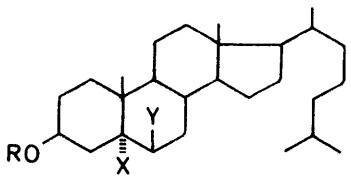
On Steroids. Part 209. Formation of 6β-Bromo-5-chloro-5α-cholestan-3β-ol on Addition of Bromine Chloride to Cholesterol

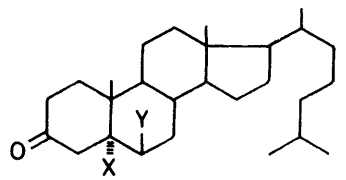
By **Alexander Kasal**, Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague, Czechoslovakia

On treatment with phosphorus tribromide 3β-acetoxy-5-chloro-5α-cholestan-6β-ol (6) yielded 3β-acetoxy-6β-bromo-5-chloro-5α-cholestane (4) which was converted into the corresponding 3β-hydroxy-derivative (2) and the 3-oxo-derivative (14). Dehydrohalogenation of compound (14) gave the known 6β-bromo-4-cholesten-3-one (15). Compound (2) was found as a product of bromine chloride addition to cholesterol. Results are discussed in terms of stereochemical control of addition of an electrophile to the Δ^5-double bond.

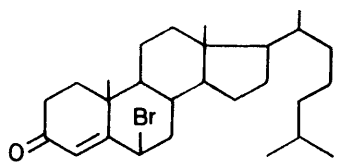
A VARIETY of electrophilic reagents add to Δ^5-unsaturated steroids with the formation of mixtures in which the product of initial electrophilic attack from the more exposed α-side usually predominates.[1] In 1952 Ziegler [2] described the addition of bromine chloride [3] to cholesterol and this reaction has since been regarded as a stereospecific synthesis of 5-bromo-6β-chloro-derivatives of the type (1). The presence of a small amount of the isomer (2) was occasionally suspected [4] but has never been proved. Recently de la Mare [4,5] reported electrophilic addition reactions to cholest-5-en-3-one: both bromine chloride and perbenzoic acid were found to add from both sides in comparable yields (*ca.* 1.3 : 1 and 2 : 1, respectively, in favour of the α-attack) which again questioned the measure of stereoselectivity of the electrophilic addition of bromine chloride to cholesterol. Since 5α,6β-dihalogeno-steroids are known to be isomorphic compounds exhibiting undepressed mixed melting points [2] a small amount of compound (2) in the bulk of isomeric (1) might easily evade detection. Synthesis



(1) R = H, X = Br, Y = Cl
(2) R = H, X = Cl, Y = Br
(3) R = Ac, X = Br, Y = Cl
(4) R = Ac, X = Cl, Y = Br
(5) R = Ac, X = Br, Y = Br
(6) R = Ac, X = Cl, Y = OH
(7) R = Ac, X = Cl, Y = OMes
(8) R = Ac, X = Cl, Y = OPH(OH)O
(9) R = Bz, X = Br, Y = Cl
(10) R = Bz, X = Cl, Y = Br
(11) R = H, X = Br, Y = F
(12) R = H, X = F, Y = Br



(13) X = Br, Y = Cl
(14) X = Cl, Y = Br



(15)

[1] D. N. Kirk and M. P. Hartshorn, 'Steroid Reaction Mechanisms,' ed. C. Earborn and N. B. Chapman, Elsevier, London, 1968, p. 94.
[2] J. B. Ziegler and A. C. Shabica, *J. Amer. Chem. Soc.*, 1952, **74**, 4891.
[3] R. E. Buckles, *J. Amer. Chem. Soc.*, 1949, **71**, 1157.
[4] P. B. D. de la Mare and R. D. Wilson, *Tetrahedron Letters*, 1975, 3247.
[5] P. B. D. de la Mare and R. D. Wilson, *J.C.S. Perkin II*, 1977, 975.

of 6β-bromo-5-chloro-5α-cholestan-3β-ol (2) therefore seemed desirable.

Consistent with an earlier report [6] the reaction of olefins with *N*-chloroacetamide in the presence of bromide ions is not applicable to the synthesis of bromochlorides: under the conditions described cholesteryl acetate gave 3β-acetoxy-5,6β-dibromo-5α-cholestane [7] (5) in almost quantitative yields. Attempts at substitution of the tertiary bound atom of bromine in 5α,6β-dibromo-derivatives on treatment with copper chloride [8] were unsuccessful. Attempts at substitution of the 6β-methylsulphonyloxy-derivative (7) lead to olefinic products only.

