Our interest in intermolecular complexes between derivatives of purines and pyrimidines is related to the central role of hydrogen bonding in the transfer of information in biological systems. In the present case, however, the intermolecular complexes between adenine derivatives and the barbiturates are of interest because these interactions may provide some insight into the varied and profound biochemical effects of the barbiturates when they are present in biological systems. The present structure shows a somewhat unusual and extensive system of hydrogen bonding which is a reflection in the solid state of the highly selective hydrogen bonding affinity that is observed between the barbiturates and adenine-containing compounds.

Acknowledgment. This research was supported by grants from the National Science Foundation and the National Institutes of Health. We thank the General Electric Corporation for allowing us to use their XRD-490 diffractometer and are grateful to Mr. Howard Pickett for his assistance with that instrument.

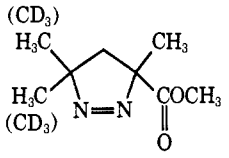
Communications to the Editor

Decomposition of Azo Compounds *via* Cationic Intermediates. Elucidation of the Mechanism of Ionization and Nitrogen Elimination

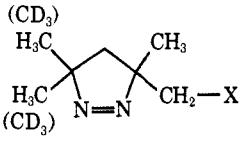
Sir:

Recently we reported the first two cases of azo compounds which eliminate nitrogen by mechanisms involving cationic intermediates.[1] The results clearly showed that for a structurally suitable system the –N=N– group anchimerically assists ionization.[1] However, the preliminary work did not provide for a definitive mechanistic description of nitrogen loss. This has stimulated us to begin a general investigation of the scope and mechanistic details of such reactions. In this communication we wish to report the acetolysis of the new system IIb-OBs and a detailed analysis of ionization–nitrogen elimination for this reaction.

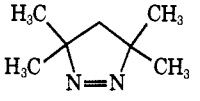
Addition of 2-diazopropane[2] to methyl methacrylate afforded I in excellent yield, bp 67–73° (1.5 mm).[3]



I



IIa, X = OH
b, X = OBs
c, X = OAc

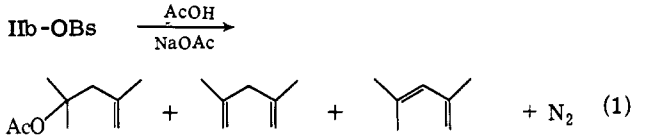


III

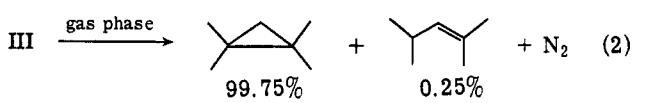
Reduction of I with lithium aluminum hydride followed by oxidation with yellow mercuric oxide gave IIa-OH, bp 88–90° (1.2 mm).[3] Reaction of IIa-OH with sodium hydride followed by treatment with *p*-bromobenzenesulfonyl chloride produced IIb-OBs, mp 109–110°. 2-Diazopropane-d_6[4] was converted in an analogous manner to IIb-OBs-d_6. Treatment of IIa-OH with acetic anhydride and pyridine afforded IIc-OAc.

Azo *p*-bromobenzenesulfonate IIb-OBs was solvolyzed in dry acetic acid buffered with sodium acetate. Rate measurements were made by the usual sealed ampoule technique. Titration of the developing *p*-bromobenzenesulfonic acid was performed with a Metrohm Potentiograph Model E-436 high-precision automatic titrator. All of the rate constants were nicely first order. The kinetic data are summarized in Table I. A reactivity comparison of IIb-OBs acetolysis with the gas-phase thermolysis of structurally related III also is included. Another reactivity comparison was made by subjecting IIc-OAc to the acetolysis conditions at 130°. The azo acetate was stable for at least 25 acetolysis half-lives of IIb-OBs.

p-Bromobenzenesulfonate IIb-OBs produced a quantitative yield of nitrogen and a mixture of the acetate and dienes shown in eq 1; no IIc-OAc was detected.



IV V VI (1)



99.75% 0.25% (2)

Product identification was based on glpc and nmr comparisons with authentic samples of IV,[5] V,[6] and VI.[7] Product yields and ratios are summarized in Table II. Equations 1 and 2 compare the products of IIb-OBs acetolysis and the gas-phase thermolysis of III.[8]

The best available evidence indicates that decomposition of III occurs by a mechanism which involves a

(1) E. L. Allred and C. R. Flynn, *J. Amer. Chem. Soc.*, **92**, 1064 (1970).

(2) A. C. Day, P. Raymond, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. C*, 467 (1966).

