Alkyllithium Compounds and Nonconjugated Olefins. The Nature of a Norbornyllithium Compound

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In diethyl ether solution at −40° *t*-butyllithium and norbornene after carbonation give 4,4-dimethylpentanoic acid, a product arising from addition of *t*-butyllithium to liberated ethylene from the solvent. Under the same conditions *t*-butyllithium adds to vinyltrimethylsilane yielding, after carbonation, 2-trimethylsilyl-4,4-dimethylpentanoic acid (VII). In ligroin or triethylamine *t*-butyllithium adds to norbornene. The n.m.r. spectra of the products from hydrolysis or carbonation show that the product in the former case is *exo*-2-*t*-butylnorbornane (Ia) and in the latter case, *exo*-3-*t*-butylnorbornane-2-carboxylic acid (II). The norbornyl carbanion is discussed.

Ziegler first showed that organolithium compounds add to conjugated olefins.[1] Some time later it was shown by Ziegler that *n*-butyllithium will add to ethylene at high pressrue.[2] More recently, Bartlett, Friedman, and Stiles[3] reported that secondary and tertiary organolithium compounds are considerably more reactive than their primary analogs and add to ethylene at atmospheric pressure and low temperature.

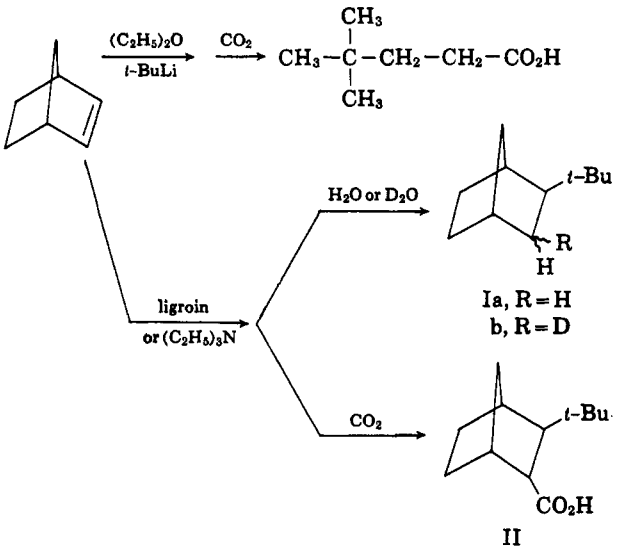
Organolithium compounds in hydrocarbon media polymerize isoprene to natural rubber, the *cis*-1,4 polymer, a process which must involve a repeated series of *cis*-1,4 additions of the growing organometallic chain to the conjugated olefins.[4]

The stereochemistry of alkyllithium addition to nonconjugated olefins is not known, although this information is necessary in understanding the reaction mechanism. It was hoped that the more reactive secondary and tertiary organolithium compounds would react rapidly in nonpolar solvents with suitable olefins so that the addition stereochemistry could be determined.

Results and Discussion

The enhanced reactivity of the secondary and tertiary lithium compounds toward ethylene did not manifest itself in similar reactions with substituted olefins such as cyclopentene, cyclohexene, cyclooctene, or 1-hexene. These olefins were treated with *t*-butyllithium in diethyl ether at −50° or in ligroin at 60–80° for approximately 24 hr. Hydrolysis or carbonation of the reaction mixture resulted in recovery of starting materials and not more than traces of other compounds. The reactions in diethyl ether were not carried out at higher temperatures because under such conditions *t*-butyllithium rapidly reacts with this solvent to produce ethylene and ethoxide ion followed by addition of the *t*-butyllithium to the liberated ethylene.[3]

