dioxide liberated in the usual way from barium carbonate (638.5 mg., 3.23 mmoles, containing 2.007 mc. of C^{14}) was then added to the Grignard solution (frozen in liquid nitrogen) and allowed to react at −20° for 80 minutes and overnight at room temperature. Unreacted carbon dioxide (1.39 mmoles 43%) was recovered by sweeping the apparatus with nitrogen led finally through traps containing aqueous sodium hydroxide. Note that although 43% was recovered, the excess of carbon dioxide over titration-determined Grignard was only 26.3% of the total introduced.[29] The reaction mixture was treated with 6 *N* HCl (contact of the reaction product with air was avoided in this and in all subsequent operations) and acidic and neutral products were separated by conventional methods. Titration of an aliquot of the acidic product indicated a 40% yield (based on Grignard,[29] 31% based on V, 29.3% based on barium C^{14}-carbonate) of crude 1-C^{14}-linoleic acid. Although the low yield based on unrecovered carbon dioxide might be attributed to reaction with two or three equivalents of Grignard (giving neutral materials of ketonic or tertiary alcoholic nature), assay of the neutral products (365 mg.) of the reaction for radiactivity showed them to contain only 0.12% of that originally present in the barium carbonate. Infrared absorption spectra of neutral materials formed in the analogous reconstitution of stearic acid[13] also demonstrate the essential absence of ketonic and alcoholic products.

Crude reconstituted linoleic acid from a "cold run" conducted in the same manner was a pale yellow oil which crystallized readily on standing in a refrigerator. The neutralization equivalent of this product was 298 (theory 280), indicating the presence of about 6% neutral material. The ultraviolet absorption spectrum of this crude "cold" linoleic acid indicated the presence of 3.9% conjugated diene[20] and 0.7% conjugated triene. The origin of the triene contaminant is obscure; samples of linoleic acid as ordinarily prepared by the action of zinc on the 115° tetrabromostearic acid (I) also frequently contain small amounts of such materials. The infrared absorption spectrum of this reconstituted linoleic acid was essentially identical with that[3b] of the authentic (zinc regenerated) substance, absorption at 10.3 μ indicating the presence of about 15% *trans* isomer. A stream of nitrogen was employed to pass a slight excess of bromine into a solution of 0.29 g. of reconstituted linoleic acid in 10 ml. of 60–70° petroleum ether at 0°, precipitating crude I. Washed twice with 5-ml. portions of ice-cold petroleum ether and dried *in vacuo*, the precipitate weighed 0.175 g. (60% yield)[30] and melted at 110–113°; recrystallization from ethylene chloride raised the melting point to 114–115°, mixed melting point with authentic I (m.p. 115–116°) 115–116°.

Esterification of the acidic products of the "hot run" was accomplished by treatment with an ethereal solution of diazomethane. Solvent and excess diazomethane were removed *in vacuo* and the residual crude ester passed with 60–70° petroleum ether through a 10 × 2 cm. column of 1:1 (by weight) alumina–Celite prewashed with the same solvent. Under these conditions the desired ester is eluted rapidly (collected in about 200 ml. of eluate) while autoxidation products and traces of acidic material are retained on the adsorbent. Removal of solvent from the eluate gave 250 mg. of methyl 1-C^{14}-linoleate (90% based on crude linoleic acid found by titration). On a superficial mass yield basis, this quantity of ester is calculated to contain 0.529 mc. of C^{14}. Direct counting[31] of a small sample highly diluted with corn oil indicated the presence of 0.462 mc. in the total material; combustion of another aliquot followed by count of barium carbonate from the carbon dioxide thus formed showed a 0.501-mc. content.

Acknowledgment.—The authors are indebted to Dr. Harry M. Walborsky for assistance in preliminary investigation of the conversion of III to V; and to Dr. Edwin R. Buchman for his encouragement and wise counsel while this approach to the carboxyl-labeling of unsaturated fatty acids was being planned.

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(30) *I.e.*, 60% of the theoretical 50% yield of the petroleum ether insoluble isomer.

(31) The method of C. Entenman, S. R. Lerner, I. L. Chaikoff and W. G. Dauben (*Proc. Soc. Exp. Biol. and Med.*, **70**, 364 (1949)) was employed.

