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).

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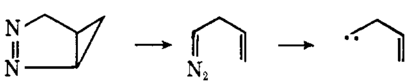
Photolysis of Substituted Derivatives of 2,3-Diazabicyclo[3.1.0]hex-2-ene. A Simple Route to Certain Bicyclo[1.1.0]butanes[1]

Sir:

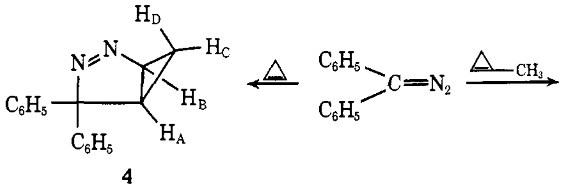
Recently, Eaton, Bergman, and Hammond reported[2] that the photochemical decomposition of derivatives of 2,3-diazabicyclo[3.1.0]hex-2-ene (**1**) produced products



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]



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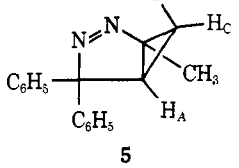


5

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.

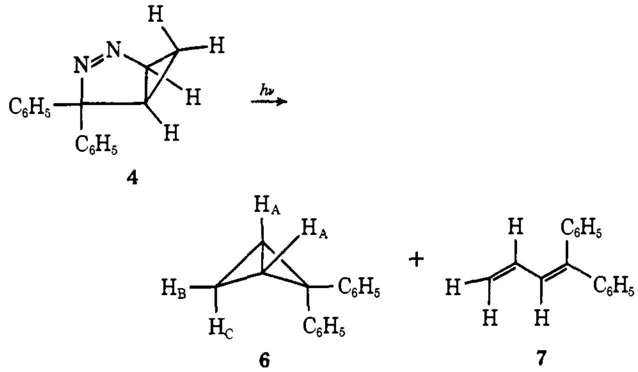
[4] G. L. Closs and K. D. Krantz, *J. Org. Chem.*, 31, 638 (1966).

[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).

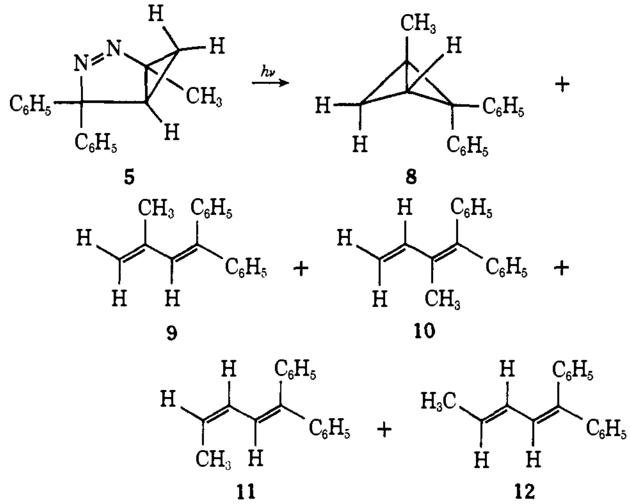
[7] The nmr assignments were based on an extensive study of the nmr spectra of various substituted and deuterium labeled 2,3-diazabicyclo[3.1.0]hex-2-enes. A detailed analysis will be presented in a full paper on this subject.

[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.