Norbornene is a highly reactive olefin because of angle strain. However, after 24 hr. at −40° in diethyl ether, *t*-butyllithium and norbornene yielded only, after carbonation, 13% of 4,4-dimethylpentanoic acid (the *t*-butyllithium-ethylene product) and no norbornene derivative. Under these conditions ethylene (liberated from the solvent) is more reactive than the bicyclic compound. If the same reaction is carried out in ligroin at 60–70° or in refluxing triethylamine a 30–45% yield of *exo*-3-*t*-butylnorbornane-2-carboxylic acid was isolated after carbonation. Hydrolysis yielded *exo*-3-*t*-butylnorbornane. The fact that only a single



II

carboxylic acid or hydrocarbon was obtained was shown in the former case by the isolation of a single sharp melting *t*-butylnorbornanecarboxylic acid. In addition esterification of the crude acid product with diazomethane revealed the presence of only one ester (other than methyl pivalate from unchanged *t*-butyllithium) by v.p.c. In the hydrolysis experiments, using either triethylamine or ligroin as solvent, v.p.c. again indicated only one bicycloheptyl product. The structures of the products were shown to be I and II by examination of their n.m.r. spectra (see below). Thus there is no evidence to indicate that this norbornyllithium compound is either nonclassical or in equilibrium with the isomeric form shown below. This is in contrast to results with both cyclopropylcarbinyl[5] and cyclobutylcarbinyl[6] organometallics which are probably classical[5c] but easily rearrange to open-chain forms. Bornyl Grignard reagents are known not to rearrange,[7] but in

(1) K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, *Ann.*, **473**, 1 (1929); K. Ziegler and H. Colonius, *ibid.*, **479**, 135 (1930); K. Ziegler, F. Dersch, and H. Wollthan, *ibid.*, **511**, 13 (1934); K. Ziegler, H. Wollthan, and A. Weriz, *ibid.*, **511**, 64 (1934); see also A. C. Cope and M. R. Kinter, *J. Am. Chem. Soc.*, **73**, 3424 (1951).

(2) K. Ziegler and H.-G. Gellert, *Ann.*, **567**, 179, 185, 195 (1950).

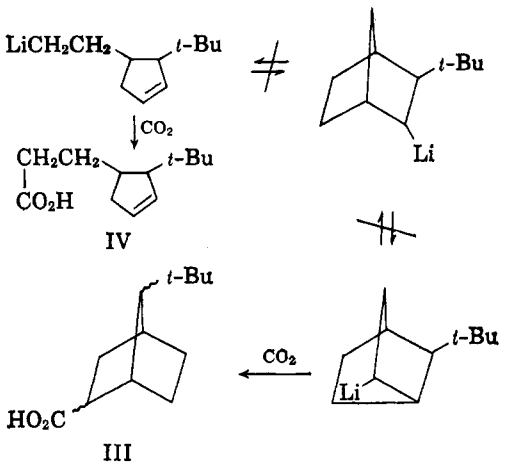
(3) P. D. Bartlett, S. Friedman, and M. Stiles, *J. Am. Chem. Soc.*, **75**, 1771 (1953). Greater reactivity of tertiary organolithium compounds was also observed in the recently discovered addition of organolithium compounds to aromatics; J. A. Dixon and D. H. Fishman, *ibid.*, **85**, 1356 (1963).

(4) H. Hsieh and A. V. Tobolsky, *J. Polymer Sci.*, **25**, 2451 (1957).

(5) (a) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); (b) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960); (c) P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. D. Sidler, *ibid.*, **86**, 2247 (1964).

(6) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963).

(7) C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, **77**, 6039 (1955), and references therein.



this case rearrangement would require a transformation of a secondary carbanion-like substance to the less stable tertiary carbanion-like compound.

An attempt was made to prepare compound II by a Diels–Alder reaction between β-*t*-butylacrylic acid and cyclopentadiene. However, the expected product from this reaction would be an extremely crowded molecule and no reaction occurred even after heating in a sealed tube at 200° for several days.

