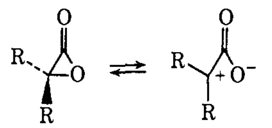
primary photochemical reaction of the α-lactone. A second photochemical reaction of the α-lactone leads to the product with the 1740-cm^{-1} absorption. The infrared spectrum of this product identifies it as the polyester **3a** which is the major product from the room temperature irradiation of **1a**.[5] Polyester **3a** is also formed when the α-lactone is warmed above $-100°$. This result is in accord with mechanisms previously suggested for polyester formation.[5]

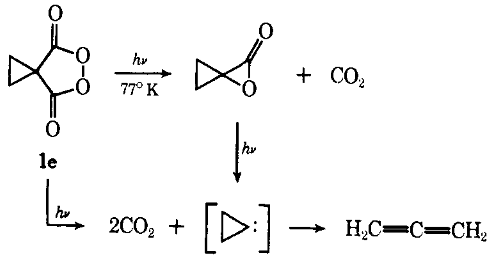
Irradiation of peroxides **1b–e** at 77°K gives in each case an α-lactone and carbon dioxide. Warming above $-100°$ again converts the α-lactones to polyesters. Irradiation of α-lactones (**2b–d**) gives carbon monoxide (2138 cm^{-1}) and the corresponding ketones.

The carbonyl stretching frequency of the α-lactones clearly shows that at 77°K they exist as the closed α-lactone structure rather than as the zwitterion. The position of $\nu_{C=O}$ is quite reasonable (Figure 3). The thermal instability of the α-lactones above $-100°$ suggests that there is a small activation barrier between the α-lactone and the zwitterion.



The very low temperatures at which the α-lactones polymerize also accounts very directly for the failures encountered in earlier attempts to observe α-lactones at temperatures as low as Dry Ice–acetone mixtures.[6] The thermal polymerization of α-lactones is in accord with earlier postulates.[3,5] The photochemical decarbonylation and polymerization of the α-lactone are unexceptional. Photodecarbonylation has been observed in α-lactams.[9]

The spirocyclopropyl α-lactone is especially interesting. The carbonyl frequency (1935 cm^{-1}) indicates a stronger than normal α-lactone carbonyl bond even though the carbonyl group bisects the cyclopropane ring in perfect fashion for conjugative overlap. Allene is a significant product in the irradiation of peroxide **1e** as well as the α-lactone. It is likely that allene is formed by way of the carbene **4**. The carbene could be formed by loss of two molecules of carbon dioxide from **1e** or by loss of carbon dioxide from the α-lactone. Preliminary evidence suggests that at 77°K the major path is that *via* the α-lactone.



Acknowledgment. The research at ISU was supported by the National Science Foundation (GP-28152X), the National Institute of Arthritis and Metabolic Diseases (AM 14624), and the Petroleum Research Fund of the American Chemical Society (5252-AC4). The research at UPR was supported by the National Science Foundation (GP-17755), the Petroleum Research Fund of the American Chemical Society (4105-A), and the A. P. Sloan Foundation.

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Internal Exchange in New Group III Metalloborane Derivatives, $(CH_3)_2AlB_3H_8$ and $(CH_3)_2GaB_3H_8$

Sir:

We wish to report the syntheses and preliminary structural studies of dimethylaluminum triborane(8) and dimethylgallium triborane(8).[1] Previously the chemistry of the $B_3H_8^-$ anion[2] has been restricted to its use in the synthesis of higher boranes[3,4] and transition metal complexes.[5,6] The relatively recent development of convenient synthetic procedures[3,7] makes this reagent potentially useful for a wide variety of chemical investigations, including the synthesis of covalent main group derivatives.