LOS ANGELES, CALIFORNIA

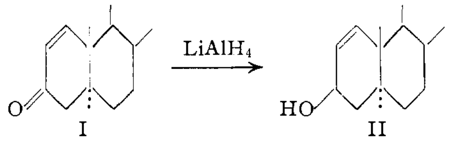
NOTES

Δ¹-Cholesten-3β-ol[1]

BY W. BERGMANN, M. KITA AND D. J. GIANCOLA

RECEIVED APRIL 22, 1954

In view of a recent publication[2] we wish to report the preparation of Δ¹-cholesten-3β-ol (II) which was carried out in this Laboratory some time ago in connection with our studies on the synthesis and photoöxidation of steroid dienes.[3] The new isomer of cholesterol is obtained readily by reduction of the well-known Δ¹-cholesten-3-one (I) with lithium aluminum hydride. As in the case of other cholestenones,[4] the reaction is predominantly, if not exclusively, stereospecific. The reduction product is precipitated quantitatively by digitonin; the sterol recovered from the digitonide[5] does not differ significantly from the product not so purified. The β-configuration of the hydroxyl group was definitely established by hydrogenation of the stenol to 3β-cholestanol.



I II

Experimental

All melting points are corrected. All optical rotations were measured in a 1-dm. tube, the sample being dissolved in 2 ml. of chloroform.

Δ¹-Cholesten-3β-ol (II).—A solution of 1.9 g. of Δ¹-cholesten-3-one (I) (m.p. 99.5°, $[\alpha]^{20}\mathrm{D}$ +60.0° $\lambda_{\max}^{\mathrm{alc}}$ 230 mμ (10.800).) in 30 ml. of anhydrous ether was added dropwise and with vigorous stirring to a solution of 0.2 g. of lithium aluminum hydride in 20 ml. of anhydrous ether. The mixture was stirred for two hours; thereafter the reaction-flask was cooled in ice, and the reduction complex and excess hydride were decomposed with cold, dilute sulfuric acid. More ether was added to the mixture, the ethereal layer separated, washed with water, aqueous sodium bicarbonate solution, water and dried. After evaporation of the solvent, the residue (1.7 g.) was recrystallized from methanol; fine needles, m.p. 131°, $[\alpha]^{25}\mathrm{D}$ +53.6°. A portion (0.209

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(1) The investigation was supported by a grant from the National Institutes of Health, U. S. Public Health Service.

(2) H. B. Henbest, G. D. Meakins and G. W. Woods, *J. Chem. Soc.*, 800 (1954).

(3) R. T. Conca and W. Bergmann, *J. Org. Chem.*, **18**, 1104 (1953).

(4) L. F. Fieser, M. Fieser and R. N. Charkavarti, THIS JOURNAL, **71**, 2226 (1949); W. G. Dauben, R. A. Micheli and J. F. Eastham, *ibid.*, **74**, 3852 (1952); Shoppee and Summers, *J. Chem. Soc.*, 687 (1950).

(5) W. Bergmann, *J. Biol. Chem.*, **132**, 471 (1940).

g.) of the crude reduction product, dissolved in boiling 90% ethanol (40 ml.), was treated with a hot 1% solution of digitonin in 90% ethanol (100 ml.). After being kept overnight, the precipitate was collected, washed and dried (0.8303 g.). The digitonide was heated on the steam-bath with pyridine (5 ml.) which was then removed *in vacuo*.[5] Exhaustive extraction of the residue with ether gave Δ^1-cholesten-3β-ol (II) which after several recrystallizations from methanol melted at 131–131.5°, $[\alpha]^{20}\mathrm{D}$ +54.9°, $[\mathrm{M}]\mathrm{D}$ +213.

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found (average): C, 83.81; H, 11.76.

The acetate was prepared by adding excess acetic anhydride to a solution of the stenol in pyridine, keeping the mixture at room temperature overnight, and precipitation of the reaction product with water. It was recrystallized several times from ether–methanol, m.p. 87°, $[\alpha]^{21}\mathrm{D}$ +60.0°, $[\mathrm{M}]\mathrm{D}$ +257, Δ_{Ac} +47.

Anal. Calcd. for $C_{29}H_{48}O_2$: C, 81.25; H, 11.29. Found: C, 81.23; H, 11.25.

The benzoate was prepared by treating a solution of the stenol in pyridine with benzoyl chloride. After standing overnight at room temperature, the mixture was diluted with methanol and the precipitate recrystallized from ether and ethyl acetate; hard needles, m.p. 141°, $[\alpha]^{25}\mathrm{D}$ +94.5°, $[\mathrm{M}]\mathrm{D}$ +464, Δ_{Be} +251.

Anal. Calcd. for $C_{34}H_{50}O_2$: C, 83.21; H, 10.27. Found: C, 82.83; H, 10.23.

Hydrogenation of Δ^1-Cholesten-3β-ol.—The stenol II was hydrogenated in ethyl acetate and at atmospheric pressure with a platinum catalyst. The 3β-cholestanol thus obtained, m.p. 141–142°, $[\alpha]^{21}\mathrm{D}$ +28.1°, was converted into the benzoate which melted at 136° to an opalescent liquid which cleared at 154.5–155.5°, $[\alpha]^{22}\mathrm{D}$ +22°. It gave no depression of the melting points when mixed with authentic material.