By comparing the n.m.r. spectra of the hydrolyzed, deuterolyzed, and carbonated products as well as the methyl ester of the carbonated product with that of norbornane[8] and *endo*-norbornane-2-carboxylic acid, structures I and II were established. In the spectra listed in Tables I and II, unless otherwise stated, the τ-values refer to the middle of broad bands arising from spin–spin splittings. However, the envelopes are sufficiently well resolved to allow a separation to be made. The cyclopentene derivative IV may be immediately eliminated as a possible structure since the product is saturated.

TABLE I

N.M.R. SPECTRA OF NORBORNANES

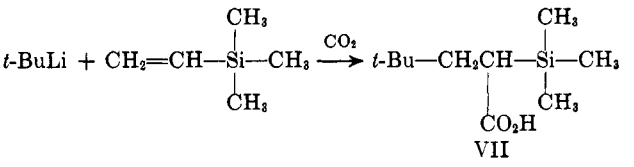
Compd.	τ_{max}	Relative integrated intensity	Assignment
Norbornane[a]	7.80	2	Bridgehead
	8.45, 8.62	4	*exo*
	8.81, 8.92	6.4	*endo* + bridge
exo-2-*t*-Butylnor-	7.88	2.0	Bridgehead
bornane (Ia)	8.44, 8.62	3.0	*exo*
	8.79, 8.96	6.4	*endo* + bridge
	9.18 (singlet)	8.7	*t*-Butyl
exo-2-*t*-Butylnor-	7.90	1.7	Bridgehead
bornane-3*d* (Ib)	8.47, 8.64	2.4	*exo*
	8.82, 8.96	5.9	*endo* + bridge
	9.20 (singlet)	8.9	*t*-Butyl

[a] See ref. 8.

Inspection of Table I reveals that the hydrolysis and deuterolysis product correlate well for *exo*-2-*t*-butylnorbornane. Especially to be noticed is the 2-3-6 integration pattern for the ring hydrogens. If this product were 7-*t*-butylnorbornane, the ring hydrogen integration pattern would have been 2(bridgehead)–4(*exo*)–5(*endo* + bridge). The presence of only three *exo* hydrogens also establishes the *exo* orientation of the *t*-butyl group. The same argument applies for the deuterated compound (Ib) (calcd. 5.0 atom % of D; found 4.1 atom % of D). The compound contains a little bit less than one deuterium atom per molecule and probably contains a mixture of *exo* and *endo* deuterium.

The n.m.r. spectrum of the carbonated product is also in accord with II as indicated by comparison with that of *endo*-norbornane-2-carboxylic acid (Table II). In the latter compound the lowest field signal is assigned to the protons at bridgehead C-1 and the carbon α to the carboxyl group (C-2). The next lowest field signal (relative integration intensity 1.0) must be the bridgehead proton at C-4. In *endo*-norbornane-2-carboxylic acid, the *endo* and *exo* proton signals are not clearly enough resolved to make a clear distinction between them. Now returning to the carbonated product II and its methyl ester, the three lowest field protons may be assigned in an analogous manner and the next two signals at higher field are the *exo* and (*endo* + bridge) protons, respectively. The integration pattern for the ring hydrogens is 2-1-2-5. The rearranged product V should give a ring hydrogen pattern of 2-1-3-4. Once again, the presence of only two *exo* hydrogens (besides the proton α to the carboxyl group) establishes that the *t*-butyl group is in the *exo* position. The n.m.r spectra of both the hydrolyzed and carbonated products are consistent with an unrearranged product with an *exo* *t*-butyl group. Thus, the *t*-butyl group adds from the less hindered *exo* side of the molecule. The stereochemistry of the carboxyl group in II can not be assigned on the basis of the n.m.r. spectrum. However, it is very likely *trans* to the *t*-butyl group since models indicate that a *cis* compound would be extremely strained. Under the conditions of the reaction the norbornyllithium compound initially formed would certainly not be expected to maintain its configuration[9] and thus the stereochemistry of the addition can not be ascertained.[10]

The activating effect of a silicon atom adjacent to a double bond is apparent in the reaction of vinyltrimethylsilane and *t*-butyllithium. Reaction between these reagents occurs at −40° in diethyl ether to give a 25% yield of VII. Under these conditions, norbornene



does not react. The orientation of the addition is assigned on the basis of similar work by Cason and Brooks.[11]

(8) H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961).

