1.000) for the *exo* series **1** and −4.52 (correlation coefficient 1.000) for the *endo* series **2**.

In contrast to the 6-methoxy derivatives,[7] the *exo/endo* rate ratios are essentially constant, exhibiting values of 3300 for *p*-anisyl, 2900 for phenyl, 2700 for *p*-trifluoromethylphenyl, and 2800 for *m,m'*-bis(trifluoromethyl)phenyl.

In both the *exo* series and the *endo* series the rates at 25° vary over a range of approximately 10^8. This represents an enormous range of electron demand by the carbonium ion center. If the original postulate that participation should increase with increasing electron demand[2] is valid, there does not appear to be any reasonable way to avoid the conclusion that π participation cannot be a major factor in these tertiary 2-arylbenzonorbornen-2-yl derivatives.

If π participation is not a major factor in the high *exo/endo* rate ratio observed for these derivatives, what can be the cause?

The ground-state energies of a 2-aryl and 2-*p*-nitrobenzoate substituent appear to be very similar.[9] Consequently, differences in ground-state energies cannot be a significant factor.

We appear to be forced to steric hindrance to ionization in the *endo* isomer as the explanation for the high *exo/endo* rate ratios in these tertiary systems.[10]

The apparent absence of π participation in these tertiary derivatives does not rule out the possibility that π participation may be a factor in the *exo/endo* rate ratio for the secondary isomer. This could account for the effect of the (6,7)-nitro substituent in greatly decreasing the *exo/endo* rate ratio of the parent secondary system. Unfortunately, this problem has now become involved in the more general question as to the precise nature of the solvolysis process for secondary alkyl arenesulfonates and may well require a resolution of that question before a satisfactory understanding of the behavior of the secondary derivatives is attained.

We are further testing the validity of the present interpretation by examining the *exo/endo* rate ratios in 2-arylbenzonorbornen-2-yl derivatives containing deactivating substituents in the benzo moiety.

Since the present results indicate that the 2-aryl-*exo*-norbornenyl derivatives are not influenced significantly by π participation, it is of interest to use these compounds as standards against which the rate accelerations produced by a 6-methoxy substituent can be measured. As pointed out earlier, the rate acceleration, as measured by the value of $k_{6\text{-OMe}}/k_{6\text{-H}}$, increases with increasing electron demand: 2.0 for *p*-anisyl, 4.9 for phenyl, 34 for *p*-trifluoromethylphenyl, and 40 for *m,m'*-bis(trifluoromethyl)phenyl.[7]

Indeed, the rate constants for the 6-methoxy tertiary derivatives plot linearly against the rate constants for the corresponding unsubstituted benzo derivatives (Figure 1). Surprisingly, the line defined by the tertiary *p*-nitrobenzoates correlates quite well the calculated rate constants for the corresponding secondary *p*-nitrobenzoates.[11] If the 2-methyl derivatives also obey this correlation, a rate enhancement of 39 at 25° would be predicted for 6-methoxy-2-methyl-*exo*-benzonorbornenyl *p*-nitrobenzoate.

The present data for the tertiary derivatives argue strongly for the absence of significant π participation in the 2-arylbenzonorbornen-2-yl derivatives. The observation that the data for the secondary derivatives are correlated so well with the data for the tertiary derivatives suggests that π participation may not be a major factor even in the parent secondary benzonorbornen-2-yl system. However, it is necessary to understand the large effect of the (6,7)-nitro substituent on the *exo/endo* rate ratio before a final decision can be reached.

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[11] These were calculated using a factor of 3×10^5 to estimate the rates of the *p*-nitrobenzoates from those of the chlorides.[4d]

[12] Postdoctorate research associate on a grant (GP 6492 X) supported by the National Science Foundation.