The preparation of $(CH_3)_2AlB_3H_8$ and $(CH_3)_2GaB_3H_8$ involves the reaction of $(CH_3)_2GaCl$ or $(CH_3)_2AlCl$ with salts of $B_3H_8^-$. In a typical reaction, excess NaB_3H_8[2] was stirred in a vacuum with 4.7 mmol of solid $(CH_3)_2GaCl$ for 15 min at room temperature, during which time a mobile liquid was formed. The product, $(CH_3)_2GaB_3H_8$, was then purified by high-vacuum fractional distillation; it distils slowly through a $-45°$ trap and is essentially completely condensed by a $-63°$ trap. The yield of purified $(CH_3)_2GaB_3H_8$ was 2.95 mmol, 63%. The use of $(CH_3)_4N^+$ and $(n\text{-}C_4H_9)_4N^+$ salts of $B_3H_8^-$ produces similar yields of the product. The $(CH_3)_2AlB_3H_8$ was prepared using the same procedures and similar yields were obtained. The volatilities of these compounds suggest that they are monomers, at least in the vapor phase. As their apparent thermal stability is marginal, vapor pressure measurements are not reliable purity criteria.

$(CH_3)_2AlB_3H_8$: 0°, 13 Torr; 19°, 35 Torr
$(CH_3)_2GaB_3H_8$: 0°, 4 Torr; 24°, 13 Torr

The gas-phase infrared spectra of $(CH_3)_2AlB_3H_8$ and $(CH_3)_2GaB_3H_8$ are virtually identical in the stretching region, indicating that their vapor-phase structures are probably very similar: $(CH_3)_2AlB_3H_8$ (cm^{-1} ± 10)

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ent origin. At 77°K the polyester undergoes a slow conversion to carbon monoxide and ketone. It may be that polyester is the source of the small amount of ketone observed at room temperature.

(9) E. R. Talaty, A. E. Du Puy, Jr., and T. H. Golson, *Chem. Commun.*, 49 (1969).

(1) In accordance with IUPAC "Nomenclature of Inorganic Boron Compounds," No. 8, 1970, it appears that these compounds could be referred to by the names 2,2-dimethyl-2-aluminatetraborane(10) and 2,2-dimethyl-2-gallatetraborane(10). However, it was felt this nomenclature might be misleading.

(2) W. V. Hough, L. J. Edwards, and A. D. McElroy, *J. Amer. Chem. Soc.*, **80**, 1828 (1958).

(3) H. C. Miller, N. E. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1456 (1964).

(4) D. F. Gaines, *J. Amer. Chem. Soc.*, **91**, 6503 (1969).

(5) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, 7, 1051 (1968).

(6) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *ibid.*, 7, 2272 (1968).

(7) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Nucl. Chem. Lett.*, **6**, 765 (1970).

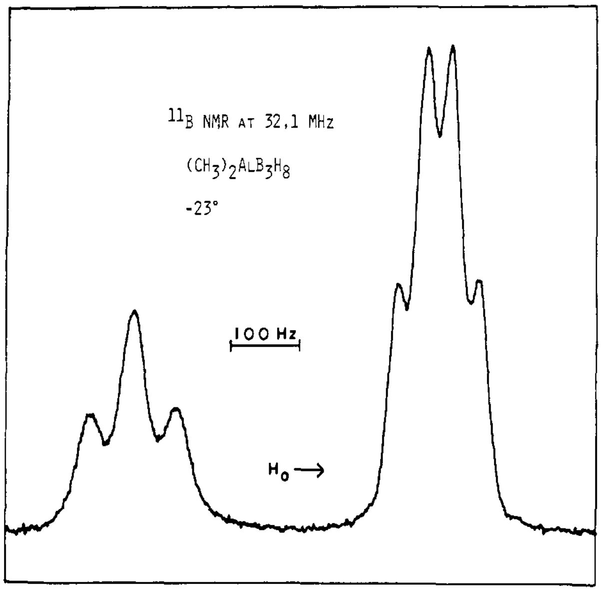

Figure 1. The 32.1-MHz ^{11}B nmr spectrum of $(CH_3)_2AlB_3H_8$ at $-23°$. Low-field triplet: $\delta = 14.0$ ppm and $J = 125$ Hz, relative area 1.0. High-field group: $\delta = 41.4$ ppm and spacings of 78, 70, and 78 Hz, relative area 2.1.

2970 (m), 2920 (w), 2850 (w), 2560 (vs), 2510 (s), 2200 (vs); $(CH_3)_2GaB_3H_8$ 3050 (sh), 2970 (m), 2910 (m), 2550 (vs), 2480 (s), 2140 (vs).