4, 6, 7

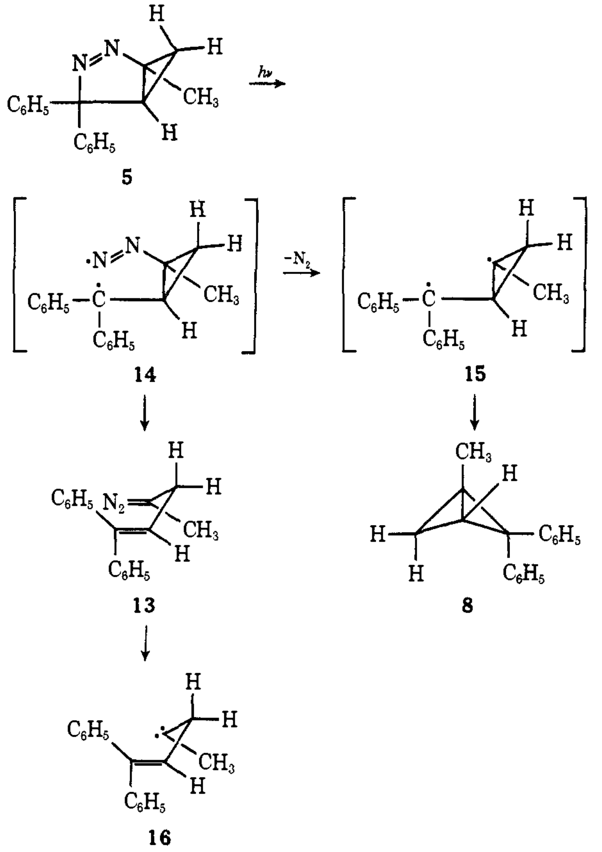
and the monoozonide of 7 was dissolved in ether and reduced with lithium aluminum hydride at −30°. Powdered sodium methoxide was added and the ether was removed under vacuum. The residue was dissolved in pentane, filtered through Celite, and the solvent was removed under vacuum to give pure **6** (23% based on **4**). The nmr spectrum of **6** showed absorptions at τ 2.5–3.1 (10 H, mult, aromatic protons), 7.98 (2 H, doublet of doublets; H_A, $J_{AB} = 3.1$, $J_{AC} = 1.2$ cps), 8.38 (1 H, triplet of doublets; H_B, $J_{AB} = 3.1$, $J_{BC} = 1.2$ cps), and 9.23 (1 H, quartet; H_C, $J_{AC} = J_{BC} = 1.2$ cps).

Similar irradiation of **5** for 18 hr gave 51% of **8** in addition to *ca.* 30%[9] of a mixture of **9**, **10**, **11**, and **12**.


5, 8, 9, 10, 11, 12

All five of these compounds were identified through comparison with authentic samples.[10,11]

The formation of **6** and **8** as a major products in the irradiation of **4** and **5**, respectively, appeared to require a modification of the previous mechanistic speculation[2] for cases where phenyl substituents are present. In order to obtain a more satisfactory picture of the overall reaction, we followed the course of the photodecomposition of **5** by nmr spectroscopy. After irradiation for 20 min the reaction mixture contained 27–33% of **8**,[12] 20–30% of **5**, only trace amounts of **9**–**12**, and substantial amounts of a previously unobserved component. After 1 hr the irradiated solution contained 44–50% of **8**,[12] less than 5% of **5**, only small amounts of olefinic materials, and approximately 26–30% of a component which has been tentatively assigned structure **13**. At this point the solution was pink.[13] In view of these observations, we feel that the photolysis of **5** yields **8** and **13** as initial products. The formation of **8** and **13** can be viewed in terms of a process involving initial carbon–nitrogen bond cleavage to yield **14**, followed by loss of nitrogen to yield **15**, or cyclopropyl bond cleavage to produce **13**. The diradical, **15**, would be expected to close to form **8**.[14,15] The slow photochemical loss of nitrogen from **13** should give the carbene **16**, which would account for the formation of the observed olefinic products. Small amounts of **9** and **10** may be derived from either a thermal or a catalyzed isomerization of **8**.


5, 14, 15, 13, 8, 16

In summary, we have found that certain derivatives of 2,3-diazabicyclo[3.1.0]hex-2-ene can yield derivatives of bicyclo[1.1.0]butane in a synthetically useful reaction. We suggest that the process may involve the formation

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[9] The total yield of olefins and the relative proportions varied with the time of irradiation. Prolonged irradiation led to a slow decline in the diene yield. No change in the yield of **8** occurred on prolonged irradiation.

[10] Again, it was observed that **8** was decomposed by most separation techniques. However, **8** could be obtained free of the olefinic impurities *via* the ozonolysis technique described above.

