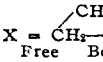
groups and aromatic rings.[1] In addition, single examples of such intramolecular bonding between *acidic* phenolic groups and acetylenes (*o*-ethynylphenol[2]), olefins (*o*-allylphenol[3]) and benzene rings (*o*-phenylphenol[4]) are available. The present broad extensions of this phenomenon are of considerable importance from both a theoretical and from a practical point of view, since they suggest many potential applications in the determination of structure and stereochemistry.

The concentration-independent[1-5] free and π-bonded OH bands observed for representative homologous primary alcohols are summarized in Table I. The values for similar aromatic alcohols[1b] have been included for comparison.

TABLE I[a,b]

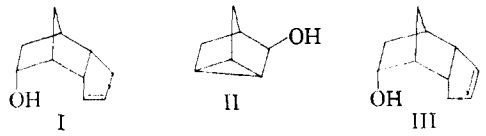
POSITIONS OF ABSORPTION BANDS OF UNSATURATED ALCOHOLS (CM.$^{-1}$)

Compound type	X = CH_2=CH— Free	Bonded	Δν	X = HC≡C— Free	Bonded	Δν
X-CH_2OH	3631sh	3618	13	none	3620	(11–18)[c]
X$(CH_2)_2OH$	3634	3594	40	3640	3598	42
X$(CH_2)_3OH$	3637	none	..	3638	3588w	50

Compound type	X =  Free	Bonded	Δν	X = C_6H_5— Free	Bonded	Δν
X-CH_2OH	3621sh	3615	16	3632sh[d]	3615	17
X$(CH_2)_2OH$				3634	3606	28
X$(CH_2)_3OH$				3638	none	..

[a] Perkin–Elmer Model 21 Spectrometer, LiF prism, *ca.* 0.005 *M* in CCl_4 solution. [b] Abbreviations: sh = shoulder, w = weak. If the bands are not of about equal intensity, the stronger of each pair is underlined. [c] Estimated by comparison with the free peaks of 1-propanol (ν = 3638) and of allyl alcohol. [d] The asymmetry of the benzyl alcohol absorption has been observed before without comment.[1a] Other groups have been reported mistakenly as the "free" peak the "bonded" position.[1c,2]

The intensity of the bonded relative to the non-bonded band decreases as the number of methylene groups separating the two functional groups is increased, while at the same time the strength of the hydrogen bond increases (larger $\Delta\nu$). The incorporation of the functional groups into a rigid molecule can result in an orientation favorable for intramolecular hydrogen bonding (I, $\Delta\nu$ = 49 cm.$^{-1}$)[6] or in an unfavorable arrangement (II, ν = 3622 cm.$^{-1}$, no intramolecular bond). The



I II III

fact that this intramolecular bonding is strongly conformationally and configurationally dependent is of great potential utility in structure elucidation. By way of illustration some polycyclic examples have been included in Table II.

TABLE II

DIFFERENTIATION OF ISOMERS (CM.$^{-1}$)

Compound	Free	Bonded	Δν
Cholesterol (Δ^5-cholesten-3β-ol)	3621	none	..
epi-Cholesterol (Δ^5-cholesten-3α-ol)	3619	3589	30
Δ^4-Cholesten-6β-ol[7]	3614	none	..
Δ^4-Cholesten-6α-ol[7]	3619	3605sh	14
i-Cholesterol (3,5-cyclocholestan-6β-ol)[8]	3614[a]	none	..
epi-i-Cholesterol (3,5-cyclocholestan-6α-ol)[8]	3628	3612sh	16
2-Norbornen-5-*endo*-ol[9]	3622	3592	30
5-*endo*-Methyl-2-norbornen-5-*exo*-ol[10]	3610	none	..
Compound I[6,b]	3624	3575	49
Compound III[6,b]	3622	3591	31

[a] Tentative assignment. [b] Assignment of structure based upon the difference in the observed $\Delta\nu$'s.

The effect of substituent groups in the acyclic, cyclic and aromatic series, extension to other proton donor groups besides the hydroxyl function[11] and a full discussion of the above examples will be presented in subsequent publications.

(1) (a) A. M. Buswell, W. H. Rodebush and R. M. Whitney, THIS JOURNAL, **69**, 770 (1947); (b) D. S. Trifan, J. L. Weinmann and L. P. Kuhn, *ibid.*, **79**, 6566 (1957); (c) I. M. Goldman and R. O. Crisler, *J. Org. Chem.*, **23**, 751 (1958); (d) E. J. Moriconi, *et al.*, Abstracts, 134th Am. Chem. Soc. Meeting, Chicago, Ill., Sept., 1958, p. 36-P; (e) H. Kwart, unpublished observations. For references to earlier work demonstrating intermolecular bonding between alcohols and other hydrogen donors and aromatic compounds, see the above papers; *cf.*, also, W. G. Schneider, *et al.*, *Can. J. Chem.*, **34**, 957, 964 (1956); **35**, 251 (1957).