(9) D. Y. Curtin and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **84**, 1967 (1962).

(10) Recently norbornadiene has been reported to react with organolithium compounds to give addition as well as metalation products: G. Wittig and J. Otten, *Tetrahedron Letters*, **No. 10**, 601 (1963); A. Streitwieser, Jr., and R. A. Caldwell, *J. Org. Chem.*, **27**, 3360 (1962); G. Wittig and E. Hahn, *Angew. Chem.*, **72**, 781 (1960). By contrast, both norbornene and norbornadiene undergo only vinylic proton abstraction with amylsodium: R. A. Finnegan and R. S. McNees, *Chem. Ind.* (London), 1450 (1961); *Tetrahedron Letters*, **No. 17**, 755 (1962).

(11) L. F. Cason and H. G. Brooks [*J. Am. Chem. Soc.*, **74**, 4582 (1952); *J. Org. Chem.*, **19**, 1278 (1954)] report that carbonation of the reaction mixture of alkyllithiums and vinylsilanes results in the formation of a hydrolysis rather than a carbonation product. The reason for the difference in their work and ours is not known.

TABLE II

N.M.R. SPECTRA OF NORBORNANECARBOXYLIC ACIDS AND ESTER

Compd.	τ_{max}	Relative integrated intensity	Assignment
endo-Norbornane-2-carboxylic acid	7.38	2.1	Bridgehead (C-1) and hydrogen α to $-CO_2H$
	7.72	1.0	Bridgehead (C-4)
	8.29, 8.42	~3.3[a]	Remaining *exo*
	8.62	~4.6[a]	*endo* + bridge
3-*t*-Butylnorbornane-2-carboxylic acid (II)	7.43, 7.51	2.1	Bridgehead (C-1) and hydrogen α to CO_2H
	7.80	1.0	Bridgehead (C-4)
	8.31, 8.40	2.1	Remaining *exo*
	8.54, 8.73	5.4	*endo* + bridge
	9.14 (singlet)	8.4	*t*-Butyl
Methyl ester of 3-*t*-butylnorbornane-2-carboxylic acid	6.42 (singlet)	2.8	$-OCH_3$
	7.54, 7.62	2.0	Bridgehead (C-1) and hydrogen α to CO_2H
	7.90	1.1	Bridgehead (C-4)
	8.36, 8.47	1.9	Remaining *exo*
	8.69, 8.83	5.4	*endo* + bridge
	9.27	8.8	*t*-Butyl

Experimental[12]

N.m.r. spectra were determined with a Varian Model A-60 (60 Mc.) spectrometer using tetramethylsilane as an internal standard in carbon tetrachloride.

Ligroin was purified by stirring overnight with sulfuric acid, washing with water, drying over magnesium sulfate, refluxing over sodium, and distillation from sodium prior to use.

Triethylamine was dried over and distilled from potassium hydroxide pellets.

t-Butyllithium was obtained in pentane solution from the Lithium Corporation of America. The concentration of the reagent was determined prior to use by the Gilman double titration method.[13]

Organolithium reactions were carried out under a helium atmosphere.

4,4-Dimethyl-2-pentenoic Acid.—Pivaloyl chloride[14] was converted to pivalaldehyde by formation of the amide from ethylenimine followed by reduction with lithium aluminum hydride.[15] Pivalaldehyde was condensed with diethyl malonate[16] and the product was saponified[17] and decarboxylated to give 4,4-dimethyl-2-pentenoic acid, b.p. 125–127° (18 mm.). After one recrystallization from petroleum ether, the acid had m.p. 60.5–62.0°; lit.[17] b.p. 126–131° (23 mm.), m.p. 62–63°.

