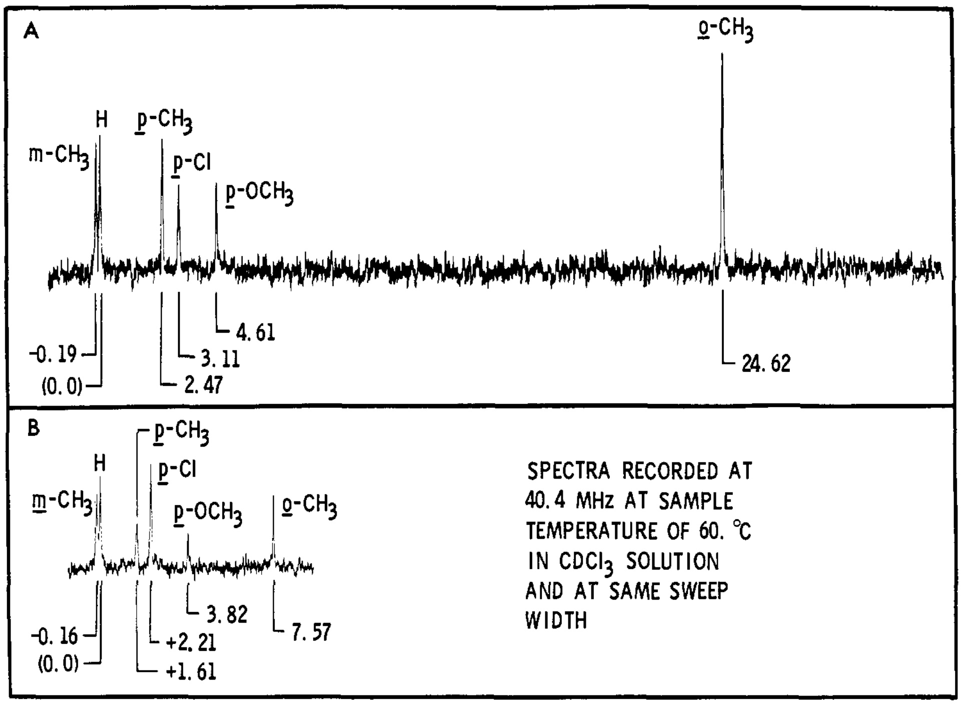


SPECTRA RECORDED AT 40.4 MHz AT SAMPLE TEMPERATURE OF 60. °C IN CDCl$_3$ SOLUTION AND AT SAME SWEEP WIDTH

Figure 1. Proton noise decoupled phosphorus-31 nmr of mixtures of triphenylphosphines (A) and phosphine selenides (B). Chemical shifts given in ppm relative to -H compound.

observed changes could not be due to anisotropy effects because of three additional C–C bonds in the vicinity of phosphorus but probably stem from a combination of two effects—steric polarization of the phosphorus valence electrons and changes in the extent of π bonding between the aromatic ring and the phosphorus orbitals. The latter no doubt involve modulation of the occupancies of the p and d orbitals of phosphorus.[7] Thus, it appears that the carbon π orbitals in the aromatic ring have more efficient interaction with ^{31}P orbitals in the phosphines than in the phosphine selenides.

For the triarylphosphine selenide, a linear correlation of directly bonded ^{31}P–^{77}Se coupling with substituent constants appears to exist.[2] The o-methyl compound, however, has a coupling whose magnitude is some 15 Hz less than expected and we attribute this diminution to a steric origin. The question of the detailed mechanism for this effect is open but significant rehybridization of both ^{31}P and ^{77}Se orbitals might be involved. Perhaps, the extent of change of ^{77}Se bonding orbitals could be sorted out from ^{77}Se chemical shift measurements. The direction of the observed change could be significant relative to the absolute sign of the coupling constant. In the cases of the directly bonded ^{13}C–^{1}H[8,9] and ^{13}C–^{19}F[9] couplings the direction of change precipitated by steric effects appears to be in the absolute negative direction. Thus, if the rehybridization and possible orbital polarization terms responsible for the observed changes in coupling constant are the same for the ^{31}P–^{77}Se coupling, this coupling would appear to be positive in absolute sign (negative J but positive K).[10]

---

(7) See, for example, the discussion of ^{31}P chemical shifts by M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.* **5**, 153 (1967).

(8) K. L. Servis, W. P. Weber, and A. K. Willard, *J. Phys. Chem.*, **74**, 3960 (1970).

