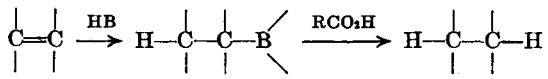
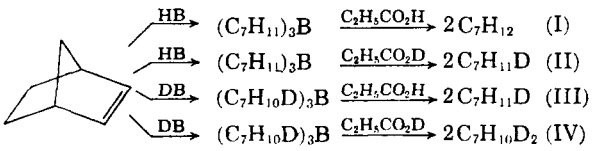
procedure for the conversion of alkenes into the corresponding alkanes.[1]



A knowledge of the stereochemistry of the protonlysis stage, similar to that now available for the hydrogen peroxide oxidation, would permit the stereospecific synthesis of alkanes and deuteroalkanes. It appeared that an NMR examination of the mono- and dideuteronorbornanes synthesized *via* hydroboration would provide evidence on this point.

The hydroboration of norbornene readily produces the corresponding organoborane (*exo*[2]) and protonlysis of two of the three alkyl groups is readily achieved with propionic acid, forming norbornane, b.p. 104–105° at 747 mm., m.p. 85.5–87°. Oxidation of the reaction residue with alkaline hydrogen peroxide converted the third group into *exo*-norborneol, m.p. 124–125°.

The deutero derivatives were prepared through corresponding reactions involving hydroboration with B_2D_6 and protonolysis with both propionic acid and deuterated propionic acid.



$$\xrightarrow{HB} (C_7H_{11})_3B \xrightarrow{C_2H_5CO_2H} 2C_7H_{12} \quad (I)$$

$$\xrightarrow{HB} (C_7H_{11})_3B \xrightarrow{C_2H_5CO_2D} 2C_7H_{11}D \quad (II)$$

$$\xrightarrow{DB} (C_7H_{10}D)_3B \xrightarrow{C_2H_5CO_2H} 2C_7H_{11}D \quad (III)$$

$$\xrightarrow{DB} (C_7H_{10}D)_3B \xrightarrow{C_2H_5CO_2D} 2C_7H_{10}D_2 \quad (IV)$$

The NMR spectrum (Varian, 60 Mc spectrometer) of the norbornane (I) indicated in order of increasing field strength a peak of relative intensity 2.0, ascribed to the two tertiary bridgehead hydrogen atoms, a doublet (resulting from splitting by the axial protons) ascribed to the four equatorial (*exo*) hydrogen atoms with a relative intensity of 4.0, followed closely by an irregular peak of intensity 6.4, attributed to overlap of the two bridge hydrogen atoms with the doublet from the four axial hydrogens.[3]

The NMR spectra of the two monodeuterated norbornanes (II and III) were identical, with the relative intensity of the equatorial doublet decreased from 4.0 to 3.0. Finally, in the case of the dideuterated derivative, IV, the relative intensity of the equatorial hydrogen doublet decreased to 2.0, the relative intensities of the three peaks changing from the 2.0:4.0:6.4 value for norbornane (I) to 2.0:2.0:6.2 for the dideuteronorbornane (IV).

These results are consistent both with the pure *cis* addition of the hydrogen-boron bond from the less hindered direction (*exo*[2]) and with the retention of configuration in the protonolysis of the organoborane.

It is not possible to generalize rigorously from the present single result with the norbornane system to all other organoboranes. However, the stereochemistry of the alkaline hydrogen peroxide oxidation has been demonstrated to proceed with retention in many systems.[2,4,5] In this reaction the organoborane from norbornene behaves the same stereochemically as all other monocyclic and acyclic systems.[2] The protonolysis of the vinylboranes from the hydroboration of acetylenes proceeds with retention of configuration.[6] Finally, numerous electrophilic substitution reactions of organomercurials have been demonstrated to proceed with retention of configuration.[7] Consequently, it appears reasonable that the protonolysis of organoboranes may proceed quite generally with retention of configuration.

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(4) W. J. Wechter, *Chem. & Ind. (London)*, 294 (1959).

(5) F. Sondheimer and M. Nussim, *Chem. & Ind. (London)*, 400 (1960).

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Synchronous Decarboxylation and Dehydration

Sir:

We wish to report evidence showing that β-*p*-methoxyphenyl-β-hydroxypropionic acid (I) undergoes facile, synchronous decarboxylation and dehydration in dilute acidic solution.

Upon heating in dilute (0.1*N*) sulfuric acid at 45°, I loses carbon dioxide in nearly quantitative yield.