Attempted Diels–Alder Reaction of 4,4-Dimethyl-2-pentenoic Acid and Cyclopentadiene.—A solution of freshly distilled cyclopentadiene (0.53 g., 0.008 mole) and 4,4-dimethyl-2-pentenoic acid (1.0 g., 0.008 mole) in 5 ml. of diethyl ether was heated under reflux for 24 hr. The reaction mixture was extracted with aqueous sodium carbonate. Acidification of the aqueous extract resulted in the recovery of 80% of the starting material.

Similar reactions in benzene at 75° for 72 hr., in decalin at 200° for 24 hr., and in xylene in a sealed tube at 185–200° for periods ranging from 2 days to a week resulted only in 80–90% recovery of starting material.

***endo*-Norbornane-2-carboxylic Acid.**—*endo*-5-Norbornene-2-carboxylic acid was hydrogenated over platinum oxide to give *endo*-norbornane-2-carboxylic acid,[18] m.p. 63.5–65.5°.

Reaction of *t*-Butyllithium and Norbornene. A. In Diethyl Ether.—A solution of 0.29 mole of *t*-butyllithium in 170 ml. of pentane was rapidly added to a stirred solution of 20.3 g. (0.216 mole) of norbornene in 250 ml. of diethyl ether at −40°. The reaction mixture was stirred at −40° for 24 hr. After slowly decanting onto crushed Dry Ice, the product was extracted with 100 ml. of 6 *N* hydrochloric acid. The remaining diethyl ether layer was then extracted with three 50-ml. portions of aqueous saturated sodium carbonate. The aqueous layer was acidified with hydrochloric acid and extracted with diethyl ether. After drying over magnesium sulfate, the diethyl ether layer was distilled to give 13% (based on *t*-butyllithium) of 4,4-dimethylpentanoic acid, b.p. 70° (1.5 mm.), $n^{29}D$ 1.4191 (lit.[19] b.p. 200–215°).

Anal. Calcd. for $C_7H_{14}O_2$: neut. equiv., 130. Found: neut. equiv., 135.

In addition to having the correct n.m.r. spectrum, the product gave an amide which after recrystallization from water had m.p. 139.0–139.5° (lit.[18] m.p. 140–141°).

B. In Ligroin.—A solution of 0.37 mole of *t*-butyllithium in 232 ml. of pentane was added to a stirred solution of 25.0 g. (0.26 mole) of norbornene in 400 ml. of ligroin (b.p. 96–110°). The pale yellow solution was heated at 64–74° for 24 hr. The ligroin solution became orange after 5 hr. Carbonation of the reaction mixture and work-up in the same manner as indicated in A resulted in a 36% yield of pivalic acid (based on *t*-butyllithium) and 32% of *exo*-3-*t*-butylnorbornane-2-carboxylic acid (II), b.p. 100–105° (0.3 mm.). After three recrystallizations from hexane the acid had m.p. 94.5–95.0°.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27; neut. equiv., 196. Found: C, 73.36; H, 10.27; neut. equiv., 191, 200.

The reaction was carried out under very nearly the same conditions and hydrolyzed by slowly adding water (external cooling). The hydrolyzed reaction mixture was washed with water, and, after drying over magnesium sulfate, the major portion of the ligroin was removed by distillation through a 50 × 1 cm. glass helix packed column. Distillation of the remaining liquid gave a 33% yield of *exo*-2-*t*-butylnorbornane, b.p. 30° (0.4 mm.), $n^{28.5}D$ 1.4588. Vapor phase chromatography indicated the presence of only one component.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.75; H, 13.25. Found: C, 86.82; H, 13.09.