Mass spectral studies have been complicated by the fact that both compounds polymerize at normal operating temperatures. Low temperature studies reduced the polymerization sufficiently to permit verification of the $(CH_3)_2MB_3H_x$ fragments, but the parent peak has not been observed (the same general problem was observed when 2,2-$(CH_3)_2B_4H_8$ was examined).[4] The following parent group fragment ions were identified for $(CH_3)_2GaB_3H_8$: $(^{12}CH_3)_2{}^{71}Ga^{11}B_3H_6$; found 140.0474 (calcd 140.0467); $(^{12}CH_3)_2{}^{71}Ga^{11}B_3H_7$; found 141.0548 (calcd 141.0545).

The ^{11}B nmr spectra (32.0 MHz) of both new compounds are temperature dependent. At normal probe temperature (*ca.* 35°) the spectrum of $(CH_3)_2GaB_3H_8$ consists of a nine-lined multiplet at δ 32.2 ± 0.3 ppm ($BF_3 \cdot O(C_2H_5)_2 = 0.0$) with $J = 34 \pm 1$ Hz. These values are surprisingly similar to those obtained for the $B_3H_8^-$ anion,[8] except that the individual resonances are noticeably narrower in $B_3H_8^-$ anion spectra. The spectrum of $(CH_3)_2AlB_3H_8$ is a slightly asymmetric singlet at δ 34.5 ppm. At 50° the resonance is more symmetrical and somewhat narrower and is shifted to δ 33.3 ppm.

The ^{1}H nmr spectra (100 MHz) of the compounds are similar at normal probe temperature, consisting of a broad unresolved hump from the hydrogens on boron and a sharp singlet from the CH_3 groups. These data indicate that the CH_3 groups, boron atoms, and boron-bound hydrogen are involved in rapid intramolecular exchange processes (on the nmr time scale) at room temperature.

An internal exchange mechanism has previously been proposed[9] for the spectroscopically similar $B_3H_8^-$ anion. Available ^{11}B nmr data indicate that the B_3H_8 moiety in $[(C_6H_5)_3P]_2CuB_3H_8$ is involved in some exchange process,[5,6,10] whereas in $[(CH_3)_4N][Cr(CO)_4B_3H_8]$ it is not.[6] Solid-state structural studies of $[(C_6H_5)_3P]_2CuB_3H_8$[11] and $[(CH_3)_4N][Cr(CO)_4B_3H_8]$[12] show that the previously determined $B_3H_8^-$ anion structure[13] is retained. The ^{11}B nmr spectra of both $(CH_3)_2GaB_3H_8$ and $(CH_3)_2AlB_3H_8$ broaden as the temperature is lowered and finally resolve into two resonances. In the case of $(CH_3)_2GaB_3H_8$, the smaller resonance is a broad hump at δ 12.9 ppm, the larger resonance is a hump at δ 41.9 ppm, and there is no visible fine structure. In the case of $(CH_3)_2AlB_3H_8$, however, the spectrum is somewhat better resolved, as is shown by the $-23°$ example in Figure 1.

Crystal structures of metal–B_3H_8 systems[11,12] show the bridging hydrogens of both B–H–B and B–H–M bonds to be closer to the borons near the metal, so the boron–bridge hydrogen bond lengths approximate those of boron–terminal hydrogens. Thus these borons in $(CH_3)_2AlB_3H_8$ may be nearly equidistant from three hydrogens, which could account for the high-field "quartet." It should be noted, however, that the quartet is slightly distorted and the intensity ratios are not ideal. The triplet would then be from the remaining boron split by its two terminal hydrogens but not by the relatively more distant bridge hydrogens. At temperatures below $-23°$ the low-field resonance collapses to a broad singlet; the high-field resonance also collapses but with some ill-defined fine structure still visible.

The ^{1}H nmr spectral changes that occur as the temperature is lowered include three related phenomena. The boron-bound hydrogens become somewhat magnetically differentiated. Nearly complete thermal decoupling[10] is observed (some slight resonance narrowing occurs when ^{11}B double irradiation is applied), with at least four environments existing for boron-bound hydrogens below $-90°$. Finally, the CH_3 resonance is resolved below $-70°$ into two equally intense peaks separated by 14 and 16 Hz, respectively, for $(CH_3)_2GaB_3H_8$ and $(CH_3)_2AlB_3H_8$.