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Relative Basicity of Phosphine and Ammonia in the Gas Phase[1]

Sir:

Phosphine in aqueous solution has been estimated[2a] to be 17–23 p*K* units less basic than its congener ammonia. Differences in energies of solvation, rehybridization, electronegativity, and possibly nonbonded repulsions may all play a role in influencing the relative basicities.[2] A quantitative gas-phase determination of the basicities (proton affinities) of PH_3 and NH_3 is desirable to estimate the relative importance of the above factors.

The proton affinity (PA) of a species, M, is the negative of the enthalpy change for the process $M + H^+ \rightarrow MH^+$. Recently, Haney and Franklin[3] have reported a value of 207 kcal/mol for the proton affinity of NH_3. The proton affinity of PH_3 is less well known. Previous estimates[4-7] for its value range from 153 to 209 kcal/mol. Clearly, new and more reliable data are desirable. Consider the general gas-phase proton-transfer reaction of eq 1. Ion–molecule reactions

$$M_1 + M_2H^+ \rightleftarrows M_1H^+ + M_2 \qquad (1)$$

proceed with negligible activation energy.[8] Thus reaction 1 will proceed to the right *only if* $PA(M_1) \geq PA(M_2)$.[9] We have derived the proton affinity of phosphine by determining the course of reaction 1 in mixtures of phosphine with compounds of known proton affinity.

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[1] This research was supported by the U. S. Atomic Energy Commission under Grant AT(04-3)767-8.

[2] (a) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, p 16; (b) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 304–308, 315–322 (1963).

[3] M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969). In agreement with these authors, we have recently obtained a value of $PA(NH_3) = 207 \pm 3$ kcal/mol employing procedures similar to those described in the present communication: J. L. Beauchamp and W. T. Huntress, unpublished results.

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[5] A. Giardini-Guidoni and G. G. Volpi, *Nuovo Cimento*, **17**, 924 (1960).

[6] Y. Wada and R. W. Kiser, *J. Phys. Chem.*, **68**, 2294 (1964).

[7] T. C. Waddington, *Trans. Faraday Soc.*, **61**, 2652 (1965).

[8] F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. Reaction Kinetics*, **1**, 67 (1961).

[9] J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968). The instrumentation and techniques employed are described herein.

Table I. Proton-Transfer Reactions Observed in Phosphine Mixtures at 12 eV

Reaction observed	$PA(PH_3)^a$	Ref
$PH_4^+ + NH_3 \rightarrow NH_4^+ + PH_3$	≤ 207	3
$PH_4^+ + (CH_3)_2CO \rightarrow (CH_3)_2COH^+ + PH_3$	≤ 189	12
$CH_3CHOH^+ + PH_3 \rightarrow PH_4^+ + CH_3CHO$	≥ 182	12
$H_3O^+ + PH_3 \rightarrow PH_4^+ + H_2O$	≥ 164	3, 9
$C_2H_5^+ + PH_3 \rightarrow PH_4^+ + C_2H_4$	≥ 158	9
$CH_5^+ + PH_3 \rightarrow PH_4^+ + CH_4$	≥ 124	13

[a] All values in kcal/mol.

Phosphine, generated *in vacuo* by transferring water onto excess magnesium aluminum phosphide, $Mg_3P_2 \cdot 2AlP$, was shown to contain less than 0.1% impurities by mass spectrometry at 70 eV.[10] The mass spectra of binary mixtures[11] of phosphine with acetaldehyde, acetone, ammonia, methane, and water were examined by ion cyclotron resonance[9] (ICR) as a function of pressure in the range 10^{-7} to 10^{-4} Torr. At pressures greater than 10^{-6} Torr, proton-transfer reactions as generalized in eq 1 were observed and investigated for the sample enumerated above. For example, in Figure 1 a plot of ion abundance as a function of pressure is presented for a 2:1 mixture of ammonia and phosphine under conditions (12 eV) where the only ions present are PH_4^+, $PH_3\cdot^+$, NH_4^+, and $NH_3\cdot^+$. One notes that as the pressure is raised all species, and in particular PH_4^+, react to form NH_4^+. Clearly, ammonia is more basic than phosphine, that is, $PA(NH_3) \geq PA(PH_3)$. Similar pressure studies performed for other mixtures are reported in Table I. In all cases reactions were confirmed to proceed as indicated by ion cyclotron double resonance.[9] Since the proton affinities of the species listed in Table I are known,[3,9,12,13] we can assign the proton affinity of phosphine as 185 ± 4 kcal/mol.[14]

