signal attributable to olefinic protons in the NMR spectrum at 0 °C. Crystallization of the residue from petroleum ether at −30 °C gave pure 3β-benzoyloxy-14-chloro-5α,14α-cholestane (**7a**): mp 157 °C (lit.[6] mp 153–156 °C); NMR (0 °C) δ 0.92 (s, C-13 Me), 0.83 (s, C-10 Me); mass spectrum (di) *m/e* 490 (M^+ − HCl), 475, 377, 255. Anal. Calcd for $C_{34}H_{51}O_2Cl$: C, 77.5; H, 9.7; Cl, 6.7. Found: C, 77.6; H, 9.9; Cl, 6.8.

7a was also obtained in 20 min by treating a 20–25 mM solution of **1a, 2a,** or **3a** in diethyl ether at −78 °C.

A solution of **7a** (100 mg) in $CHCl_3$ (10 mL) was left at 25 °C for 2 h, cooled at 0 °C, and washed with ice–water. The aqueous solution was titrated for Cl^- ions (calcd 6.7 mg, found 6.6 mg). After usual workup of organic solution, chromatography of the residue on silica gel G–Celite–$AgNO_3$ (1:1:0.3) yielded **2b** (18 mg) and **3b** (76 mg), whose physical constants (mp, GC, and mass spectrum) were identical with those of authentic specimens. Treatment of **7a** with 0.5 M methanolic triethylamine, after usual workup, afforded pure **3b** in quantitative yields.

3β-Benzoyloxy-14-chloro-5α,14β,17β*H*-cholestane (4b). In typical experiments the benzoates **1b, 2b,** and **3b** (500 mg) in diethyl ether (100 mL) were treated with HCl at −60 °C for 5 h. The pressure in the reaction vessel was then lowered to about 20 mm without interrupting the cooling. The residue was poured into ice water and extracted with diethyl ether. The organic layer was dried (Na_2SO_4) and evaporated in vacuo to give solid 3β-benzoyloxy-14-chloro-5α,14β,17β*H*-cholestane (**4b**): mp 130–132 °C; NMR δ 1.18 (s, C-13 Me), 0.81 (s, C-10 Me); mass spectrum (di) *m/e* 490 (M^+ − HCl). Anal. Calcd for $C_{34}H_{51}O_2Cl$: C, 77.5; H, 9.7; Cl, 6.7. Found: C, 78.0; H, 9.5; Cl, 6.7.

3β-Benzoyloxy-5α,17β*H*-cholest-14-ene (6b). 3β-Benzoyloxy-14-chloro-5α,14β,17β*H*-cholestane (**4b;** 500 mg) in methanol (50 mL) and triethylamine (5 mL) was refluxed for 30 min. After usual workup, 3β-benzoyloxy-5α,17β*H*-cholest-14-ene (**6b;** 470 mg) was obtained as an oil. Crystallization from methanol gave pure **6b:** mp 67–70 °C; $[\alpha]^{21}_D$ +61.1°; NMR δ 5.08 (m, C-15 H), 1.09 (s, C-13 Me), 0.87 (s, C-10 Me); mass spectrum *m/e* 490 (M^+). Anal. Calcd for $C_{34}H_{50}O_2$: C, 83.2; H, 10.3. Found: C, 83.5; H, 10.2.

Radioactive 3β-Benzoyloxy-14-chloro-5α,14β,17β*H*-cholestane (4b). 3β-Benzoyloxy-14-chloro-5α,14α-cholestane (**7a;** 300 mg) in diethyl ether (60 mL) was treated at −78 °C with ^3HCl for 5 h. After usual workup **4b** was obtained by crystallization from petroleum ether (MR 156, unchanged after repeated crystallizations). Localization of radioactivity was determined after dilution of the product (1:9) with unlabeled **4b.**

Radioactive 3β-Benzoyloxy-5α,17β*H*-cholest-14-ene (6b). Radioactive **4b** (MR 15.6) was dehydrochlorinated as described above and tritiated **6b** was crystallized to constant radioactivity (MR 11.7; 75% of **4b**).

Radioactive 3β-Benzoyloxy-5α,17β*H*-cholestane-14α,15β-diol (8a). Osmium tetroxide (360 mg) was added to a solution of radioactive **6b** (500 mg) in diethyl ether (7 mL) containing pyridine (0.5 mL) and the mixture was allowed to stand at room temperature in the dark for 24 h. After usual workup, the diethyl ether–dichloromethane solution was shaken with potassium hydroxide (1.5 g) and D-mannitol (1.5 g) in water (15 mL). The product was isolated with the usual washing and drying procedures. Crystallization from MeOH gave 430 mg of radioactive 3β-benzoyloxy-5α,17β*H*-cholestane-14β,15β-diol (**8a**): mp 173–174 °C; $[\alpha]^{21}_D$ −11°; NMR ($CDCl_3$) δ 4.28 (m, 15α-H), 1.07 (s, C-13 Me), 0.77 (s, C-10 Me); NMR (pyridine-d_5) δ 4.4 (m, 15α-H), 1.23 (s, C-13 Me), 0.81 (s, C-10 Me); mass spectrum (di) *m/e* 506 (M^+ − 18), 354, 216; MR 11.7. Anal. Calcd for $C_{34}H_{52}O_4$: C, 77.8; H, 10.0. Found: C, 77.5; H, 9.8.