(9) S. L. Manatt, M. A. Cooper, C. W. Mallory, and F. B. Mallory, *J. Amer. Chem. Soc.*, **95**, 975 (1973).

(10) This conclusion is supported from the fact that the sign of the ^{31}P–^{77}Se coupling (*i.e.*, K) has been reported from double resonance experiments to be positive for (CH$_3$)$_2$PSeMe and (CH$_3$)$_2$PSSeMe: W. McFarlan and J. N. Hash, *Chem. Commun.*, 913 (1969).

(11) Work accomplished under a grant from the California Institute of Technology President's Fund.

Robert P. Pinnell,* Clifford A. Megerle
Joint Science Department
Scripps, Pitzer and Claremont Men's Colleges[11]
Claremont, California 91711

Stanley L. Manatt,* Paulus A. Kroon
Space Sciences Division, Jet Propulsion Laboratory[11]
California Institute of Technology, Pasadena, California 91103

Received August 21, 1972

Solvent Effects in Organic Chemistry. XVI. An Enormous Alkyl Substituent Effect in Solution[1]

Sir:

In fluorosulfuric acid (HSO$_3$F) at −52° the heats of protonation of CH$_3$SH and H$_2$S are −19.2 and −5.3 kcal/mol, respectively. The difference (13.9 ± 1.2 kcal/mol) is almost exactly the same as has been reported for their proton affinities (PA) in the gas phase (16 ± 6 kcal/mol).[2] This would represent a 10^{15}-fold substituent effect for a methyl group if converted into rates or equilibrium constants at this temperature and is many orders of magnitude greater than any such effect reported previously for a direct thermodynamic measurement in solution. Similarly, large substituent effects are also found for the solution protonation of

---

(1) Supported by National Science Foundation Grant GP-6550X.

(2) (a) M. S. Haney and J. H. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969); (b) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

Table I

Compound	$-\Delta H_{HSO_3F}$	ΔH_{inert}	$-\Delta H_i$	$-$PA
H_2S	10.4 ± 0.6[a,c]	−5.1 ± 0.2[a,d]	5.3 ± 0.8	170 ± 3,[i,j] 178 ± 2[k]
MeSH	19.2 ± 0.6[a]	0 ± 0.03[a,d]	19.2 ± 0.6	185 ± 1,[i] 186[j]
MeSMe	18.1 ± 0.7[a]	0 ± 0.3[a,d]	18.1 ± 0.7	197[j]
H_2O	12.2 ± 0.1[b]	4.33 ± 0.15[b,e]	16.5 ± 0.2	164 ± 4,[j,k] 165 ± 3[i]
MeOH	14.4 ± 0.3	2.74 ± 0.07[f]	17.1 ± 0.4	180[j], 182 ± 3[i]
MeOMe	22.9 ± 0.4	−4.68 ± 0.26[f]	18.2 ± 0.7	186[j], 187 ± 1[i]
EtOH	15.3 ± 0.3[b]	3.39 ± 0.12[f]	18.7 ± 0.4	186[j]
EtOEt	19.5 ± 0.7[b]	0.09 ± 0.06[f]	19.5 ± 0.7	199[j]
PH_3	16.9 ± 0.8[a,c]	−2.9 ± 0.6[a,c,d]	14.0 ± 1.4	185 ± 4,[l,j] 186 ± 1[i]
$C_6H_{11}PH_2$	29.9 ± 0.6[a]	0.4 ± 0.2[a,d]	30.3 ± 0.8	
$(C_6H_{11})_2PH$	31.6 ± 0.7[a]	0.92 ± 0.10[a,d]	32.5 ± 0.8	
Me_3P	44.6 ± 0.4[a]	0 ± 0.03[a,d]	44.6 ± 0.7	230 ± 3[m]
NH_3	47.3 ± 0.7[c]	−4.0 ± 0.2[c,g]	43.3 ± 0.9	207 ± 3[i,l]
$MeNH_2$	51.3 ± 0.3[c]	−5.4 ± 0.2[c,h]	46.3 ± 0.5	216.3 ± 0.6,[n] 218.4 ± 0.2[o]
Me_2NH	53.8 ± 0.5[c]	−6.0 ± 0.2[c,h]	47.8 ± 0.7	222.4 ± 0.6,[n] 224.9 ± 0.2[o]
Me_3N	53.5 ± 0.7[c]	−6.0 ± 0.2[c,h]	47.5 ± 0.9	226.6 ± 0.6,[n] 229.1 ± 0.2[o]