If the reaction mixture were treated with deuterium oxide there was obtained *exo*-2-*t*-butylnorbornane-3*d*, b.p. 34° (0.4 mm.), $n^{27}D$ 1.4584 (single peak in v.p.c.). The infrared spectrum was identical with that of 2-*t*-butylnorbornane with the exception of a band at 2200 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{19}D$: D, 5.00 atom %. Found: D, 4.15 atom %.

C. In Triethylamine.—Under very nearly the same reaction conditions, in refluxing triethylamine a 30% yield of 2-*t*-butylnorbornane was obtained after 24 hr. and a 45% yield after 72 hr. (work-up by hydrolysis).

Methyl Ester of *exo*-3-*t*-Butylnorbornane-2-carboxylic Acid.—To 0.07 mole of diazomethane[20] in 100 ml. of diethyl ether at 0° there was slowly added a solution of 9.15 g. (0.046 mole) of *exo*-3-*t*-butylnorbornane-2-carboxylic acid (II) in 40 ml. of diethyl ether. The yellow color of the diazomethane disappeared and the solution was allowed to warm to room temperature and stand

(12) Melting points are uncorrected. Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill. Vapor phase chromatography, unless otherwise noted, was carried out using an Aerograph instrument with a Dow 11 silicone-on-firebrick column. Deuterium analyses were carried out by J. Nemeth, Urbana, Ill., using the falling-drop method.

(13) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

(14) H. C. Brown, *ibid.*, **60**, 1325 (1938).

(15) H. C. Brown and A. Tsukamoto, *ibid.*, **83**, 4549 (1961).

(16) A. C. Coper and E. M. Hancock, *ibid.*, **60**, 2901 (1938).

(17) S. L. Foreman and S. M. McElvain, *ibid.*, **62**, 1438 (1940).

(18) K. Alder and G. Stein, *Ann.*, **525**, 183 (1936).

(19) R. S. Spindt and D. R. Stevens, U. S. Patent 2,470,876 (1949); *Chem. Abstr.*, **43**, 7501 (1949).

(20) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

for 2 hr. Acetic acid (0.5 ml.) was added to decompose any excess diazomethane. Distillation yielded 52% of the methyl ester of *exo*-3-*t*-butylnorbornane-2-carboxylic acid, b.p. 60–64° (0.3 mm.), single peak in v.p.c.

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.04; H, 10.32.

The methyl ester (2.5 g., 0.012 mole) was heated under reflux for 25 hr. in a solution of sodium methoxide (0.024 mole) in 13 ml. of absolute methanol. Methanol (12 ml.) was removed by distillation and the remaining solution was poured onto 20 ml. of ice–water. The ester was extracted with three 20-ml. portions of diethyl ether, and the ether extract was washed with two 10-ml. portions of saturated aqueous sodium chloride solution. The organic layer was dried over magnesium sulfate and, after removal of diethyl ether, the remaining oil gave a single peak in v.p.c. with a retention time identical with that of the starting ester.

Addition of *t*-Butyllithium to Vinyltrimethylsilane.—*t*-Butyllithium (0.13 mole) in 70 ml. of pentane was added over a period of 5 min. to a stirred solution of 10 g. (0.10 mole) of vinyltrimethylsilane in 250 ml. of diethyl ether at −40°. The reaction mixture was stirred at −30 to −50° for 24.5 hr. Carbonation by decantation and work-up in the manner described above gave 25% of 2-trimethylsilyl-4,4-dimethylpentanoic acid, m.p. 93–96°. After three recrystallizations from hexane, the acid had m.p. 98.5–99.5°; n.m.r. (20% in $CDCl_3$) τ 7.97, 8.03, and 8.13 (relative area 3.0), 9.13 (relative area 9.0), and 9.92 (relative area 9.0).

Anal. Calcd. for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96; Si, 13.88; neut. equiv., 202. Found: C, 59.54; H, 10.81; Si, 14.00; neut. equiv., 201.