Radioactive 3β-Benzoyloxy-14-hydroxy-5α,14β,17β*H*-cholestan-15-one (8b). Compound **8a** (300 mg) in pyridine (0.5 mL) was added at 0 °C to a solution of chromium trioxide (300 mg) in pyridine (3 mL) and dichloromethane (12 mL) and the mixture was stirred for 5 min. After usual workup and crystallization of the crude residue from methanol, radioactive **8b** was obtained: mp 135–137 °C; mass spectrum *m/e* (di) 522 (M^+); IR 3310, 1740, 1720 cm^{-1}; MR 7.8 (50% of **4b**). Anal. Calcd for $C_{34}H_{50}O_4$: C, 78.1; H, 9.6. Found: C, 78.3; H, 9.4.

Radioactive 3β-Benzoyloxy-14-oxo-14,15-seco-5α,17β*H*-cholestan-15-oic acid (9b). Chromium oxide (56 mg) in acetic acid (2.8 mL) was added at 0 °C to a solution of radioactive **8b** (200 mg) in acetic acid (8 mL) and benzene (1 mL). The mixture was allowed to stand at room temperature for 2 h. After usual workup and crystallization of the residue from isooctane–diethyl ether, radioactive **9b** was obtained: mp 159–161 °C; $[\alpha]^{25}_D$ −33°; mass spectrum (di) *m/e* 520 (M^+ − 18), 354 (M^+ −184); IR 1740, 1710 cm^{-1}; MR 7.8 (50% of **4b**). Anal. Calcd for $C_{34}H_{50}O_5$: C, 75.8; H, 9.3. Found: C, 75.5; H, 9.4. Me ester, mass spectrum (di) *m/e* 521 (M^+ − 31), 479 (M^+ − 73), 354 (M^+ − 196). Acid **9b** after saponification at 25 °C and rebenzoylation showed MR 3.9 (25% of **4b**).

Radioactive 3β-Benzoyloxy-14-oxo-14,15-seco-17β*H*-cholestan-15-al (9a) and its Pyrolysis. A solution of labeled **6b** (300 mg) in dichloromethane (5 mL) was ozonized at −70 °C until excess ozone was present. The solvent was removed and the residue was stirred for 2 h with acetic acid (7 mL) and Zn powder (0.5 g). After usual workup oily compound **9a** was obtained: IR 2700, 1720, 1714 cm^{-1}; NMR δ 9.67 (H_{15}, t, J = 1.5 Hz); mass spectrum *m/e* 522 (M^+), 354 (M^+ − 168). The keto aldehyde (**9a**) was heated at 15-mm pressure (capillary leak fed with N_2) to 200 °C; the temperature was raised during 2 h to 250 °C and maintained there for 3 h. The volatile product, trapped in a receiver at −30 °C, was taken up in a little diethyl ether and washed with $NaHCO_3$ solution. The solvent was removed to give the crude aldehyde **10.** This was transformed in its semicarbazone: mp 134 °C; $[\alpha]^{21}_D$ −23°; mass spectrum *m/e* 225 (M^+); MR 7.7 (49% of **4b**). Anal. Calcd for $C_{12}H_{23}N_3O$: C, 64.0; H, 10.2; N, 18.7. Found: C, 64.3; H, 9.8; N, 18.4.

(*R*)(−)-2,6-Dimethylheptanoic Acid Amide. Potassium permanganate was added to a boiling acetone solution of the semicarbazone of the unsaturated aldehyde **10.** After usual workup the acid fraction was treated with thionyl chloride. The resulting acid chloride

gave the amide, which was crystallized from *n*-hexane to yield the pure product: mp 75–77 °C;[20] MR 0.0.

3β-Benzoyloxy-12,14α-cyclo-12,13-seco-5α-cholest-13(17)-ene (5b). Compound **6b** (500 mg) was added to a mixture of anhydrous 4-toluenesulfonic acid (250 mg) and benzene (125 mL) and refluxed for 5 min. After usual workup the crude residue was chromatographed on silica gel G–Celite–$AgNO_3$ (1:1:0.3). Fractions eluted with petroleum ether gave **5b** (400 mg): oil; NMR δ 1.46 (t, J = 0.7 Hz, C-13 Me), 0.93 (d, J = 7 Hz, C-20 Me), 0.84 (d, J = 6 Hz, C-25 Me_2), 0.8 (s, C-10 Me); mass spectrum (di) *m/e* 490 (M^+), 206, 121. Anal. Calcd for $C_{34}H_{50}O_2$: C, 83.2; H, 10.3. Found: C, 83.4; H, 10.0.