[a] At −52°. [b] Reference 4. [c] Solutes which were gaseous at the temperature of solution were introduced either with a gas-tight syringe or an apparatus resembling that of C. E. Vanderzee and J. D. Nutter, *J. Phys. Chem.*, 67, 2521 (1963). [d] Inert solvent is toluene. [e] Inert solvent is *sym*-tetrachloroethane. [f] Inert solvent is C_6H_6. [g] ΔH_{inert} = av ΔH_s in C_6H_6 and *o*-dichlorobenzene. [h] ΔH_{inert} = av ΔH_s in C_6H_6, *o*-dichlorobenzene, and CCl_4. [i] Reference 2a. [j] Reference 3. [k] Reference 2b. [l] D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970). [m] Reference 13. [n] Reference 8. [o] D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4726 (1972).

phosphine compared with several alkyl phosphines. In sharp contrast are the small alkyl effects observed for protonation of the analogous oxygen and nitrogen bases in solution, although the gas-phase substituent effects on protonation as represented by PA's are roughly equivalent in all four series (N, O, S, P) of bases.[3]

Heats of ionization (ΔH_i) in fluorosulfuric acid are defined as the heat of transfer for a base from high dilution in an inert solvent to high dilution in HSO_3F.[4] Because of strong exothermic decompositions when H_2S or PH_3 were introduced into this solvent at room temperature, the calorimeter was operated at −52°[5] for the compounds so footnoted in Table I. Clean protonation for all of the compounds in Table I has been demonstrated independently by nmr.[6]

The heat of solution of the pure gaseous or liquid base in HSO_3F (ΔH_{HSO_3F}) was measured both at −52 and at 25° for several of the compounds whose conjugate acids were known to be stable at both temperatures. In no case could a statistically significant temperature effect on ΔH_{HSO_3F} be found. We therefore consider that the relatively low values of ΔH_i at −52° for H_2S and PH_3 are the result of repressing the exothermic side reactions so that the true, small heats of protonation were revealed.

ΔH_{inert} is the heat of solution of the pure gaseous or liquid base in an inert solvent (toluene, benzene, *o*-dichlorobenzene, carbon tetrachloride, and *sym*-tetrachloroethane) under the same conditions that ΔH_{HSO_3F} was determined. ΔH_{inert} was shown to be independent of the inert solvent (within ±1 kcal/mol) for all of the compounds listed which could be tested in several solvents.[7] Therefore $\Delta H_i = \Delta H_{HSO_3F} - \Delta H_{inert}$.[4]

Comparison should be made between heats of ionization in HSO_3F (ΔH_i) and the heats of ionization in the gas phase as represented by proton affinities (PA) for the same compounds. For the amines, quite exact relative PA's are known from equilibrium studies using ion cyclotron resonance (see footnoted references to values cited). For most of the bases there seems to be agreement within 3–5 kcal/mol for PA's on an absolute scale. In view of the likelihood of large absolute errors in some cases, we think it unwise to use the present data to calculate the heats of solvation of the different O, P, and S onium ions as we have done elsewhere for the ammonium ions,[8] although the present data could be used in that way.

Since the bases and the onium ions derived respectively from each central atom (*e.g.*, H_2O *vs.* H_2S) should be of similar size and shape, they should have nearly equivalent electrostatic solvation. Thus, we look to different modes of specific solvation to explain why the large substituent effects which are found for the protonation of all four series of bases (N, O, S, P) in the gas phase are selectively supressed for the nitrogen and oxygen bases in HSO_3F. We attribute the observed differences to the peculiar ability of oxonium and ammonium ions to form strong hydrogen bonds to the solvent or to its lyate anion.[9] The effect of alkyl substitution on a protonated onium ion will be to stabilize it through polarization. If, however, an onium ion is also capable of stabilization through hydrogen bonding to the solvent, the net result of replacing a hydrogen by an alkyl group will depend on the balance of what is gained through charge delocalization into the alkyl group and what is lost through decreased hydrogen bonding.[8,10] If the ion is a poor hydrogen bond donor,

---

(3) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

(4) E. M. Arnett, R. P. Quirk, and J. J. Burke, *J. Amer. Chem. Soc.*, **92**, 1260 (1970). What we call ΔH_i here corresponds to ΔH_{ab} in that article.