(3) Satisfactory elemental analyses were obtained for all of the new compounds. The nmr, ir, and uv spectral data were in complete agreement with the structural assignments.

(4) 2-Diazopropane-d_6 was prepared from acetone-d_6 of 99.5% minimum isotopic purity.[2] Nmr analysis showed I-d_6 and II-d_6 to be of greater than 98% deuterium incorporation.

(5) Prepared from 2,4-dimethyl-4-penten-2-ol obtained from Chemical Samples Co.

(6) Obtained from Chemical Samples Co.

(7) T. L. Jacobs and R. A. Meyers, *J. Amer. Chem. Soc.*, **86**, 5244 (1964).

(8) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966).

Table I. Acetolysis Rate Data for IIb-OBs and IIb-OBs-d_6[a]

Compd	Temp, °C	10^5k, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu	k_{rel}	k_H/k_D
IIb-OBs	121.0	4.12 ± 0.04			125	
	150.0	73.43 ± 0.61	32.1	+2.2		
	130.0	10.98 ± 0.10[b]				0.98 ± 0.03
IIb-OBs-d_6	130.0	11.17 ± 0.13[b]				
III	121.0	0.033[c]			1	

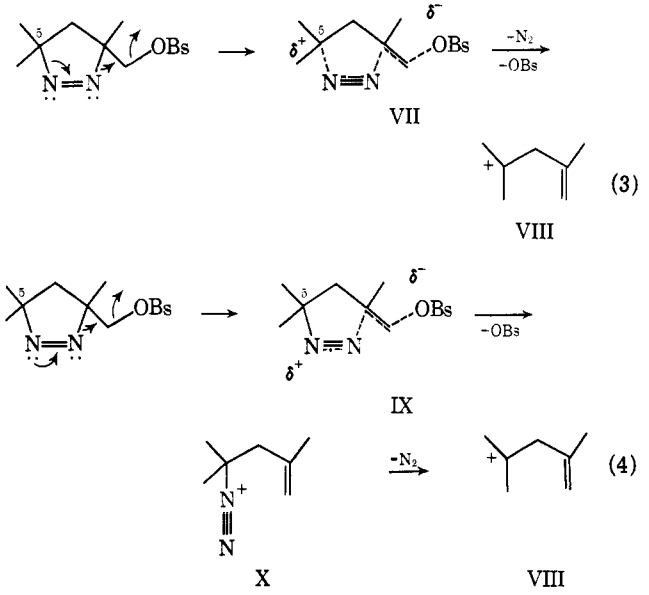
[a] Dry acetic acid with 0.016 *M* ROBs and 0.017 *M* NaOAc. [b] Average of four separate kinetic measurements. Each measurement consisted of simultaneous acetolysis of runs of IIb-OBs and IIb-OBs-d_6 under identical conditions. [c] Gas-phase decomposition data based on extrapolation from data at other temperatures.[8]

Table II. Effect of Deuterium Substitution on the Products from the Acetolysis of IIb-OBs at 130°[a]

Compd	Time, min	% acetolysis[b]	Total % product yield[c]	% product composition[c] IV-OAc	V	VI	k_H/k_D
IIb-OBs	20	9	100	16.8[d]	38.3[d]	44.9[d]	1.95 ± 0.15[f]
IIb-OBs-d_6	20	9	100	20.6[e]	24.1[e]	55.3[e]	

[a] 0.016 *M* ROBs and 0.017 *M* NaOAc. [b] Product measurements were made after 9% acetolysis due to the instability of IV-OAc upon prolonged heating. Under the reaction conditions decomposition of IV-OAc is negligible. [c] Determined by glpc using internal standards of tridecane for IV-OAc and *n*-octane for V and VI. Reproducibility better than ±2%. [d] Values are the average of four experiments. [e] Values are the average of three experiments. [f] Calculated from the product ratios of V and VI from IIb-OBs and IIb-OBs-d_6 according to the procedure of Silver.[9]

diradical-like intermediate.[8-10] It is evident from the higher reactivity and the differences in products that IIb-OBs solvolyzes by an entirely different reaction process.[11] A consideration of the nature of the products suggests that IV, V, and VI are the consequence of a cationic pathway involving the 2,4-dimethyl-4-penten-2-yl cation VIII. Two attractive possibilities for ionization–nitrogen elimination leading to VIII are illustrated by eq 3 and 4.