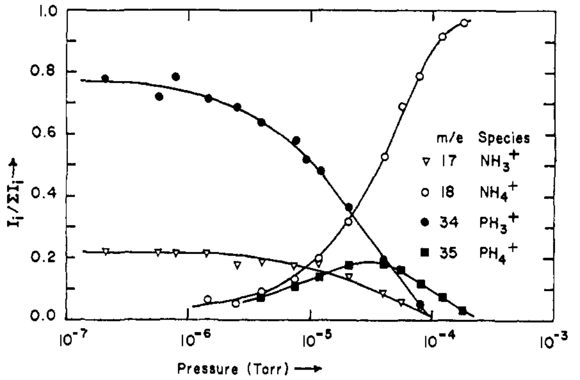

Figure 1. Variation of ion densities (reported as normalized single-resonance intensities) with pressure for a 2:1 mixture of PH_3 and NH_3 at 12 eV.

The proton affinity of PH_3 is 22 kcal/mol less than that of NH_3, a difference comparable to the aforementioned basicity difference of 23–32 kcal/mol in aqueous solution. Thus, solvation appears to play a minor role in the relative basicities of PH_3 and NH_3 in aqueous solution, a somewhat surprising conclusion. It is of interest to note that the proton affinities[3,9] of H_2O (164 kcal/mol) and H_2S (170) show a relative ordering opposite from that of NH_3 (207) and PH_3 (185). Unfortunately, the solution basicities of H_2O and H_2S are not known.[15]

The present work allows the calculation of some interesting thermochemical quantities. The proton and hydrogen affinities of a molecule and its corresponding ion are interrelated[9] by ionization potentials as shown in eq 2. The hydrogen affinity, $HA(M^+)$, is

$$PA(M) - HA(M^+) = IP(H) - IP(M) \qquad (2)$$

simply the $H-M^+$ bond strength, $D(H-M^+)$. A summary of hydrogen affinities and bond strengths for isoelectronic species is presented in Table II. As expected, the M–H bond strength increases in proceeding to the isoelectronic ion. Enhancement of a similar magnitude is noted for congeners in moving from the first to the second row of the periodic table. The correlation observed is only semiquantitative, however.

Table II. Bond Strengths of Some Isoelectronic Species[a]

Ion	Hydrogen affinity[b]	Neutral	Bond energy[c]	Δ^d
NH_4^+	128	CH_4	103	25
PH_4^+	102	SiH_4	80	22
Δ^e	26		23	
OH_3^+	141	NH_3	105	36
SH_3^+	97	PH_3	85	12
Δ^e	44		20	

[a] All values in kcal/mol. [b] $HA(M^+)$ from eq 2. Ionization potentials from J. L. Franklin and J. G. Dillard; H. M. Rosenstock, J. T. Herron, and K. Draxl; and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. Values for 298°K. [c] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials, and Electron Affinities," translated from the Russian by Scripta Technica Ltd., St. Martin's Press, New York, N. Y., 1966. [d] Difference in M–H bond strengths for isoelectronic species. [e] Difference in M–H strengths for congeners.

The ion chemistry of PH_3 is exceedingly rich. For example, at 70 eV and pressures above 10^{-6} Torr, condensation reactions in phosphine generate ions

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(10) The authors gratefully acknowledge the gift of a sample of $Mg_3P_2 \cdot 2AlP$ from Rocky Mountain Research, Inc., Denver, Colo.

