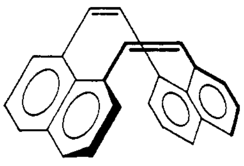
nmr spectra[10] of **7** and **8** are unusual, presumably due to steric effects in the ten-membered ring.

Solutions of **6** (pentane, chloroform, benzene, etc.) gradually became red. The change was found to involve initial isomerization to 7,14-dihydrozethrene (**9**),[12] which in the presence of air is then oxidized to zethrene (**10**).[13] The same changes occurred also in the solid state, most rapidly by pyrolysis; the crystals quickly became pink on the surface even on standing at room temperature, but could be stored with little decomposition at −15° in the dark for several weeks. In preparative experiments, **9** (yellow needles, mp 232–234° dec) was obtained in over 90% yield from **6** by allowing an unstoppered solution in CD_2Cl_2 (nmr sample) to stand at room temperature without protection from diffuse daylight for 5–60 min,[14] or in ~50% yield by pyrolysis of the solid in air at 200° for 1 min. Substance **10** (red-violet needles, mp 262–263°) was obtained in 30% yield from **6** by allowing an unstoppered solution in $CDCl_3$ (nmr sample) to stand for 10 days, or in 40% yield by pyrolysis of the solid at 200° for 15 min. Structures **9** and **10** (supported by the nmr and mass spectra) are based on the correspondence of the melting points and the detailed ultraviolet spectra with the reported data.[12,13]

Reaction of **6** with bromine or chlorine did not result in simple addition, but gave derivatives of zethrine (**10**).

The structure of **6** follows unequivocally from the above-described properties and reactions. We tentatively assign the *cis,cis* configuration A to the compound, in view of the presence of only a very weak infrared band (at 968 cm^{-1}) in the 1000–920-cm^{-1} region.[15] We hope that more definite stereochemical information will be provided by an X-ray crystallographic analysis, which is now being carried out by Mrs. O. Kennard and co-workers.



A

The properties of **6** indicate that it is a nonplanar molecule and that it does not represent an annelated delocalized ten-π-electron system.

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(12) E. Clar, "Aromatische Kohlenwasserstoffe," Vol. 2, Springer-Verlag, Berlin, 1952, p 387.

(13) E. Clar, K. F. Lang, and H. Schulz-Kiesow, *Chem. Ber.*, **88**, 1520 (1955); see also C. A. Coulson and C. M. Moser, *J. Chem. Soc.*, 1341 (1953); C. A. Coulson, C. M. Moser, and M. P. Barnett, *ibid.*, 3108 (1954).

(14) The time required for the formation of **9** (which precipitated directly) was found to vary, and we believe that the reaction is radical initiated.

(15) By comparison, medium or strong infrared bands at ~960 cm^{-1} are shown by *trans*-stilbene and *trans*-1,2-bis(α-naphthyl)ethylene,[16] as well as by some related macrocyclic compounds containing *trans*-stilbene groupings.[17]

(16) Prepared according to G. Drefahl, D. Lorenz, and G. Schnitt, *J. Prakt. Chem.*, **23**, 143 (1964).

(17) *Inter al.*, see E. D. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 4281 (1953); C. E. Griffen, K. R. Martin, and B. E. Douglas, *J. Org. Chem.*, **27**, 1627 (1962); H. A. Staab, F. Graf, and B. Junge, *Tetrahedron Letters*, 743 (1966).

(18) Recipient of a Science Research Council Research Studentship.

R. H. Mitchell,[18] F. Sondheimer
University Chemical Laboratory
Cambridge, England

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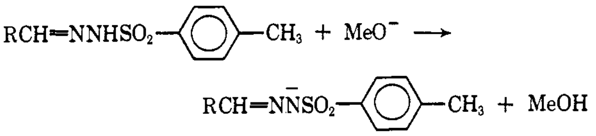
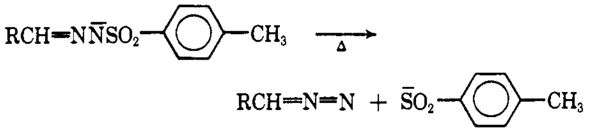
The Effect of Solvent on the Course of the Bamford–Stevens Reaction[1,2a]

