P, 10.00. Found: P, 9.78). Di-*n*-octylphosphine oxide, m.p. 85–6° (lit.[6] m.p. 85°) was characterized by its reaction with acrylonitrile to give 2-cyanoethyldi-*n*-octylphosphine oxide, m.p. 51–52° (lit.[7] m.p. 53.4–54.2°). Bis-(2-cyanoethyl)-phosphine oxide, m.p. 98–99°, (calcd. for $C_6H_9N_2OP$: C, 46.15; H, 5.80; P, 19.84. Found: C, 46.32; H, 5.95; P, 19.94) was characterized by reaction with chloral hydrate to give bis-(2-cyanoethyl)-1-hydroxy-2,2,2-trichloroethylphosphine oxide, m.p. 159–160° dec. (calcd. for $C_8H_{10}Cl_3N_2O_2P$: C, 31.65; H, 3.32. Found: C, 31.76; H, 3.35). Additional examples and experimental details will be given in a subsequent publication.

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ISOTOPIC EVIDENCE FOR THE MECHANISMS OF DECARBONYLATION OF THREE CARBOXYLIC ACIDS IN SULFURIC ACID

Sir:

As reaction mechanisms are often determined from the form of the observed acid catalysis, it is significant that the mechanism[1] of decarbonylation of triphenylacetic acid proposed on this basis is not supported by isotopic evidence. Complete equilibrium of the oxocarbonium ion with water[1] and carbon–carbon bond cleavage as the rate determining step[1] are not supported since: (I) this decarbonylation in oxygen-18 enriched 95.5% sulfuric acid yielded carbon monoxide having an oxygen-18 enrichment of only about one-fifth that of the sulfuric acid,[2] and (II) no measurable isotope effect was found in the decarbonylation of triphenylacetic-2-C^{14} acid.

For the decarbonylation of formic acid the mechanism,[3]

A. $RCOOH + H_2SO_4 \rightleftharpoons RC(=O)(OH)H^{\oplus} + HSO_4^{\ominus}$

B. $RC(=O)(OH)H^{\oplus} \xrightarrow{\text{slow}} RCO^{\oplus} + H_2O$

C. $RCO^{\oplus} + H_2O \longrightarrow RC(=O)(OH^{\oplus})H$

D. $RCO^{\oplus} + H_2SO_4 \longrightarrow (R{\cdot}H_2SO_4)^{\oplus} + CO$

E. $(R{\cdot}H_2SO_4)^{\oplus} + 2H_2O \xrightarrow[\text{up}]{\text{work-}} ROH + H_3O^{\oplus} + H_2SO_4$

accounts for the facts: (III) log of pseudo-first order rate constant linearly related to H_0[3]; (IV) Large carbon-14 isotope effect (k_{12}/k_{14} = *ca.* 1.09),[4] (V) secondary deuterium isotope effect (k_H/k_D = *ca.* 1.5) with formic-*d* acid, undoubtedly due to stretching of the carbon–hydrogen bond during the slow step, B, and (VI) carbon monoxide of normal isotopic composition formed during reaction in oxygen-18 enriched sulfuric acid. Step C fails to occur because of its unfavorable competition with D, the rapid proton transfer to the sulfuric acid.

For the triphenylacetic acid decarbonylation the scheme, A, B, C, D, E, adequately accounts for facts I and II. Some back reaction of the oxocarbonium ion with water, C, can occur by favorably competing with D which is an attack by sulfuric acid on the hindered number 2 carbon atom with ejection of carbon monoxide, and which is understandably slower than the analogous proton transfer in the formic acid decarbonylation. Since the oxygen-18 study indicates that C is slower than D, however, the mechanism is closer to that of formic acid[3] than to the other extreme proposed by Deno and Taft.[1] The reported[5,6] non-integral slope of the plot of log k *vs.* H_0 may be due to the intermediate character of the mechanism with neither B nor D strictly rate controlling.

The proposed mechanism[6] of decarbonylation of benzoylformic acid can explain the results of isotopic studies: (VII) the large isotope effect[7] with benzoylformic-1-C^{14} acid (k_{12}/k_{14} = *ca.* 1.1) due to carbon-14–oxygen bond cleavage in the rate step, VIII. A smaller effect (k_{12}/k_{14} = *ca.* 1.036) with benzoylformic-2-C^{14} acid, probably due to the effect of isotopic substitution at the number 2 carbon on the equilibrium constant of the reversible protonation involving the *alpha*-keto group, and IX. unenriched carbon monoxide from decarbonylation of benzoylformic acid in oxygen-18 enriched sulfuric acid, reasonable by analogy with the formic acid decarbonylation mechanism.

Non-radioactive carbon monoxide from decarbonylation of benzoylformic-2-C^{14} acid confirmed an earlier report[8] that the carbon monoxide came only from the carboxyl group.

Helpful suggestions of John D. Roberts and F. A. Long are acknowledged.

(1) N. C. Deno and R. W. Taft, THIS JOURNAL, **76**, 248 (1954).

(2) Although the two oxygen positions in carboxylic acids are not exactly equivalent, they should rapidly equilibrate through the symmetrical form, $R-C(OH)(OH)^{\oplus}$. Hence, the proposed[1] equilibrium involving the oxocarbonium ion and water should result in completely enriched carbon monoxide.

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 283.

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(7) B. Fingerman and M. Lemmon, Bio-Organic Chemistry Report, Radiation Lab., Univ. of California, Berkeley, Calif., 1958, UCRL-8204.

(8) K. Banholzer and H. Schmid, *Helv. Chim. Acta*, **39**, 548 (1956).

(9) Chemistry Division, Oak Ridge National Laboratory, Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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INTRAMOLECULAR HYDROGEN BONDING INVOLVING DOUBLE BONDS, TRIPLE BONDS AND CYCLOPROPANE RINGS AS PROTON ACCEPTORS

Sir:

We wish to report evidence which demonstrates the occurrence of intramolecular hydrogen bonding between proton donors and unsaturated linkages, including cyclopropane rings, as proton acceptors. Recently, similar observations have been reported for intramolecular interactions between hydroxyl

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]

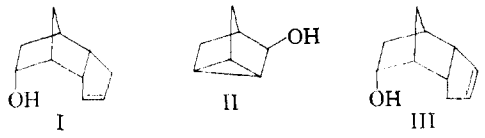
POSITIONS OF ABSORPTION BANDS OF UNSATURATED ALCOHOLS (CM.$^{-1}$)

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 = CH_2(cyclo)CH— 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.

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(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.

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

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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.

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