(5) E. M. Arnett and J. W. Larson, *ibid.*, 90, 791 (1968).

(6) G. A. Olah and C. W. McFarland, *J. Org. Chem.*, 34, 1832 (1969); G. A. Olah and A. M. White, *Chem. Rev.*, 70, 561 (1970).

(7) Slightly larger differences between ΔH_s in benzene *vs.* carbon tetrachloride were seen for methanol (1.6 kcal/mol) and ethanol (1.1 kcal mol) probably reflecting slight exothermic formation of a weak hydrogen bond to benzene; see E. M. Arnett *et al.*, *J. Amer. Chem. Soc.*, **92**, 2365 (1970), Tables VI and VII. We have used benzene as the inert medium for these compounds in order to conform with other bases which were subsequently run in toluene.

(8) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

(9) A close linear correlation between heats of solvation of ammonium ions in HSO_3F and H_2O has been found and will be reported independently.

(10) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

stabilization by alkyl polarization will be the dominating result of substitution in solution and in the gas phase. We therefore attribute the large difference between the heat of protonation of H_2S and CH_3SH or between PH_3 and $C_6H_{11}PH_2$ to the large gain of internal stabilization of the onium ion by delocalization into the alkyl group with little or no loss in stabilization due to specific solvation. Further substitution of alkyl groups leads to further stabilization of phosphonium ions.[11]

There is precedent for the dramatically low basicity of phosphine compared to alkyl phosphines or the other bases shown.[12] However, the cited value for the PA of $(CH_3)_3P$[13] seems to be surprisingly high compared to the effects of methyl groups in the N, O, and S analogs. If it were lower by 11 kcal/mol it would give complete agreement between PA and ΔH_i differences and conform almost exactly to the pattern expected from the other series.

The results and our interpretation of them clearly indicate that oxygen compounds would be exceptionally weak bases in solution were it not for the hydrogen bonding ability of their conjugate acids. The consequences of this fortunate circumstance are nearly unlimited.

Acknowledgment. We are glad to acknowledge the many contributions of Mr. Kenneth Stanko and Mr. John Pezdek in performing the experiments reported here.

---

(11) We will not account for the relatively low heat of ionization of dimethyl sulfide at this time, but the small effect of the second methyl group appears to be genuine.

(12) R. E. Weston, Jr., and J. Bigeleisen, *J. Amer. Chem. Soc.*, **76**, 3074 (1954); W. A. Henderson, Jr., and C. A. Streuli, *ibid.*, **82**, 5791 (1960); H. C. Brown, *ibid.*, **67**, 503 (1945).

(13) D. H. McDaniel, N. B. Coffman, and J. M. Strong, *ibid.*, **92**, 6697 (1970).

* Address correspondence to this author at the University of Pittsburgh.

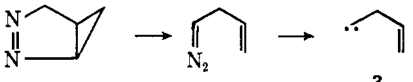
Edward M. Arnett,* J. Fredrick Wolf
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15213
Mellon Institute of Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Received November 7, 1972

Photolysis of Substituted Derivatives of 2,3-Diazabicyclo[3.1.0]hex-2-ene. A Simple Route to Certain Bicyclo[1.1.0]butanes[1]

Sir:

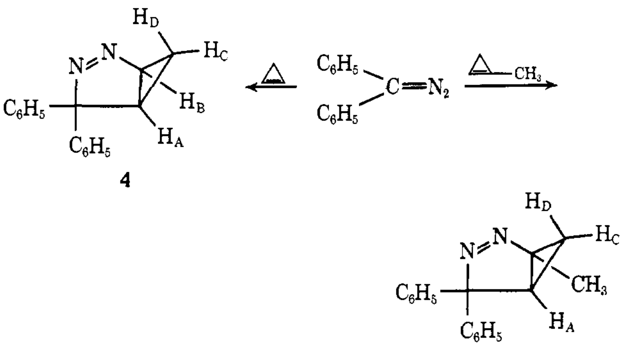
Recently, Eaton, Bergman, and Hammond reported[2] that the photochemical decomposition of derivatives of 2,3-diazabicyclo[3.1.0]hex-2-ene (**1**) produced products



1 **2** **3**

which were readily explained in terms of the initial formation of a diazoalkene, **2**, followed by loss of nitrogen to give the carbene, **3**, and subsequent rearrangements to yield olefins. They concluded that their observations "unambiguously implicate carbene formation as a major decomposition path in the diazabicyclo[3.1.0]hex-2-ene system." We now wish to report results on the photochemical decomposition of derivatives of 2,3-diazabicyclo[3.1.0]hex-2-ene, which contrast strongly with those previously reported.[2] Our results indicate that the total mechanistic picture for the photochemical decomposition of derivatives of 2,3-diazabicyclo[3.1.0]-hex-2-ene can be changed dramatically by the presence of phenyl substituents.