(11) Reagent grade commercial chemicals were employed and were subjected to several freeze–pump–thaw cycles before use.

(12) Calculated using recent data given by (a) A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966); (b) K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, **48**, 5205 (1968).

(13) P.-M. Guyon, *J. Chim. Phys.*, **66**, 468 (1969).

(14) It is recognized that the participation of excited reactant ions in the proton-transfer processes listed in Table I might lead to the establishment of an improper limit on $PA(PH_3)$. The examination of the kinetics of reaction 1, as exemplified in Figure 1, serves to provide evidence against the participation of excited reactants. At the higher pressures in Figure 1, conditions where excess internal energy should be removed by collisional stabilization, there is no evidence of a reversal in the direction of proton transfer.

(15) Reference 2b, pp 283–285, 309–310.

containing two and three atoms of phosphorus. These reactions, as well as the ion chemistry observed in mixtures of phosphine with other molecules, will be the subject of a forthcoming publication.

[16] Alfred P. Sloan Fellow, 1968–1970.

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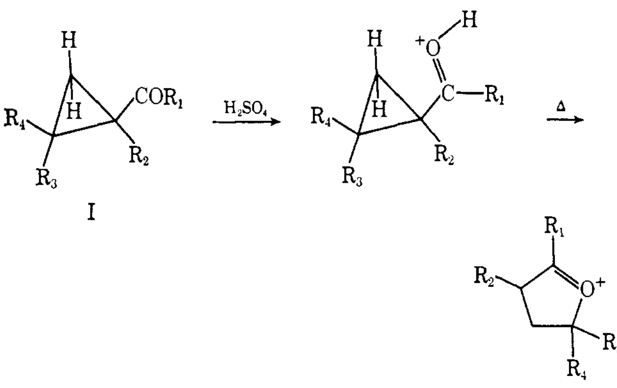
Rearrangement of Protonated Cyclopropyl Ketones to 1-Oxacyclopent-1-enyl Cations[1]

Sir:

Primary, secondary, and tertiary oxonium ions have been prepared by a variety of methods[2] since the pioneering work of Meerwein. We now describe a novel and mechanistically interesting method—the synthesis of 1-oxacyclopent-1-enyl cations from cyclopropyl ketones on heating in strong acids.

The protonation of ketones in acidic media has been studied extensively.[3] Pittman and Olah,[3f,g] in particular, have studied protonated cyclopropyl ketones in strong acids, but no further reactions beyond O-protonation were observed. When cyclopropyl methyl ketone (Ia) was added to 90% H_2SO_4 at room temperature, quantitative O-protonation occurred. On heating the solution to 81° complete conversion to 2-methyl-1-oxacyclopent-1-enyl cation (IIa) occurred in 3000 sec. Ion IIa was identified by its nmr spectrum (Figure 1), which exhibited a singlet at 3.48 ppm (three protons), a triplet at 4.28 ppm, $J = 7.8$ Hz (two protons), a pentet at 3.03 ppm, $J = 7.8$ Hz (two protons), and a triplet at 6.13 ppm, $J = 7.8$ Hz (two protons).[4] Drowning of ion IIa in excess dilute NaOH solution generated only 5-hydroxy-2-pentanone.[5,6] Oxonium ion formation proved to be general as illustrated by the rearrangement, in acid solution, of ketones Ia–h[7] to the respective oxonium ions IIa–h. Ions IIa–g were each formed quantitatively,[8] while IIh was obtained in only 45% yield. In the latter example, ring opening of the second cyclo-



I

II

a, $R_1 = CH_3$; $R_2, R_3, R_4 = H$
b, $R_1, R_2 = CH_3$; $R_3, R_4 = H$
c, $R_1, R_2, R_3 = CH_3$; $R_4 = H$
d, $R_1, R_3, R_4 = CH_3$; $R_2 = H$
e, $R_1 = CH_3$; $R_2, R_4 = H$; $R_3 = C_6H_5$
f, $R_1 = C_6H_5$; $R_2, R_3, R_4 = H$
g, $R_1, R_3 = C_6H_5$; $R_2, R_4 = H$
h, $R_1 = c\text{-}C_3H_5$; $R_2, R_3, R_4 = H$