Thus the low-temperature nmr data appear consistent with static structures for $(CH_3)_2AlB_3H_8$ and $(CH_3)_2GaB_3H_8$ similar to the solid state structures of $[(C_6H_5)_3P]_2CuB_3H_8$[11] and $[(CH_3)_4N][Cr(CO)_4B_3H_8]$,[12] *i.e.*, two adjacent B atoms of the B_3H_8 moiety are bound by the hydrogen bridge bonds, B–H–M, to the Al or Ga (I). Equilibration of the CH_3 resonances at temperatures at which the B_3H_8 moiety is essentially static (~0 to $-60°$) may be envisioned as a result of cleavage of one of the B–H–M bridge bonds (II) followed by rotation of the $(CH_3)_2M$ group about the remaining B–H–M bridge ($I \rightleftharpoons II$).

Methyl groups could also be equilibrated *via* a "flapping" motion; however, this seems unlikely considering the low temperatures at which the methyl groups are equivalent. At higher temperatures other exchange intermediates (III, IV, V) may also form in order to provide facile internal exchange routes ($I \rightleftharpoons II \rightleftharpoons III$, $I \rightleftharpoons II \rightleftharpoons IV$, $I \rightleftharpoons II \rightleftharpoons V$) for hydrogens

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(8) G. R. Eaton and W. N. Lipscomb, "Nmr Studies of Boron Hydrides and Related Compounds," W A. Benjamin, New York, N. Y., 1969, p 53.

(9) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 117 (1959).

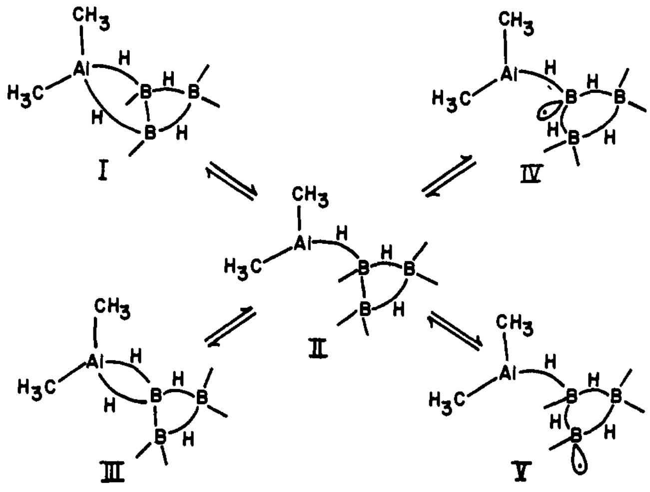
(10) C. H. Bushweller, H. Beall, M. Grace, W. J. Dewkett, and H. S. Bilofsky, *J. Amer. Chem. Soc.*, **93**, 2145 (1971).

(11) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

(12) L. J. Guggenberger, *ibid.*, **9**, 367 (1970).

(13) C. R. Peters and C. E. Nordman, *J. Amer. Chem. Soc.*, **82**, 5758 (1960).

around the B_3H_8 moiety while maintaining the CH_3 exchange. Further spectroscopic and chemical studies of these and related compounds are in progress.



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Gas-Phase Basicities and Pyridine Substituent Effects[1]

Sir:

The substantially lower base strength toward the aqueous proton of pyridine ($pK_a = 5.21$) than that of ammonia and aliphatic amines ($pK_a = 9$–11) has generally been ascribed to a greater degree of s character in the former's hybrid molecular orbital containing the lone electron pair. We wish to report that in the gas phase the basicity is substantially greater for pyridine (proton affinity, PA = 225 ± 2 kcal)[2] than ammonia (PA = 207 ± 3 kcal)[3] and comparable with aliphatic amines,[4] *e.g.*, $(CH_3)_2NH$ (PA = 225 ± 2 kcal). This observation clearly establishes that the stability afforded the pyridinium ion by differential polarization[5] of the π molecular orbital between gas and aqueous phases, as well as other solvation effects,[6] is as large or larger than the hybridization effect.

Such a substantial inversion in base strengths of ammonia and pyridine between gas and aqueous phases makes substituent effects on gas-phase proton affinity particularly significant. Do substituent constants, based upon observations in aqueous solution, apply in the gas phase? What is the quantitative attenuation of substituent effects due to aqueous solvent? How useful are approximate molecular orbital treatments in such problems?