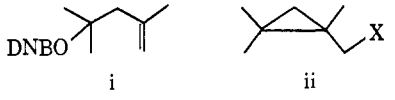
The isotope effect results from IIb-OBs and IIb-OBs-d_6 provide criteria for distinguishing between pathways 3 and 4 and for describing the details of the mechanism. If C_5–N bond breaking and charge development at C_5 are important in the rate-determining transition state (VII, eq 3), the kinetic β-deuterium isotope effect will be large; if there is little C_5–N bond breaking in the rate-determining transition state (IX, eq 4), the effect will be near unity.[12,13] The observed k_H/k_D value of 0.98 ± 0.03 rules out concerted pathway 3 and supports the stepwise pathway 4. While the rate-determining step remains essentially unchanged upon deuterium substitution, the product proportions change markedly. This amounts to a product k_H/k_D value of 1.95.[14] Lack of a kinetic isotope effect but the presence of a product isotope effect is unambiguous evidence for the intervention of a product-determining intermediate after the rate-determining step. Candidates for the intermediate are diazonium ion X and carbonium ion VIII. Since diazonium ions lose nitrogen with very low energies of activation[15] and since nitrogen departs from a tertiary carbon in X,[15,16] we conclude that VIII is responsible for the product isotope effect.

In summary, all of the observations, enhanced reactivity, the nature of the products, lack of a kinetic isotope effect, and occurrence of a product isotope effect, taken collectively point to and are entirely consistent with the acetolysis of IIb-OBs *via* mechanistic pathway 4. It is worth noting that solvolysis of azo

(9) M. C. Silver, *J. Amer. Chem. Soc.*, **83**, 3487 (1961).

(10) R. J. Crawford and A. Mishra, *Can. J. Chem.*, **47**, 1515 (1969); R. J. Crawford and D. M. Cameron, *ibid.*, **45**, 691 (1967); R. J. Crawford and G. L. Erickson, *J. Amer. Chem. Soc.*, **89**, 3907 (1967); and other papers in the series.

(11) Acetolysis of i-dinitrobenzoate i produces IV, V, and VI as the only products, whereas acetolysis of cyclopropylcarbinyl derivative ii gives IV, V, and VI and significant amounts of three additional products. The details of this will be reported in the full paper.



i ii

(12) The magnitude of the kinetic β-deuterium isotope effect has been used to assess the degree of charge development at carbon in transition states of solvolysis reactions. See: A. Streitwieser and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969), and references cited therein; V. J. Shiner and W. Dowd, *J. Amer. Chem. Soc.*, **93**, 1029 (1971), and other papers in the series.

(13) For charge development at tertiary carbon the k_H/k_D value for six β deuteriums can be expected to be above *ca.* 1.5 at 130°. For example, see: V. J. Shiner, *ibid.*, **83**, 240 (1961); G. J. Frisone and E. R. Thornton, *ibid.*, **86**, 1900 (1964).

(14) This value is in line with the product β-deuterium isotope effect of *ca.* 1.6 observed for the *tert*-pentyl carbonium ion formed from deamination of *tert*-pentylamine in acetic acid.[9]

(15) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Wiley, New York, N. Y., 1968, p 440 ff.

(16) R. A. Moss, *Chem. Eng. News*, **49** (48), 28 (1971).

compounds suggests a uniquely different approach to the generation of diazonium ions. Study of appropriate reactions offers the possibility of providing valuable new mechanistic information about the intriguing questions associated with deamination chemistry. This is now under investigation.

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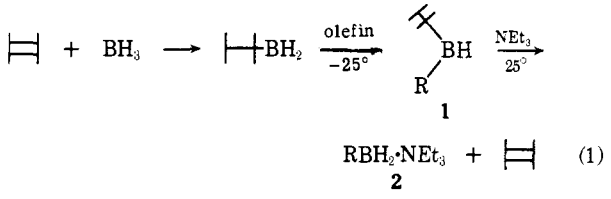
Remarkably Facile and Selective Dehydroboration of Tetramethylethylene from Thexylmonoalkylboranes under the Influence of Triethylamine. A Novel, Convenient Synthesis of Monoalkylboranes as Triethylaminates

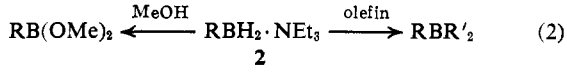
Sir:

Thexylmonoalkylboranes (**1**), readily obtainable by the hydroboration of olefins with an equimolar quantity of thexylborane,[1] react rapidly at 25° with triethylamine to produce the corresponding triethylamine–monoalkylboranes (**2**) in nearly quantitative yields (eq 1).