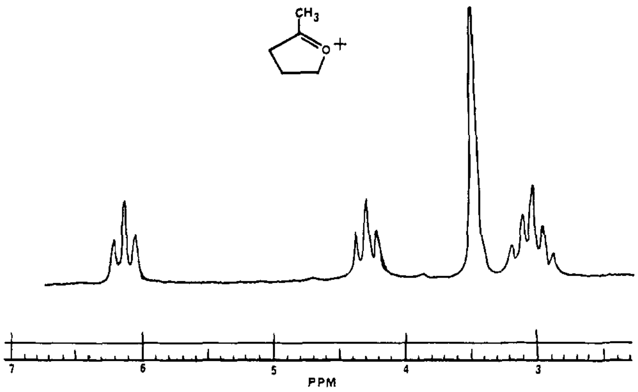


Figure 1.

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[1] (a) Acid-Catalyzed Cyclization Reactions. VI. For paper V, see S. P. McManus and C. U. Pittman, Jr., in press; (b) this work was supported by a University of Alabama Research Committee Grant and at Huntsville by Grant 3501-B from the Petroleum Research Fund, administered by the American Chemical Society, and by NASA Grant NGL 01-002-001.

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[3] (a) S. Nagakwa, A. Minegishi, and K. Stanfield, *J. Am. Chem. Soc.*, **79**, 1033 (1957); (b) R. Stewart and K. Yates, *ibid.*, **80**, 6355 (1958); (c) H. J. Campbell and J. T. Edward, *Can. J. Chem.*, **38**, 2109 (1960); (d) R. Stewart, M. R. Granger, R. B. Moodie, and J. J. Muenster, *ibid.*, **41**, 1065 (1963); (e) T. Birchall and R. J. Gillespie, *ibid.*, **43**, 1045 (1965); (f) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 2998 (1965); (g) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 5123 (1965); (h) T. J. Sekur, *Tetrahedron Letters*, 4793 (1966); (i) T. G. Bonner and J. Phillips, *J. Chem. Soc., B*, 650 (1966); (j) T. D. J. D'Silva and H. Ringold, *Tetrahedron Letters*, 1505 (1967); (k) M. Brookhart, G. C. Levy, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1735 (1967); (l) G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967); (m) G. A. Olah and M. Calin, *ibid.*, **90**, 938 (1968); (n) G. A. Olah and M. Calin, *ibid.*, **90**, 4672 (1968).

[4] (a) The simplicity of this spectrum results from the equivalence of the *cis* and *trans* vicinal coupling constants between the 3,4 and the 4,5 positions. This was expected in analogy with the 2,3-dihydrofuran system (*cf.* L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 87) and the previously reported 1-oxacyclopent-1-enyl cations.[2n,s] (b) All spectra were taken on a Varian HA-100 instrument and positions are reported relative to TMS (internal capillary).

[5] L. Joris and P. von R. Schleyer, *J. Am. Chem. Soc.*, **90**, 4599 (1968).

[6] Addition of authentic 5-hydroxy-2-pentanone[5] to 90% H_2SO_4 generated ion IIa quantitatively.

[7] Ketones were prepared by standard methods [*cf.* J. M. Conia, *Angew. Chem. Intern. Ed. Engl.*, 7, 570 (1968)] or were purchased. All compounds reported here were fully characterized.

[8] The nmr bands of protonated ketones disappear completely and are replaced by bands completely attributable to the corresponding oxonium ion. With the exception of IIh, no other bands are found in the spectra and the total number of protons measured by integration agrees with quantitative generation of cations IIa–g. The rates of rearrangement were monitored by observing both the disappearance and the appearance of characteristic bands.