4,4-Diphenyl-2,3-diazabicyclo[3.1.0]hex-2-ene (**4**),[3]



4

5

mp 118–119°, was prepared in 90% yield *via* the addition of gaseous cyclopropene[4] to a pentane solution of diphenyldiazomethane[5] at 0°. In a similar manner, addition of 1-methylcyclopropene[6] to an ethereal solution of diphenyldiazomethane gave a 99% yield of 4,4-diphenyl-1-methyl-2,3-diazabicyclo[3.1.0]hex-2-ene (**5**). The structure of **4** was established on the basis of its spectroscopic properties which gave absorptions in the nmr at τ 2.25–3.10 (10 H, mult, aromatic protons), 5.04 (1 H, heptet; H_B,[7] $J_{AB} = 4.5$, $J_{BC} = 8.0$, $J_{BD} = 2.5$ cps), 7.75 (1 H, octet; H_A, $J_{AB} = 4.5$, $J_{AC} = 8.0$, $J_{AD} = 5.0$ cps), 8.87 (1 H, hextet; H_C, $J_{AC} = 8.0$, $J_{BC} = 8.0$ $J_{CD} = 5.0$ cps), and 9.93 (1 H, hextet; H_D, $J_{AD} = 2.5$, $J_{BD} = 5.0$, $J_{CD} = 5.0$ cps). The uv of **4** showed $\lambda_{max}^{ethanol}$ 334 nm (ϵ 202) while the near-ir spectrum showed $\lambda_{max}^{CCl_4}$ 1.636 μ (ϵ 0.682) for a cyclopropyl methylene unit. Similar spectroscopic analysis of **5** showed nmr absorptions at τ 2.25–3.10 (10 H, mult, aromatic protons), 8.11 (1 H, quartet; H_A, $J_{AC} = 8.0$, $J_{AD} = 5.0$ cps), 8.13 (3 H, singlet, methyl), 9.08 (1 H, quartet; H_C, $J_{AC} = 8$, $J_{CD} = 5$ cps), and 9.93 (1 H, triplet; H_D, $J_{AD} = 5$, $J_{CD} = 5$ cps). The uv spectrum of **5** showed $\lambda_{max}^{ethanol}$ 333 nm (ϵ 170).

Irradiation of a solution of 3 g of **4** in 3 l. of pentane in a Pyrex vessel for 12 hr with a 450-W Hanovia lamp gave a mixture consisting of **6** (35% yield) and **7** (51% yield). The identity of **7** was established by a comparison of its spectral properties with those of an authentic sample. Since standard separation techniques led to the decomposition of **6**, the mixture of **6** and **7** was ozonized with 1 equiv of ozone at −78° to yield a mixture of **6** and the stable monoozonide of **7**.[8] The mixture of **6**

---

(1) Paper XXXVI in a series on The Chemistry of Bent Bonds. For the preceding paper in this series, see P. G. Gassman, T. J. Atkins, and J. T. Lumb, *J. Amer. Chem. Soc.*, **94**, 7757 (1972).

(2) D. F. Eaton, R. G. Bergman, and G. S. Hammond, *ibid.*, **94**, 1351 (1972).

(3) Satisfactory elemental analysis or exact mass molecular weights were obtained on all new compounds except **13** which was not isolated.

(4) G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966).

(5) L. I. Smith and K. L. Howard, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 351.

(6) F. Fisher and D. E. Applequist, *J. Org. Chem.*, **30**, 2089 (1965).

(7) The nmr assignments were based on an extensive study of the nmr spectra of various substituted and deuterium labeled 2,3-diazabicyclo[3.1.0]hex-2-enes. A detailed analysis will be presented in a full paper on this subject.

(8) The nmr of the mixture of **6** and the monoozonide of **7** showed that the ozonide was identical with that obtained from an authentic sample of **7** and 1 equiv of ozone.