[11] We wish to thank Dr. Takeshi Nakai for providing us with authentic samples of **8**–**12**.

[12] The analytical method used to determine the per cent compositions involved nmr integration of the well-separated methyl resonances of **5**, **8**, and **13** *vs.* an internal standard which was added to an aliquot of the solution. The percentages quoted represent five determinations.

[13] Attempts to isolate and purify **13** have been unsuccessful thus far.

[14] An alternate process which cannot be ruled out would involve concerted loss of nitrogen from **5** to yield **8** directly. This would require two competitive photochemical processes, one which promotes cleavage of one C–N bond and one which promotes cleavage of two C–N bonds. For a relevant discussion of one bond scission, see N. A. Porter, M. E. Landis, and L. J. Marnett, *J. Amer. Chem. Soc.*, **93**, 795 (1971).

[15] The absence of significant amounts of olefins at this stage indicated that if **15** was the precursor of **8**, the closure of the diradical must be an efficient process. Control experiments showed that significant amounts of bicyclo[1.1.0]butane were not obtained from irradiation of the olefinic products under the reaction conditions.

of a "cyclopropylmethylene" diradical[16] of the general formula **17** as an intermediate.

17

We are continuing to investigate both the synthetic and mechanistic aspects of 2,3-diazabicyclo[3.1.0]hex-2-ene photochemistry.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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[16] R. Srinivasan, *J. Amer. Chem. Soc.*, **90**, 4498 (1968); J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).

[17] National Science Foundation Undergraduate Research Participant, summer 1971.

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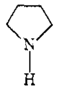
The Remarkable Fast Reaction of Potassium Hydride with Amines and Other Feeble Organic Acids. A Convenient Rapid Route to Elusive New Superbases[1]

Sir:

Potassium hydride exhibits remarkable activity toward weak organic acids such as amines, sulfoxides, and hindered tertiary carbinols. At 25–50°, this insoluble saline hydride reacts smoothly to form mono- and dialkylamides, a previously unknown class of extremely vigorous "superbases" soluble in organic solvents. Other important strong bases such as "dimsyl" anion and hindered tertiary alkoxides are also formed with unprecedented ease.

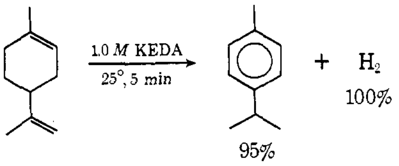
Pyrrolidine is inert toward fine (<0.5 mm) potassium sand at 50° for 24 hr; in refluxing amine, 20% of the potassium reacts in 8 hr with considerable darkening of the reaction mixture and decomposition of the amine. In contrast, KH (50.0 mmol, 2.0 g) in 50 ml of dry pyrrolidine at 25° reacts completely in 2 hr. The yield of amide is 93% by titration (triphenylmethane indicator). Sodium hydride is far more sluggish, as shown in Figure 1. Kaliation of some representative amines is summarized in Table I.

Table I. Kaliation of Amines with KH in Excess Amine[a]

Amine	Temp, °C	Time	Yield, % H$_2$[b]	Yield, % Amide[c]
	25	2 hr	95	93
$H_2NCH_2CH_2NH_2$[d]	25	5 min	100	95
$(CH_3)_2CHCH_2NH_2$[d]	50	1 hr	105	92

[a] 50.0 ml of amine, 50.0 mmol of KH. [b] ±5%. [c] Minimum values from titration with triphenylmethane indicator, compared to titration of total base after quenching with water. [d] Monometalation.

Potassium mono- and dialkylamides appear unknown in the literature. These elusive materials—now readily available *via* kaliation with KH—are bases of exceptional reactivity for prototropic reactions. Thus, 1.0 *M* *N*-kaliopyrrolidine in excess amine isomerizes 2-methyl-1-pentene with $k_{isom} > 10^{-2}$ sec^{-1}, much faster than KO-*t*-Bu–DMSO.[2] *N*-Kalioethylenediamine (1.0 *M* in excess amine) aromatizes limonene in 5 min at 25°. The lithium analog[3a] fails to aromatize limonene in 1 hr under comparable conditions.[3b] Investigations of these base systems for isomerization, elimination, and aromatization reactions are in progress.