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C-19 Functional Steroids. VIII.[1a,b] Studies in the Synthesis of the A/B Ring System of Sarmentosigenin E[1c]

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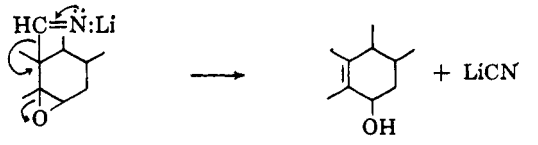
Oxidation of 5α-chloro-*syn*-19-oximinocholestane-3β,6β-diol 3-acetate gave 5α-chloro-3β-hydroxy-6-oxocholestane-19-nitrile 3-acetate which was allowed to react with alcoholic potassium hydroxide to form 3β,5β-dihydroxy-6-oxocholestane-19-nitrile. This diol was reduced with sodium borohydride to afford 3β,5β,6β-trihydroxycholestane-19-nitrile which on treatment with methanolic hydrogen chloride followed by hydrolysis furnished 3β,5β,6β-trihydroxycholestan-19-oic acid 6,19-lactone embodying the A/B ring system of sarmentosigenin E. Reduction of 5β,6β-epoxy-19-oximinocholestan-3β-ol or the corresponding 19-nitrile with lithium aluminum hydride afforded 19-norcholest-5(10)-ene-3β,6β-diol *via* a fragmentation reaction.

Cardiac glycosides are of major importance in drug therapy and methods for their synthesis not only are of interest *per se*, but also as a means for obtaining analogs of potential pharmacological importance. Syntheses of digitoxigenin[2] and periplogenin[3] have been disclosed recently. Neither of these aglycones has a functional group at C-19, and analysis[4,5] of the relationship between chemical constitution and biological activity in the cardiac glycosides indicates that concomitant oxygenation at C-19 and C-5 enhances cardiotonic action.

This article describes the synthesis of the A/B ring system of sarmentosigenin E (3β,5,6β,14-tetrahydroxy-5β-card-20(22)-enolide-19-oic acid 6,19-lactone),[6] utilizing the 19-oximino-5α-chloro-6β-hydroxy steroid intermediates which have been prepared in this laboratory.[7–9] These intermediates possess functionality at both C-5 and C-19, and are readily available from conventional steroids.

5β,6β-Epoxy steroids, which have the desired 5β-oxygen linkage, are available from 5α-chloro-6β-hydroxy steroids, and in principle it would be possible to reduce a 5β,6β-epoxide to the desired 5β-ol with lithium aluminum hydride.[10] Treatment of I with alkali gave the epoxide III which on lithium aluminum hydride reduction gave the 19-norsteroid VII. Moreover, the nitrile IV, prepared from I by successive treatment with hot acetic anhydride and alkali, on treatment with lithium aluminum hydride also gave VII. Presumably, in both cases this fragmentation[11] is owing to formation of an intermediate imine–metal complex, in which the electron deficiency resulting from ionization of the 5β-bond is neutralized by heterolysis of the 10β-bond, and by donation of the lone pair of electrons on the nitrogen.



After these experiments were completed, the formation of VII by treatment of V with alkali was described.[12]

(1) (a) From the undergraduate and graduate research of J. A. Muñoz. This research was supported by University funds and by a Public Health Service research grant (AM-05016) from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service. The n.m.r. spectrometer used in this study was provided by a grant (NSF-G-21268) from the National Science Foundation. (b) Paper VII: M. E. Wolff and W. Ho, *J. Med. Chem.*, **7**, 681 (1964). (c) A preliminary account of portions of this work has been presented: M. E. Wolff and J. A. Muñoz, *Chem. Ind.* (London), 1312 (1964).

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(11) For a discussion of fragmentation reactions, consult C. A. Grob, *Bull. soc. chim. France*, 1360 (1960).

(12) M. Akhtar and D. H. R. Barton, *J. Am. Chem. Soc.*, **86**, 1528 (1964). This article appeared after completion of our work and includes several related reactions in the 5α-bromo series.