(1)

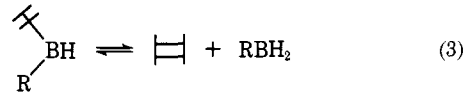
Thus tetramethylethylene serves as a temporary blocking agent to achieve the simple monoalkylation of borane. The triethylamine–monoalkylboranes (**2**) function as monoalkylboranes in disguise. They can readily be solvolyzed to form the corresponding boronic acids and their derivatives, and can hydroborate olefins to produce a variety of mixed trialkylboranes (eq 2).



(2)

Partially alkylated boranes and mixed organoboranes are essential to the maximum application of organoborane chemistry to organic synthesis.[2] Except with a very limited number of olefins, such as tetramethylethylene (TME),[3] simple hydroboration does not lead to predominant formation of monoalkylboranes.[4] We recently reported the first general synthesis of free monoalkylboranes.[5] However, a simpler, more convenient synthesis has been desired.

While studying the reaction of thexylborane with olefins, we observed dehydroboration to minor extents of TME from thexylmonoalkylboranes even at 0° (for example, 5 and 25% with isobutylene and cyclohexene, respectively).[1b] If this involved an equilibrium reaction, as shown in eq 3, either distillation of the



(3)

volatile TME or selective complexation of the monoalkylboranes would provide a simple synthesis of monoalkylboranes or their addition compounds. Our attempts to obtain pure monoalkylboranes by the removal of TME have not been successful. Addition of pyridine to thexyl(2-methylcyclopentyl)borane results in an instantaneous and complete formation of complexes as indicated by ir. However, no extensive dehydroboration of TME takes place. Evidently, pyridine quenches the entire reaction mixture.

On the other hand, treatment of thexyl(2-methylcyclopentyl)borane with 4 equiv of triethylamine at 25° for 1 hr results in the regeneration of 98% of TME without the concurrent formation of 1-methylcyclopentene. Oxidation[6] of the reaction mixture with alkaline hydrogen peroxide provides *trans*-2-methylcyclopentanol in 97% yield along with traces (≤1% each) of the cis isomer, 2,3-dimethyl-1-butanol, and 2,3-dimethyl-2-butanol. Evaporation of the volatile substances at 15 mm for 2 hr produces triethylamine–(2-methylcyclopentyl)borane (**3**): pmr (benzene, TMS) δ 0.86 (t, J = 7 Hz, 9 H), 1.28 (d, J = 6 Hz, 3 H), 1.4–2.2 (m, *ca.* 8 H), and 2.46 (q, J = 7 Hz, 6 H) ppm; ir (neat) 2350 (s) cm^{-1}. The following procedure is adaptable to all cases reported. To 5.65 ml (10 mmol) of 1.77 M thexylborane[1] was added 0.82 g (10 mmol) of 1-methylcyclopentene at −25°. One hour later 5.6 ml (40 mmol) of triethylamine was added and the mixture was stirred for 1–2 hr at 25°. For most purposes direct use of this reaction mixture is satisfactory as described later. Clearly, the present synthesis is exceedingly simple and convenient.

Treatment of the reaction mixture containing 10 mmol of triethylamine–(2-methylcyclopentyl)borane (**3**) with 40 mmol (100% excess) of methanol evolves 19.8 mmol (99%) of hydrogen within 30 min at 25° indicating the presence of 2 equiv of active hydride per boron. Glpc examination of the methanolysis product on a 2-ft SE-30 reveals the presence of 18.6 mmol (93%) of dimethyl 2-methylcyclopentylboronate (**4**). These results clearly support the formation of **3** as an essentially pure substance. Unlike free monoalkylboranes[5] triethylamine–monoalkylboranes appear quite stable to disproportionation. Thus, no noticeable disproportionation of **3** is observed at least for 1 week at 25° as evidenced by glpc after methanolysis. The experimental results of the preparation and characterization of triethylamine–monoalkylboranes are summarized in Table I.

These triethylamine–monoalkylboranes have proven to be highly useful intermediates. Thus, distillation

(1) (a) G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, **85**, 2066 (1963); (b) unpublished results with E. Negishi and J. J. Katz. We have not so far been able to obtain thexylmonoalkylboranes cleanly from monosubstituted terminal olefins.

(2) See, for example, H. C. Brown, *Proc. Int. Congr. Pure Appl. Chem., XXIIIrd*, **2**, 27 (1971).

(3) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).

(4) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(5) H. C. Brown and S. K. Gupta, *J. Amer. Chem. Soc.*, **93**, 4062 (1971).

(6) *Caution!* Hydrogen peroxide (30%) should be added after completing the destruction of active hydride (25°, 0.5–1 hr) with 3 N sodium hydroxide. Premature addition of hydrogen peroxide to the unhydrolyzed monoalkylborane can result in minor explosions.