(2) V. Prey and H. Berbalk, *Monatsh. Chem.*, **82**, 990 (1951).

(3) R. West, Abstracts, 134th Am. Chem. Soc. Meeting, Chicago, Ill., Sept., 1958, p. 79-P and THIS JOURNAL, submitted. Herein also is reported intermolecular phenol-olefin and acetylene hydrogen bonding. See also A. W. Baker and A. T. Shulgin, *ibid.*, **80**, 5358 (1958).

(4) O. R. Wulf, U. Liddel and S. B. Hendricks, THIS JOURNAL, **58**, 2287 (1936); *cf.*, W. Lüttke and R. Mecke, *Z. physik. Chem.*, **196**, 56 (1950); V. v. Keussler and G. Rossmy, *Z. Elektrochem.*, **60**, 136 (1956).

(5) *Cf.* R. N. Jones and C. Sandorfy in W. West, Ed., "Chemical Applications of Spectroscopy," Interscience Publisher, Inc., New York, N. Y., 1956, p. 422 f.

(6) R. S. Barnes, Jr., Ph.D. Thesis, Harvard University, 1950; P. von R. Schleyer, Ph.D. Thesis, Harvard University, 1956.

(7) E. J. Becker and E. S. Wallis, *J. Org. Chem.*, **20**, 353 (1955).

(8) The assignments of structure correspond with those currently accepted. *Cf.* E. M. Kosower and S. Winstein, THIS JOURNAL, **78**, 4347 (1956), for a discussion.

(9) P. Hirsjarvi, *Acta Chem. Scand.*, **10**, 249 (1956).

(10) P. Mälkönen and N. J. Toivonen, *Suom. Kemistilehti*, **B31**, 146 (1958); P. von R. Schleyer and R. E. O'Connor, Abstracts, 134th Am. Chem. Soc. Meeting, Chicago, Ill., Sept., 1958, p. 39-P.

(11) *E.g.*, the NH group similarly has been observed to hydrogen bond intramolecularly with olefins, as in N-allylaniline.

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RECEIVED SEPTEMBER 2, 1958

THE MICROWAVE SYNTHESIS OF DIGERMANIUM HEXACHLORIDE

Sir:

We wish to report the microwave discharge synthesis of digermanium hexachloride (Ge_2Cl_6). This compound first was prepared by Schwarz and Baronetzky,[1] who obtained 5 mg. per week by the reduction of germanium tetrachloride with germanium metal. By using a microwave discharge method similar to that which Frazer and Holzmann[2] used for the preparation of B_2Cl_4 from BCl_3, we have prepared digermanium hexachloride in yields of 250 mg. per hour.

(1) Robert Schwarz and Egon Baronetzky, *Z. anorg. allgem. Chem.*, **275**, 1 (1954).

(2) J. W. Frazer and R. T. Holzmann, THIS JOURNAL, **80**, 2907 (1958).

Germanium tetrachloride vapor was passed at the rate of 30 mmoles/hr. through 10 mm. o.d. Pyrex tubing which passed through a microwave resonance cavity similar to that described by Zelikoff, *et al.*[3] The pressure of germanium tetrachloride vapor at the entrance to the cavity was approximately 0.1 mm. At the immediate exit of the discharge cavity, a yellow solid and a viscous pale yellow oil collected in an amount roughly equal to that of the Ge_2Cl_6 collected. These relatively non-volatile products have not been further characterized. The effluent vapors passed, successively, through a −18° trap (which condensed the Ge_2Cl_6), a −78° trap (which condensed the undecomposed $GeCl_4$), and a −196° trap (which condensed the chlorine).

Digermanium hexachloride is a colorless, crystalline material which is sublimed easily at room temperature; the observed melting range is 40–42°. A sample has been analyzed for germanium after hydrolysis and oxidation with hydrogen peroxide by titration of the germanic acid in the presence of mannitol. Chlorine analyses have been performed after hydrolysis both by the Mohr method and by titration of the liberated hydrochloric acid. The average oxidation state of the germanium has been measured by titrating a 3 *M* HCl solution of a sample with iodine. *Anal.* Calcd. for Ge_2Cl_6: Ge, 40.57; Cl, 59.43; ox. state of Ge, +3. Found: Ge, 44.9; Cl, 59.2 (Mohr) and 57.9 (from HCl); ox. state of Ge, +3.04.

We wish to thank Mr. Jack Frazer for the use of the Baird Associates' Hg 198 Exciter. This work was performed under the auspices of the U. S. Atomic Energy Commission.

(3) M. Zelikoff, P. H. Wyckoff, L. M. Aschenbrand and R. S. Loomis, *J. Opt. Soc. Am.*, **42**, 818 (1952).