From the decarboxylative dehydration, *p*-methoxystyrene has been isolated (largely as a colorless waxy polymer) along with a small amount of anis-

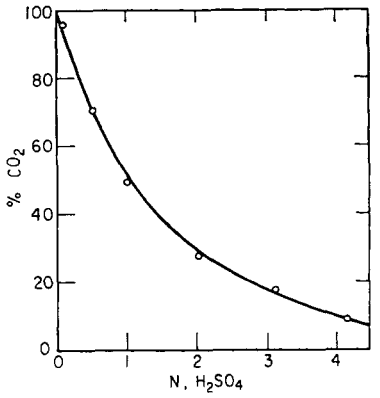


Fig. 1. Percentage decarboxylation as a function of acid concentration, 45°

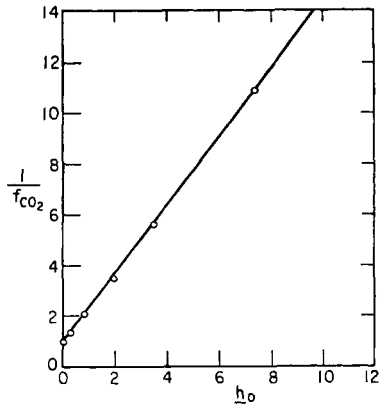
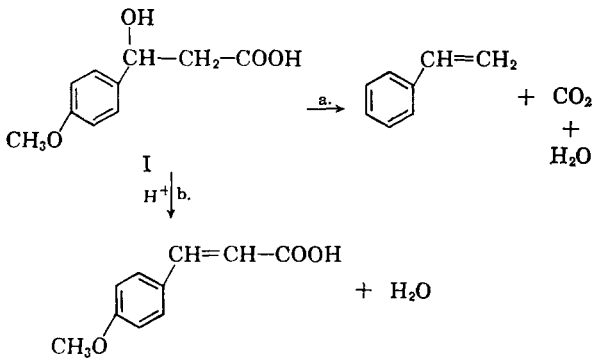


Fig. 2. Correlation of fraction decarboxylation with acidity of medium

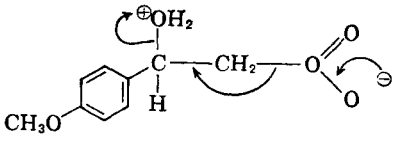
ylmethylcarbinol. In progressively more concentrated solutions, the yield of carbon dioxide decreases, becoming less than 10% in 4*N* sulfuric acid. (Fig. 1). At the higher acidities, simple acid-catalyzed dehydration becomes the predominant course of reaction. In all cases, *p*-methoxycinnamic acid is stable under the reaction conditions. Thus two different reaction pathways are observed, as outlined, in Chart I.

Chart I



Preliminary kinetic investigation shows that the rate of the decarboxylation reaction (path *a*) is nearly independent of the acid concentration, while the rate of simple dehydration (path *b*) is closely parallel to the acidity function (h_0).

The reaction pathway for the synchronous decarboxylation and dehydration can be most attractively formulated as proceeding through the zwitterion of I, (II) which, by the indicated electron migration may collapse directly to the products.



This *decarboxylative dehydration* will be observed in dilute acid, sufficient merely to suppress the self-ionization of the carboxylic acid.

It is easily shown that for two competing pathways, the percentage of carbon dioxide evolved is given by Equation 1:

$$\%CO_2 = \frac{k_{-CO_2}}{k_{-CO_2} + k_{-H_2O}(h_0)} \quad (1)$$

and thus that the reciprocal of the fraction of carbon dioxide evolved should be a linear function of the acidity of the medium, Equation 2:

$$1/f_{CO_2} = 1 + [k_{-H_2O}/k_{-CO_2}]h_0 \quad (2)$$

Our data are plotted in Fig. 2.

This decarboxylative dehydration appears to be general, and parallel is drawn to several analogous reports in the literature. The decomposition of β bromo acids, for which the mechanism has been carefully elucidated by Cristol and Norris,[1] Grovenstein and Lee,[2] and Grovenstein and Theophila,[3] is of course analogous with bromide, rather than water, being the leaving group at the β-carbon. The spontaneous decomposition of β-isovalerolactone[4] in neutral solution likewise represents a close parallel, as does the reported formation of *t*-butyl alcohol upon heating β-hydroxyisovaleric acid.[5]

Further indications of the generality of this reaction are shown in the several reports of thermal decomposition of β-phenyl-β-hydroxy fatty acids to give substituted styrenes, at temperatures well below those at which cinnamic acids decompose.[6,7] Further studies of these systems are in progress.

(1) S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 632 (1953); **75**, 2645 (1953).
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(3) E. Grovenstein, Jr., and S. P. Theophila, *J. Am. Chem. Soc.*, **77**, 3795 (1955).
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Gas Chromatographic Separations of Sapogenins

Sir:

Gas chromatographic techniques have recently been developed for steroid separations. Suitable conditions have been found for the chromatography of a variety of steroids including plant and animal sterols, sex hormones, bile acids, adrenal cortical steroid hormones, steroidal amines and provitamins D_2 and D_3.[1] These methods may be used in many ways, but they are particularly useful for work with complex mixtures of natural origin. Among the naturally occurring steroids not previously investigated are the sapogenins; this group has now been studied. In addition to a spiroketal system, these compounds have a varying degree of substitution with hydroxyl and keto groups.