We have made a CNDO/2 calculation[7] of the relative proton affinities of 4-substituted pyridines using conventional geometries and bond distances. These calculations show a rough linear potential energy–free energy relationship between the calculated gas-phase proton affinities and the corresponding experimental free energies of aqueous ionization of slope ~3.6 (*cf.* Table I).

Table I. 4-Substituent Effects

	Aqueous solution		Gas phase	
Substituent	pK_a	$\delta_R\Delta G°$, kcal	$\delta_R\Delta E$,[c] kcal	δ_RPA, kcal ± 2.0
MeO	6.58[a]	1.87	5.6[d]	8.0
Me	6,03[a]	1.12	6.9	5.0
H	5.21[a]	(0.00)	(0.0)	(0.0)
CF_3	2.63[b]	−3.52	−15.3	−11.0
NO_2	1.39[a,e]	−5.21	−21.4	−17.0

[a] A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 3591 (1964). [b] H. B. Yang, unpublished result. We are indebted to Dr. W. A. Sheppard for a sample. [c] CNDO/2 calculation. [d] Calculation for OH. [e] We are indebted to Dr. J. Lyle for a sample.

PA's have been determined using ion cyclotron resonance intensity-pressure plots[8a] and double resonance techniques[8b] with aliphatic and fluoroaliphatic amine standards which have been separately established.[4] Each pyridine was compared to at least three standards and its assigned PA is that of the amine for which proton transfer was observed with negative $(dk/dE_{ion})_0$ in both directions. Relative values of PA, δ_RPA, for the 4-substituted pyridines are listed in Table I.

Figure 1 illustrates the satisfactory linear enthalpy–free energy relationship which exists between gaseous δ_RPA and aqueous $\delta_R\Delta G°$. The slope of this relationship, 3.5 ± 0.5, provides the first quantitative measurement on protonation equilibria of the attenuation in the effects of distant substituents due to the aqueous medium. The extent of agreement with the CNDO/2 calculation supports the predictive value of the method in this application. The attenuation factor may be attributed to three effects: (a) the higher effective dielectric constant[9] in the aqueous phase and the hydration of (b) the pyridines[6c] and (c) the pyridinium ions[6] by hydrogen bonding. The latter interactions lead to partial protonations of the pyridines and partial deprotonations of the pyridinium ions. Each of the three effects evidently involves a proportionality with the intrinsic (gas phase) base strengths, thus accounting for the linearity of Figure 1.

The substituent effects on ionization of 4-substituted pyridinium ions, H_2O, 25°, between various treatments, are best fitted by the relationship:[10] $\log (K/K_0) = 5.15\sigma_I + 2.69\sigma_R{}^+$. Converting the PA's to log K units gives for gaseous ionization: $\log (K/K_0) =$

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(1) This work was supported in part by grants from the Public Health Service, the National Science Foundation, and the Atomic Energy Commission.

(2) W. L. Jolly, University of California, LBL-182, 1971, p 15, has estimated PA = 222 for C_5H_5N based upon core electron binding energies from X-ray photoelectron spectroscopy. The agreement is in apparent support of the concept of equivalence of equally charged cores.

(3) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969).

(4) W. G. Henderson, J. L. Beauchamp, and R. W. Taft, unpublished results.

(5) The polarization of the π molecular orbital of pyridinium ion is an effect analogous to polarization of alkyl groups in ammonium ions. The latter effect has been shown to be of importance in the PA of aliphatic amines: *cf.* J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Amer. Chem. Soc.*, 93, 3914 (1971).

(6) (a) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949); (b) R. G. Pearson and D. C. Vogelson, *J. Amer. Chem. Soc.*, 80, 1038 (1958); (c) F. E. Condon, *ibid.*, 87, 4481 (1965).

(7) *Cf.* J. A. Pople and M. Gordon, *ibid.*, 89, 4253 (1967).

(8) (a) D. Holtz and J. L. Beauchamp, *ibid.*, 91, 5913 (1969); (b) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, 48, 1783 (1968).

(9) J. G. Kirkwood and F. H. Westheimer, *ibid.*, 6, 506 (1938).

(10) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, unpublished results.