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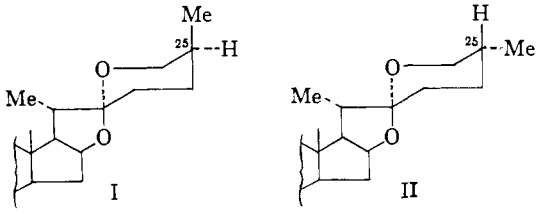
RECEIVED NOVEMBER 1, 1958

THE MECHANISM OF THE ISOMERIZATION OF STEROIDAL SAPOGENINS AT C-25

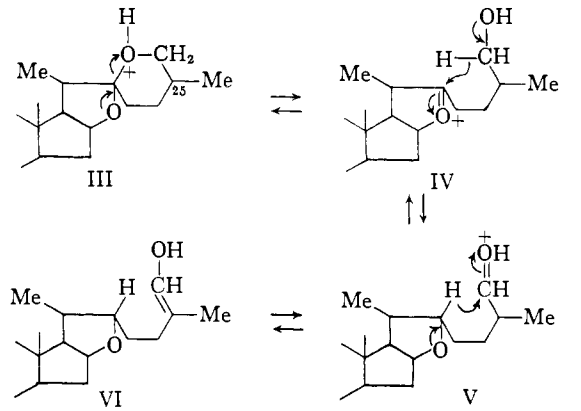
Sir:

Extensive previous investigations have established that the normal (I) and the iso (II) sapogenins differ in configuration only at C-25.[1] In the light of this fact, the acid-catalyzed inter-

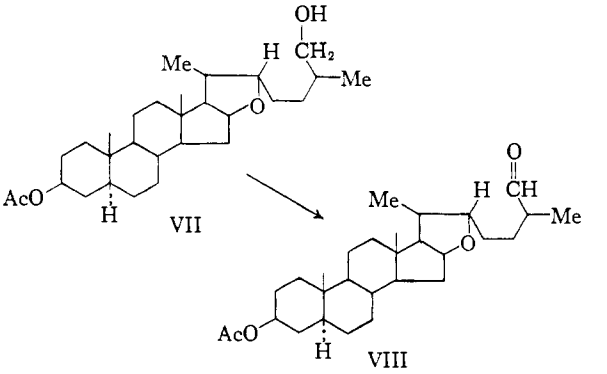


conversion[2] of the isomers appears remarkable. Cornforth has suggested[1,3] that the reaction might involve bimolecular displacement by a proton, with inversion, but such a reaction is without parallel in organic chemistry.

We consider that the isomerization proceeds by an oxidation–reduction mechanism. The key step in the change is a reversible hydride transfer involving the oxonium compounds (IV) (available by the simple change III ⇄ IV) and (V).[4] Since the conjugate acid V may be expected to be in readily established equilibrium with the corresponding enol VI, change in configuration at C-25 is simply accommodated.



We have found powerful support for our mechanism in the observation that the change V → IV does in fact occur readily. Dihydrotigogenin 3-monoacetate (VII)[5] in benzene was oxidized by



sodium dichromate in aqueous sulfuric acid/acetic acid. Chromatography of the reaction mixture on alumina gave an oily mixture of the aldehydes VIII, isomeric at C-25, from which one pure component [m.p. 86–87°, $[\alpha]_D$ −16° ($CHCl_3$), λ_{max} 3.62 μ; Found: C, 75.81; H, 10.30] separated. Re-chromatography of the crystalline isomer regenerated the stereoisomeric mixture. When the crystalline aldehyde, or the mixture, was subjected under nitrogen to the conditions ordinarily used[2] to bring about the interconversion of I and II (concentrated hydrochloric acid in boiling ethanol), tigogenin admixed with some neotigogenin was produced in over 75% yield in two hours. From this mixture, pure tigogenin [m.p. 202–204°, $[\alpha]_D$ −49° (C_5H_5N)], identical with authentic

(1) R. K. Callow and P. N. Massy-Beresford, *J. Chem. Soc.*, 2645 (1958), and earlier references there cited.

(2) R. E. Marker and E. Rohrmann, THIS JOURNAL, **61**, 846 (1939); R. K. Callow and V. H. T. James, *J. Chem. Soc.*, 1671 (1955); M. E. Wall, S. Serota and L. P. Witnauer, THIS JOURNAL, **77**, 3086 (1955).

(3) J. W. Cornforth, *Ann. Repts. on Progr. Chem.* (*Chem. Soc. London*), **50**, 219 (1953).

(4) It may be noted that hydride-transfer reactions of a related type are known (*cf.* P. D. Bartlett and J. D. McCollum, THIS JOURNAL, **78**, 1441 (1956)).

(5) Y. Sato and H. G. Latham, *ibid.*, **78**, 3150 (1956).