The desired compound (4) was eventually prepared in a low yield by reaction of the 6β-hydroxy-derivative (6) with phosphorus tribromide. Elemental analysis of the major product was consistent with the formula $C_{29}H_{50}ClO_5P$, its i.r. spectrum was compatible with structure (8) while its ^1H n.m.r. spectrum showed that the configuration at the 3- and 6-carbons was unchanged. The minor component of the mixture (4) was of the same polarity as compound (3), its melting point was identical with that of compound (3), and a mixed melting point was undepressed.

On hydrolysis the bromo-chloride (4) afforded the corresponding hydroxy-derivative (2) which was characterized as the benzoyloxy-derivative (10). The hydroxy-compound (2) was oxidized according to Jones [9] to 6β-bromo-5-chloro-5α-cholestan-3-one * (14). Optical rotatory dispersion properties compare well with those of other 5α,6β-dihalogeno-5α-cholestan-3-ones [10] (see Table 1). Dehydrohalogenation of the ketone (14) leads to the known 6β-bromocholest-4-en-3-one (15).

TABLE 1

O.r.d. data for 5,6β-dihalogeno-5α-cholestan-3-ones [a]

Compound	Amplitude [b]
5,6β-Dichloro-5α-cholestan-3-one [c]	−8
5-Bromo-6β-chloro-5α-cholestan-3-one [c]	−15
6β-Bromo-5-chloro-5α-cholestan-3-one (14)	−31
5,6β-Dibromo-5α-cholestan-3-one [c]	−33

[a] For solutions in dioxan. [b] Cotton effect of the $n\rightarrow\pi^*$ transition of the carbonyl group at 292 nm is involved. [c] Values are taken from ref. 2.

Properties of the two series of isomers are very close to each other. Melting points and polarities are identical for each pair, specific rotation values are very similar though for the 5-bromo-6β-chlorides they are slightly more negative than for their counterparts (see Table 2). I.r. spectra differ particularly in the region of halogen-sensitive bands [11] (see Experimental section) though no simple generalizations were made. The simplest diagnostical means is offered by ^1H n.m.r. spectroscopy (see Table 3): the C-19 protons signal for the 5-bromo-6β-chlorides (1), (3), (9), and (13) are systematically found at higher field than those for the corresponding 6β-bromo-5α-chlorides (2), (4), (10), and (14).

TABLE 2

Specific rotation of 5,6β-dihalogenocholestanes

Compound	$[\alpha]_D^{20}$ (°)
5-Bromo-6β-chloro-5α-cholestan-3β-ol (1) [a]	−47
6β-Bromo-5-chloro-5α-cholestan-3β-ol (2)	−35
3β-Acetoxy-5-bromo-6β-chloro-5α-cholestane (3) [b]	−43
3β-Acetoxy-6β-bromo-5-chloro-5α-cholestane (4)	−38
3β-Benzoyloxy-5-bromo-6β-chloro-5α-cholestane (9) [a]	−35
3β-Benzoyloxy-6β-bromo-5-chloro-5α-cholestane (10)	−29
5-Bromo-6β-chloro-5α-cholestan-3-one (13) [b]	−45
6β-Bromo-5-chloro-5α-cholestan-3-one (14)	−38

[a] The data are taken from ref. 17. [b] The data are taken from ref. 2.

TABLE 3

^1H N.m.r. spectra for 5,6β-disubstituted 5α-cholestanes.[a] The spectra were recorded in deuteriochloroform with tetramethylsilane as internal reference on a Tesla 60 (60 MHz) spectrometer. Chemical shifts are given in δ units