Treatment of 3β-Benzoyloxy-12,14α-cyclo-12,13-seco-5α-cholest-13(17)-ene (5b) with Hydrogen Chloride. The spiro olefin (**5b**;[17] 200 mg) was dissolved in hydrogen chloride saturated ether (20 mL) at −78 °C. The solution was poured instantaneously into a $NaHCO_3$ saturated solution and extracted with diethyl ether; the organic layer was dried (Na_2SO_4) and evaporated in vacuo to give 3β-benzoyloxy-14-chloro-5α,14β,17β*H*-cholestane (**4b**).

Acknowledgments. This research was supported by the Italian Research Council. We thank Professor G. Galli, Institute of Pharmacology and Pharmacognosy, University of Milan, for mass spectra.

Registry No.—**1a,** 2465-00-1; **1b,** 4356-22-3; **2a,** 6562-21-6; **2b,** 6673-65-0; **3a,** 40446-06-8; **3b,** 6673-66-1; **4b,** 66792-81-2; **5b,** 66792-87-8; **6b,** 66808-37-5; **7a,** 66808-38-6; **8a,** 66792-86-7; **8b,** 66792-85-6; **9a,** 66792-84-5; **9b,** 66792-83-4; **9b** methyl ester, 66792-82-3; **10,** 66792-88-9; **10** semicarbazone, 66792-89-0; (*R*)(−)-2,6-dimethylheptanamide, 66792-90-3.

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Importance of the Structure of the Phosphorus Functionality in Allowing Dihedral Angle Control of Vicinal ^{13}C–^{31}P Coupling. Carbon-13 NMR Spectra of 7-Substituted Bicyclo[2.2.1]heptane Derivatives[1]

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Received February 16, 1978

Carbon-13 NMR spectra were obtained on norbornenes with the 7 position bearing the following substituents: Cl_2P (syn and anti), Me_2P (syn and anti), $Me_2(S)P$ (anti), Me_3P^+ (anti). Norbornanes with 7-Cl_2P and 7-Me_2P were also studied. For the groups $Me_2(S)P$ and Me_3P^+, vicinal C–P coupling was clearly controlled by dihedral angle relations; carbons anti to P were strongly coupled (about 16 Hz), while carbons syn to P showed no coupling. This result is consistent with observations made previously for rigid cyclohexanes bearing these substituents in equatorial or axial positions, respectively. However, the trivalent groups Cl_2P and Me_2P showed no indication of their vicinal coupling (absolute), being minimized at the same dihedral angle; with these groups in either the syn or anti 7 position of norbornene or in the 7 position of norbornane, coupling to the two sets of vicinal carbons differed very little. Again this result is consistent with observations from cyclohexanes and leads to the conclusion that dihedral angle control of vicinal (C–P) coupling is not general in phosphorus chemistry. One-bond ^{13}C–^{31}P coupling was also considered; there was no consistent relation with steric crowding in the compounds studied. Chemical shifts of the phosphorus compounds followed the expected trends, with γ-gauche carbons shifted relatively upfield and anti carbons relatively downfield from the corresponding bicyclo[2.2.1]heptane. Curiously, in *syn*-7-bromonorbornene both types of γ carbon were shifted upfield.

From a study[2] of the effect of phosphorus functions on the ^{13}C NMR spectra of the cyclohexane ring came an indication that three-bond ^{13}C–^{31}P coupling was under steric control in a Karplus-like relation for tetravalent phosphorus functions (e.g., $Me_2(S)P$ and Me_3P^+) but not for some trivalent functions (e.g., Cl_2P and Me_2P). To illustrate, ^{31}P coupling to ring carbons 3 and 5 was 13 Hz when $Me_2(S)P$ was placed in the equatorial position of 4-*tert*-butylcyclohexane (dihedral angle about 180°), but only 4 Hz when in the axial position (dihedral angle about 60°), strongly suggestive of a Karplus effect. On the other hand, Cl_2P similarly placed gave $^3J_{PC}$ values of 11 and 9 Hz, respectively, and Me_2P gave values of 11 and 8 Hz. However, uncertainty about dihedral angles in the axially substituted cyclohexanes, which might be capable of distortion to skew-boat conformations, left the situation unclear. We also[3] encountered cases among some phosphorinane derivatives (**1–4**) where a dihedral angle control of vicinal coupling was suggested. Thus, two $^3J_{PC}$ path-

0022-3263/78/1943-3508$01.00/0