Other useful bases such as "dimsyl" anion[4a] and hindered tertiary alkoxides[5] are also readily formed.

Dry dimethyl sulfoxide (DMSO) reacts vigorously at 25° with KH[6] to yield a clear, pale yellow solution of "dimsyl" potassium; hydrogen evolution is quantitative in 8 min. In contrast, NaH is much more sluggish.[6b,7]

The solutions of "dimsyl" potassium react analogously to "dimsyl" sodium.[4,8] Kaliation with KH provides the only rapid direct route to "dimsyl" solutions with a completely inert, noncondensable, and insoluble by-product.[9]

Hindered tertiary alcohols also react vigorously with quantitative liberation of hydrogen. Thus, 50 ml of 3-ethyl-3-pentanol reacts with 50.0 mmol of KH upon contact to yield a clear, colorless solution of potassium triethyl carboxide. Potassium metal sand is more sluggish and fails to react completely unless heated vigorously; moreover, highly colored solutions occur unless the potassium is carefully freed of superoxide coating.[5a,10] Sodium hydride is nearly inert to hindered alcohols (Figure 2).

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[1] Kaliation. I.

[2] S. Bank (*J. Org. Chem.*, 37, 114 (1972)) reports $k_{isom} \approx 2 \times 10^{-4}$ at 55°.

[3] (a) L. Reggel, S. Friedmen, and I. Wonder, *J. Org. Chem.*, **23**, 1136 (1958); (b) at 90°, over 2 hr is required for aromatization of limonene by excess $LiNHCH_2CH_2NH_2$.

[4] (a) E. J. Corey and M. Chaykowski, *J. Amer. Chem. Soc.*, **84**, 866 (1962); *ibid.*, **87**, 1345 (1965), and references therein; (b) L. F. Fieser and M. F. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 310; Vol. II, 1969, p 166; Vol. III, 1972, p 123.

[5] For example, see: (a) S. P. Acharya and H. C. Brown, *Chem. Commun.* 305 (1968); (b) H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, **75**, 4112 (1953); (c) H. C. Brown, J. H. Kawakami, and S. Misumi, *J. Org. Chem.*, **35**, 1360 (1970); (d) H. C. Brown and B. Carlson, private communication (reactions of organoboranes with halo compounds).

[6] (a) Optimum temperature for preparation of "dimsyl" sodium is reported[4a] to be 70–75°; decomposition occurs over 80°.[4a,6b] Sjöberg reports that solutions prepared at the recommended temperature are unstable; stable "dimsyl" Na solutions are obtained only by reaction of NaH with DMSO under prolonged ultrasonic aggitation at 25°.[6c] (b) C. C. Price and T. Yukuta, *J. Org. Chem.*, **34**, 2503 (1969); (c) K. Sjöberg, *Tetrahedron Lett.*, 6383 (1966).

[7] Corey and Chaykowsky[4a] report heating at 70–75° for 45 min. We find that at 25°, less than 5% of the hydrogen is evolved in 20 min. At temperatures above 75°, the reaction is faster but decomposition occurs.[4a,7b] Even at 70° some decomposition occurs, rendering the "dimsyl" solutions unstable with time.[6c]

[8] However, some differences as titrating agents have been reported; see ref 9a.

[9] Past preparations of "dimsyl" potassium: (a) DMSO + KNH_2, E. C. Steiner and M. C. Gilbert, *J. Amer. Chem. Soc.*, **85**, 3054 (1963); (b) DMSO + KO-*t*-Bu, G. J. Mikol and G. A. Russell, *Org. Syn.*, **48**, 109 (1968); (c) DMSO + K, A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1964). This latter procedure yields $CH_3S^-K^+$ and K^+OH^- along with the dimsyl anion.

[10] D. E. Pearson and O. D. Keaton, *J. Org. Chem.*, **28**, 1557 (1963).