Substance	Signals of protons in positions 3	6	18	19	Additional signals
(1)	4.45 [b]	4.53 [c]	0.70 [d]	1.38 [d]	
(2)	4.29 [b]	4.54 [c]	0.71 [d]	1.44 [d]	
(3) [g]	5.40 [b]	4.60 [c,j]	0.69 [d]	1.39 [d]	2.02 [e]
(4)	5.36 [b]	4.53 [c]	0.71 [d]	1.45 [d]	2.03 [e]
(5)	5.47 [b]	4.83 [c]	0.71 [d]	1.46 [d]	2.03 [e]
(6)	5.33 [b]	3.92 [c]	0.68 [d]	1.28 [d]	2.01 [e]
(7)	5.50 [b]	4.83 [c]	0.68 [d]	1.22 [d]	2.01 [e], 3.00
(8)	5.20 [b]	4.65 [h]	0.68 [d]	1.20 [d]	2.02 [e]
(9)	5.71 [b]	4.64 [c]	0.71 [d]	1.45 [d]	7.51 and 8.09
(10)	5.93 [b]	4.55 [c]	0.71 [d]	1.50 [d]	7.40 and 8.07
(13)		4.56 [c]	0.73 [d]	1.62 [d]	
(14)		4.51 [c]	0.75 [d]	1.58 [d]	

[a] The methyl groups in the side-chain, unless overlapped by other signals, display doublets at 0.86 (6 H) and 0.90 (3 H) ±0.01 p.p.m. [b] Broad multiplet. [c] Narrow multiplet, $W_{1/2}$ = 7 Hz. [d] Singlet (3 H). [e] Singlet of OAc group. [f] Singlet of OSO_2CH_3 group. [g] Angular methyl singlets were found at δ 1.39 and 0.72 (J. C. Jacquesy, R. Jacquesy, L. Jevisalles, J. P. Pete, and H. Rudler, *Bull. Soc. chim. France*, 1964, 2224). [h] Pair of narrow multiplets, $J_{2,6H}$ = 10 Hz. [j] Multiplets of the aromatic ring. [i] The 6-H signal was found at δ 5.82 (quartet) (V. Hatch, *Steroids*, 1973, **21**, 245).

Having established the physicochemical properties of the new compounds we began our search for compound (2) in the product of bromine chloride addition to cholesterol: in the ^1H n.m.r. spectrum of the adduct a small peak appears in the region of the C-19 protons which might arise from the presence of compound (2). The adduct was acetylated and the ^1H n.m.r. spectra of the product could again be interpreted as superposition of the spectra of compounds (3) and (4). Results of earlier experiments with the dibromide (5) show [12] that of the

* Prepared but not characterized by de la Mare. No spectroscopic data were reported; see ref. 4.

[6] E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1952, 1116.
[7] D. H. R. Barton and E. Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 1066.
[8] M. Ishikawa, M. Misono, and Y. Yoneda, *Chem. Letters*, 1976, 1229.
[9] K. Bowden, J. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39.
[10] C. S. Barnes and C. Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1962.
[11] D. H. R. Barton, J. E. Page, and C. W. Shoppee, *J. Chem. Soc.*, 1956, 331.
[12] A. Kasal and A. Trka, *Coll. Czech. Chem. Comm.*, 1974, **39**, 603.

two bromine atoms the one bound to the tertiary carbon is more reactive on treatment with silver fluoride than the other. Hence, of the two isomers (3) and (4), the former, containing a tertiary-bound bromine atom, ought to react faster with silver salts; thus the less reactive isomer (4) would accumulate * in unchanged material. The mixture of acetates (3) and (4) was treated [14] with silver nitrate and triethylamine at 50 °C. Portions were taken from the reaction mixture and worked up, the cholesteryl acetate formed being oxidized with *m*-chloroperbenzoic acid and separated from unchanged material by t.l.c. Samples of unchanged material were examined by ^{1}H n.m.r. spectroscopy. After the disappearance of compound (3) the unchanged material was found to be identical in all respects with compound (4) prepared from the chlorohydrin (6). The concentration of (4) in the starting mixture was assessed from the n.m.r. spectrum of the latter (see Experimental section): in the ^{13}C n.m.r. spectrum C-5 signals of both isomers (3) and (4) were easily assigned. Integration of the corresponding signals indicated that the isomers are formed in the ratio 4.5: 1.

The ratio of α- to β-electrophilic attack [(1) : (2)] is not only higher than in other cases of electrophilic addition (*e.g.* epoxidation) but also higher than in the closely related addition of bromine fluoride to 5-unsaturated steroids. This can be interpreted in terms of the reversible nature of the electrophilic addition of hypobromous acid derivatives: [15] opening of the 5β,6β-bromonium intermediate is, apparently, slowed down by the non-bonding interactions of the approaching [16] chloride anion with the 1α, 3α, 7α, and 9α axial hydrogen atoms.