CONTRIBUTION NO. 1224 FROM THE
STERLING CHEMISTRY LABORATORY
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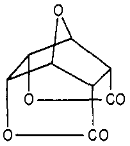
Infrared Spectra of Some Tricyclic and Tetracyclic Lactones[1]

BY JEROME A. BERSON

RECEIVED MARCH 25, 1954

The carbonyl group of simple 5-membered lactones is characterized by absorption in the infrared at or near 5.65 μ and that of 6-membered lactones by absorption in the same region as open-chain esters, *i.e.*, at or near 5.75 μ.[2,3] In connection with other studies, we have prepared a number of tricyclic lactones derived from cyclopentadiene–maleic acid and furan–maleic acid Diels–Alder adducts. The unusual steric requirements of these substances as well as the lack of direct evidence on the size of the lactone rings[4] prompted us to examine the infrared spectra. The data settle the question of ring size and provide information on the effect of confinement of the lactone function in the relatively strained environment of the tricyclic system.

Table I gives the absorption maxima and band assignments in the carbonyl region for the substances concerned.



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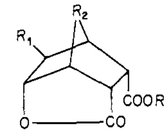
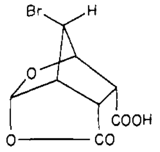
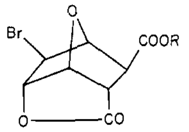


IIa $R_1,R_3 = H$; $R_2 = CH_2$
b $R_1 = Br$; $R_2 = CH_2$; $R_3 = H$
c $R_1 = Br$; $R_2 = CH_2$; $R_3 = CH_3$
d $R_1 = Br$; $R_2 = O$; $R_3 = H$
e $R_1 = Br$; $R_2 = O$; $R_3 = CH_3$



III



IVa R = H
b R = CH_3

TABLE I

INFRARED MAXIMA (μ)

	Lactone	Ester or carboxyl		Lactone	Ester or carboxyl
I[a]	5.62	. .	IId[c]	5.66	5.82
IIa[b]	5.64	5.82	IIe[c]	5.61	5.77
IIb[b,e]	5.66	5.73, 5.84	III[d]	5.68	5.78
IIb[b,f]	5.69	5.86	IVa[c]	5.68	5.73
IIc[b]	5.61	5.75	IVb[c]	5.61	5.77

[a] J. A. Berson and R. Swidler, THIS JOURNAL, **75**, 1721 (1953). [b] Reference 6. [c] O. Diels and K. Alder, *Ann.*, **490**, 243 (1931). [d] R. B. Woodward and H. Baer, THIS JOURNAL, **70**, 1161 (1948). [e] Anhydrous bromolactonic acid, m.p. 157°, $C_9H_9O_4Br$. [f] Bromolactonic acid hydrate, m.p. 116°, $C_9H_{11}O_5Br$.

While it might possibly be argued *a priori* that the strain introduced by the bicyclic system would have an appreciable effect on the lactone C=O stretching frequency, this does not seem to be the case. The dilactone I in which the lactone rings are necessarily 5-membered shows the normal 5-membered lactone absorption. The average position of the lactone band for all the substances of Table I is 5.65 ± 0.03 μ. Using I as a model, it is clear that all of the lactones examined here are 5-membered. The result is in agreement with general experience on the preference for γ- as against δ-lactone formation.[5]

The assignment[6] of a bromohydrin structure V to the substance $C_9H_{11}O_5Br$, m.p. 116°, obtained on bromination of *endo-cis*-3,6-endomethylene-Δ^4-tetrahydrophthalic acid, already disputed[4] on chemical grounds, is definitely invalidated by the strong lactone absorption in the infrared (Table I). This substance is therefore a crystal hydrate of the lactonic acid IIb, m.p. 157°.

It may be significant that the lactone C=O bands for the lactonic acids of the series appear at slightly longer wave lengths than those of the corresponding esters. It seems likely that this effect is associated with hydrogen bonding between the lactone and carboxyl functions.

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[1] Paper VI in the series "The Structure and Stereochemistry of Bicyclic Derivatives."

[2] *Cf. inter alia* (a) R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949); (b) R. N. Jones, P. Humphries and K. Dobriner, *ibid.*, **72**, 956 (1950).

[3] It has been pointed out [R. B. Woodward, *ibid.*, **72**, 3327 (1950)] that the assignment of the region 5.48–5.50 μ to lactone absorption in the useful and informative reference work by H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, is based on the spectra of oxazolones and should not be taken as applying to lactones in general.

[4] *Cf.* J. A. Berson and R. Swidler, *ibid.*, **76**, 4060 (1954).

[5] *Cf.* H. C. Brown, J. H. Brewster and H. Schechter, *ibid.*, **76**, 467 (1954).

[6] K. Alder and G. Stein, *Ann.*, **504**, 216 (1933).