The conditions selected for a study of sapogenin separations involved use of a nonpolar phase (silicone polymer SE-30) at 225°. All of the compounds gave single, well defined peaks with no evidence of decomposition. The relative (to cholestane) retention times are in Table I. A sample of tigogenin recovered after chromatography was found to be unchanged (infrared comparisons) and repeated chromatography of the sample showed no indication of thermal alteration. Figure 1 shows the behavior of several sapogenins under these conditions.

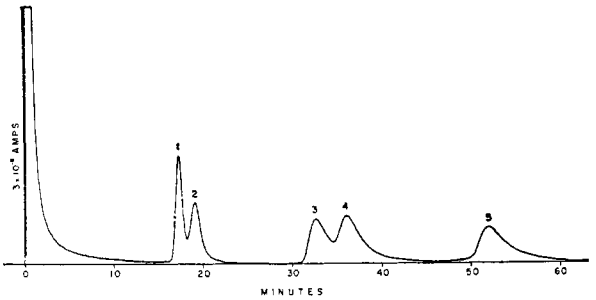

Fig. 1. Gas chromatographic behavior of (1) smilagenin, (2) tigogenin, (3) gitogenin, (4) chlorogenin, and (5) mexogenin. The conditions are those described for Table I

TABLE I[a]

Compound	C_{22}[b]	C_5[c]	Substituents	Time[d]
Sarsasapogenin	neo	β	3β-OH	2.57
Smilagenin	iso	β	3β-OH	2.47
Yamogenin	neo	Δ^5	3β-OH	2.66
Diosgenin	iso	Δ^5	3β-OH	2.64
Tigogenin	iso	α	3β-OH	2.71
Yuccagenin	iso	Δ^5	2α,3β-$(OH)_2$	4.68
Gitogenin	iso	α	2α,3β-$(OH)_2$	4.81
Chlorogenin	iso	α	3β,6α-$(OH)_2$	5.40
Hecogenin	iso	α	3β-OH 12-keto	4.96
Mexogenin	iso	β	2β,3β-$(OH)_2$ 12-keto	7.82
Manogenin	iso	α	2α,3β-$(OH)_2$ 12-keto	8.76
Kammogenin	iso	Δ^5	2α,3β-$(OH)_2$ 12-keto	8.33
Cholestane				1.00[e]

[a] Conditions: Column, 6 ft. × 5 mm.; 0.75% SE-30 polymer on 100–140 mesh Gas-Chrom P; 225°; 14 p.s.i.; argon ionization detector. [b] The configurations are 25L or neo and 25D or iso. [c] The notation refers to 5-H. [d] Relative to cholestane. [e] Time, 7.0 min.

Several correlations between structure and relative retention times may be seen from the data in Table I. The introduction of an additional substituent group (hydroxyl or carbonyl) leads to a relatively large increase in the retention time, and consequently the extent of substitution may be recognized from the chromatographic behavior. Compounds with differing ring A/B relationship were separated; the 5α-H isomer had a longer retention time than the 5β-H compound (compare tigogenin and smilagenin). Compounds with a Δ^5 structure gave retention times different from those observed for the corresponding saturated compounds. The effect of a change in configuration of the methyl group at C-25 was relatively small; in two examples the *iso*-series showed the lower retention times. The relatively small effect observed here parallels previous observations on the behavior of C-25 epimers in the steroidal amine series.

These results suggest that gas chromatographic techniques may be useful in studies of the occurrence, structure, and reactions of sapogenins. A number of steroid hormones are synthesized from

(1) W. J. A. VandenHeuvel, C. C. Sweeley, and E. C. Horning, *J. Am. Chem. Soc.*, **82**, 3481 (1960) (steroids); W. J. A. VandenHeuvel, C. C. Sweeley, and E. C. Horning, *Biochem. Biophys. Res. Comm.*, **3**, 33 (1960) (sex hormones and bile acids); W. J. A. VandenHeuvel and E. C. Horning, *Biochem. Biophys. Res Comm.*, **3**, 356 (1960) (adrenal cortical steroid hormones); W. J. A. VandenHeuvel, C. C. Sweeley, and E. C. Horning, *Separation of Steroids by Gas Chromatography*, Symposium on Drugs Affecting Lipid Metabolism, Milan, Italy, June 2–4, 1960 (sterols and sterol esters); C. C. Sweeley and E. C. Horning, *Nature*, **187**, 144 (1960) (steroids); W. J. A. VandenHeuvel, E. C. Horning, Y. Sato, and N. Ikekawa, *J. Org. Chem.*, in press (steroidal amines); E. O. A. Haahti, W. J. A. VandenHeuvel and E. C. Horning, *J. Org. Chem.*, in press (polyester phases for steroids); H. Ziffer, W. J. A. VandenHeuvel, E. O. A. Haahti, and E. C. Horning, *J. Am. Chem. Soc.*, in press (Vitamins D_2 and D_3); R. K. Beerthius and J. H. Recourt, *Nature*, **186**, 372 (1960) (sterols).