EXPERIMENTAL

M.p.s were determined on a Kofler block. Samples for analysis were dried at room temperature for 24 h over phosphorus pentaoxide. I.r. spectra were measured in the form of potassium bromide discs unless otherwise stated. Specific rotation was measured in chloroform, n.m.r. spectra were recorded for deuteriochloroform solutions, and o.r.d. data were determined for solutions in dioxan with a JASCO spectrometer.

3β-*Acetoxy*-5,6β-*dibromo*-5α-*cholestane* (5).—A solution of cholesteryl acetate (120 mg) in chloroform (10 ml) was shaken with *N*-chloroacetamide (350 mg) and lithium bromide (800 mg) at room temperature. After 15 min the mixture was washed with aqueous sodium thiosulphate and water and dried over sodium sulphate. The solution was concentrated under reduced pressure and the residue crystallized from ethyl acetate–methanol; m.p. 118—121 °C (127 mg), $[\alpha]_D^{20}$ −46° (lit.,[7] 112—114 °C, −46°) (Found: C, 59.9; H, 8.35; Br, 26.8. $C_{29}H_{48}Br_2O_2$ requires C, 59.18; H, 8.22; Br, 27.16%).

3β-*Acetoxy*-6β-*bromo*-5-*chloro*-5α-*cholestane* (4).—(a) Cholesterol (50 g) was treated [2] with *N*-bromoacetamide and hydrogen chloride to give a mixture of the bromo-chlorides (1) and (2) (49 g), m.p. 138—139 °C (from ethyl acetate–methanol). Part of the crystalline product (3 g) was dissolved in hot pyridine (20 ml) and treated with acetic anhydride (15 ml). After 18 h the mixture was worked up and the mixture of the acetates (3) and (4) was crystallized from ethyl acetate–methanol; m.p. 118—121 °C (2.86 g). A solution of silver nitrate (5.22 g) in acetonitrile (32 ml) and triethylamine (13 ml) was stirred at 50 °C and then the above described mixture of acetates (3) and (4) (0.8 g) in tetrahydrofuran (10 ml) was added. After 55 min the mixture was poured into dilute hydrochloric acid (5%, 100 ml) and the precipitated product was extracted with chloroform. The extract was washed with aqueous potassium hydrogen carbonate and dried over sodium sulphate. The crude product was dissolved in chloroform (5 ml) and treated with *m*-chloroperbenzoic acid (0.5 g) at 0 °C. After 48 h the mixture was diluted with toluene (30 ml) and washed with the solution of potassium hydrogen carbonate and brine. The dried organic layer was concentrated under reduced pressure to small volume and applied on p.l.c. (silica gel). Plates were developed with a mixture of benzene–ligroin (1 : 1), sprayed with methanolic solution of morin (0.02%), and inspected under u.v. light. The band corresponding in polarity to compound (3) was collected and eluted with ether. The extract (70 mg) was crystallized from ethyl acetate–methanol to give the product, m.p. 118—121 °C, $[\alpha]_D^{20}$ −38°; $\nu_{max.}$ (CCl_4) 677vw, 634vw, 614m, 602w, 578w, and 545vw cm^{-1} (Found: C, 63.85; H, 8.95; Br, 14.35; Cl, 6.35. $C_{29}H_{48}BrClO_2$ requires C, 64.02; H, 8.89; Br, 14.69; Cl, 6.52%).

(b) A solution of the chlorohydrin (6) (750 mg) in phosphorus tribromide (15 ml) was boiled under reflux for 10 min and then diluted with toluene (25 ml) and evaporated under reduced pressure. The residue was dissolved in acetone (*ca.* 1 ml) and added dropwise to a saturated solution of potassium hydrogen carbonate in water (*ca.* 50 ml). The product was taken up first in ether and then in chloroform. The ethereal extract was washed with water, dried over sodium sulphate, and concentrated to small volume. The solution was applied on t.l.c. plates and developed as described above. 3β-Acetoxy-6β-bromo-5-chloro-5α-cholestane (4) was crystallized from ethyl acetate–methanol and had m.p. 118—121 °C (29 mg); its i.r. and ^{1}H n.m.r. spectra were identical with those of compound (4) prepared as above in (a).

The chloroform extract was washed with water, dried over sodium sulphate, and evaporated to dryness. The residue was crystallized from acetone to give the ester (8) (630 mg), m.p. 195—197 °C, $[\alpha]_D^{20}$ −43°; $\nu_{max.}$ 1 730, 1 250, 1 033, 2 200—2 700, and 1 005 cm^{-1} (Found: C, 63.95; H, 9.0; Cl, 6.45; P, 5.65. $C_{29}H_{50}ClO_5P$ requires C, 63.89; H, 9.25; Cl, 6.50; P, 5.68%).

3β-*Acetoxy*-5-*bromo*-6β-*chloro*-5α-*cholestane* (3).—The hydroxy derivative (1) was acetylated under standard conditions; [2] the product had $\nu_{max.}$ (CCl_4) 677w, 633m, 611w, 601w, and 545vw cm^{-1}.

6β-*Bromo*-5-*chloro*-5α-*cholestan*-3β-*ol* (2).—A solution of the acetate (4) (45 mg) in chloroform (1 ml) and methanol (10 ml) was set aside at 37 °C for 48 h with hydrochloric acid

* Analogous dehalogenation with sodium iodide according to Barton [13] was carried out with the product of the bromine chloride addition to cholesterol. The starting material recovered was examined by ^{1}H n.m.r. spectroscopy and the proportion of both isomers (1) and (2) was found almost identical with that before the reaction.

[13] D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1951, 1048.
[14] A. Kasal, *Coll. Czech. Chem. Comm.*, 1976, **41**, 2040.
[15] C. Anselmi, G. Berti, G. Catelani, L. Lecce, and L. Monti, *Tetrahedron*, 1977, **33**, 2271.
[16] G. Belluci, G. Berti, G. Ingrosso, and E. Mastrorilli, *Tetrahedron Letters*, 1973, 3911.

(0.2 ml). The mixture was then diluted with toluene (20 ml) and concentrated under reduced pressure to *ca.* 5 ml. This was then filtered through a column of sodium sulphate and evaporated. Crystallization from ethyl acetate–methanol yielded compound (2) (34 mg), m.p. 138—141 °C, $[\alpha]_D^{20}$ −35°; $\nu_{max.}$ 622w, 605w, and 579w cm^{-1} (Found: C, 64.7; H, 9.4; Br, 15.45; Cl, 6.85. $C_{27}H_{46}BrClO$ requires C, 64.59; H, 9.24; Br, 15.92; Cl, 7.06%).

5-Bromo-6β-chloro-5α-cholestan-3β-ol (1).—This compound was prepared according to a literature method [17] and had $\nu_{max.}$ 636m and 604w cm^{-1}.

3β-Acetoxy-5-chloro-6β-methylsulphonyloxy-5α-cholestane (7).—A solution of the chlorohydrin (6) (200 mg) in pyridine (1 ml) was cooled to 0 °C and methanesulphonyl chloride (0.1 ml) was added to it. After 18 h the solution was poured onto ice, the product was taken up in ether, the organic layer was washed with dilute hydrochloric acid, brine, aqueous potassium hydrogen carbonate, and water, and the solution was dried and concentrated to dryness. Crystallization of the residue from ether–heptane yielded compound (7), m.p. 140—143 °C, $[\alpha]_D^{20}$ −32° (Found: C, 64.3; H, 9.25. $C_{30}H_{51}ClO_5S$ requires C, 64.43; H, 9.19%).

Attempted Solvolyses of the Methylsulphonyloxy-derivative (7).—(a) A solution of compound (7) (60 mg) in acetone (3 ml) was boiled under reflux for 2 h with lithium bromide (350 mg). T.l.c. (silica gel, benzene) revealed the presence of the starting compound only.

(b) A solution of compound (7) (60 mg) in dimethylformamide (5 ml) was heated under reflux with lithium bromide (500 mg) for 2 h. The mixture was worked up and individual components were separated by means of p.l.c. The component of identical polarity with the desired compound (4) was isolated (6 mg) and identified as cholesteryl acetate (^1H n.m.r. spectrum).

3β-Benzoyloxy-5-bromo-6β-chloro-5α-cholestane (9).—This compound was prepared according to a literature preparation, $\nu_{max.}$ (CCl_4) 689w, 675vw, 640m, 611m, 585vvw, and 551vw cm^{-1}.

3β-Benzoyloxy-6β-bromo-5-chloro-5α-cholestane (10).—A solution of the hydroxy-compound (2) (50 mg) in pyridine (1 ml) and benzoyl chloride (0.1 ml) was set aside at room temperature for 2 h. The mixture was poured onto ice, the product was extracted with ether, and the extract was washed with dilute hydrochloric acid, water, aqueous potassium hydrogen carbonate, and water. The dried solution was applied on p.l.c. plates and the major product was crystallized from ether–methanol; it had m.p. 123—125 °C, $[\alpha]_D^{20}$ −29.5°, $\nu_{max.}$ (CCl_4) 689w, 676vw, 658w, 628m, 606m, 584w, and 551vw cm^{-1} (Found: C, 67.2; H, 8.15; Br, 13.4; Cl, 6.0. $C_{34}H_{50}BrClO_2$ requires C, 67.37; H, 8.32; Br, 13.18; Cl, 5.85%).

6β-Bromo-5-chloro-5α-cholestan-3-one (14).—The hydroxy-derivative (2) (98 mg) was oxidized according to Jones method [9] using 10 ml of acetone at 20 °C. After 5 min the mixture was worked up and crystallized from ether–methanol at 0 °C; the product (60 mg) had m.p. 111—116 °C (decomp.), $[\alpha]_D^{20}$ −38°, $\nu_{max.}$ (CCl_4) 655vw, 632w, 602m, and 587w cm^{-1} (Found: C, 64.7; H, 9.0. $C_{27}H_{44}BrClO$ requires C, 64.86; H, 8.87%).

6β-Bromo-4-cholestan-3-one (15).—Compound (14) (28 mg) was applied in dichloromethane to a thin layer of silica gel and was set aside in the dark at 20 °C. After 20 h the plate was developed (benzene) and sprayed with methanolic morin. The major product (21 mg), crystallized from pentane, had m.p. 129—131 °C, $[\alpha]_D^{20}$ +5° (lit.,[7] 132 °C, +6°) and the mass spectrum showed *m/e* 462 (M^+) (Found: C, 69.8; H, 9.15. $C_{27}H_{43}BrO$ requires C, 70.07; H, 9.36%).

Dehalogenation of the Mixture of Bromo-chlorides (1) *and* (2).—The product of bromine chloride addition to cholesterol [2] (0.4 g) was dissolved in acetone (40 ml) and sodium iodide (10 g) was added. The mixture was stirred at room temperature for 20 h and then poured into a saturated solution of sodium thiosulphate in water (200 ml). The product was taken up in ether and the extract concentrated under reduced pressure and separated by means of p.l.c. (20% ether in benzene). The following compounds, given in order of increasing polarity, were isolated: (i) cholestenone (42 mg), i.r. and ^1H n.m.r. spectra are identical with those of a standard substance; (ii) a mixture of compounds (1) and (2), the former being the major component (21 mg; from its ^1H n.m.r. spectrum); (iii) cholesterol (222 mg), m.p. and mixed m.p. identical with a standard substance.

Estimation of the Ratio of 5,6β-Bromo-chlorides to 6β,5-Bromo-chlorides formed on Addition of Bromine Chloride to Cholesterol.—(a) The ^{13}C n.m.r. spectrum of the mixture of acetates (3) and (4) (400 mg) was recorded on the JEOL FX-60 spectrometer and for the major component (3) the signals at 87.3 and 71.7 p.p.m. were readily assigned to C-5 and C-6 respectively. These signals were accompanied by the C-5 and C-6 signals of the minor component (4) at 70.8 and 84.6 p.p.m. respectively. The ratio of (3) : (4) was calculated from both pairs of signals as 4.5 : 1.

(b) The ^1H n.m.r. spectrum of the crystalline product obtained by bromine chloride addition to cholesterol was recorded and the region 75—95 Hz was expanded. The spectrum was digitalized and the bands were separated on a Hewlett–Packard 9820A apparatus. The ratio of compounds (1) : (2) is *ca.* 3.7 : 1.

We thank Dr. P. Sedmera for the measurement of ^{13}C n.m.r. spectra and Mrs. Jelínková and Snopková for the measurement of ^1H n.m.r. spectra. Elemental analyses and i.r. and o.r.d. measurements were carried out under the supervision of Dr. J. Horáček, Dr. J. Smolíková, and Dr. S. Vaseckovă.

[8/129 *Received*, 26*th January*, 1978]

[17] D. H. R. Barton, E. Miller, and H. T. Young, *J. Chem. Soc.*, 1951, 2598.