Sir:

Tosylhydrazone anions of aliphatic and aromatic aldehydes and ketones undergo thermal decomposition to give diazoalkanes *via* α elimination (eq 1 and 2).[2] The fate of the diazoalkane intermediates as determined by product analysis was found to be mainly dependent upon the nature of the solvent in that in aprotic media such as diethyl Carbitol and diglyme diazoalkanes thermally decompose with loss of nitrogen, giving carbenes,[2b,3] while in protic solvents such as ethylene glycol and diethylene glycol competitive protonation of the diazoalkanes occurs, leading to diazonium and/or carbonium ions.[3,4]



(1)



(2)

The term "protic" has been poorly defined with regard to these reactions.[5] A study was initiated in order to obtain further information concerning the relative "protonicity," *i.e.*, proton donor ability, of various representative hydroxylic solvents in these reactions. In addition it was anticipated that base-catalyzed decomposition of several aliphatic tosylhydrazones in these solvents would yield quantitative information regarding the *extent* of competitive carbenic and cationic processes.

2-Methylpropanal and 2,2-dimethylpropanal tosylhydrazones were chosen for study since decomposition in aprotic media gives large amounts of methylcyclopropane and 1,1-dimethylcyclopropane *via* their respective carbenes.[3] However, in protic solvents conversion to cyclopropane is markedly reduced as a result of diazonium ion formation with concomitant increase in Wagner–Meerwein rearrangement products.[3,4]

It has now been found that "protonicity" of solvents is a function of their (a) relative acidity (pK_a or K_e) [K_e[6] is an acidity scale inversely related to pK_a], and (b) "proton equivalence" (PE), defined herein as milliequivalents of hydroxyl per gram of solvent.

The effects of the solvents can be followed by observing the amounts of methylcyclopropane and 1- and 2-butenes[7] formed *via* decomposition of 2-methylpropanal tosylhydrazone (I) anion. For example, methylcyclo-

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(1) Financial support from the National Science Foundation is gratefully acknowledged.

(2) (a) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); (b) W. Kirmse "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(3) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

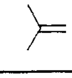
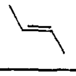
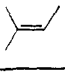
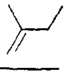
(4) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

(5) *Cf.* J. W. Wilt, C. A. Schneider, H. F. Dabele, Jr., J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, **31**, 1543 (1966).

(6) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952); P. Ballinger and F. A. Long, *ibid.*, **82**, 795 (1960); H. Shigematsu, Y. Nishikawa, and Y. Ishii, *Kogyo Kagaku Zasshi*, **65**, 945 (1962). K_e, rather than pK_a, is employed since K_e (not pK_a) has been determined for a large number of alcohols and glycols.

(7) The Wagner–Meerwein rearrangement products. *Cf.* A. T. Jurewicz and L. Friedman, *J. Am. Chem. Soc.*, **89**, 149 (1967).

Table I. Thermal Decomposition[a] of 2-Methylpropanol Tosylhydrazone (I) and 2,2-Dimethylpropanal Tosylhydrazone (II) Anions in Various Solvents

Solvent	PE	K_e	Tosylhydrazone	Yield,[b] %	Hydrocarbon products, %							
												
Diethyl Carbitol			I	53	35	64	0.5	0.2	0.3			
			II	77						90	9.0	1.0
Triethylcarbinol	8.61	<0.2	I	39	36	61	0.7	1.7	0.5			
			II							77	18	5.0
Methylisobutylcarbinol	9.78	<0.2	I	55	35	62	0.4	1.4	0.4			
			II	87						81	17	2.0
Hexanol	9.78	<0.5	I		30	65	1.6	2.2	1.1			
			II							67	27	6.0
Ethyl Carbitol	7.45	14.8	I	38	27	67	2.5	1.9	1.5			
			II							48	30	22
1,3-Butanediol	22.2	<10	I	46	18	61	10	7.2	3.9			
			II							18	42	40
1,3-Propanediol	26.3	12	I		8.1	60	15	9.9	6.2			
			II							6.2	46	48
Diethylene glycol	18.8	33	I		7.3	65	13	10	5.4			
			II							2.3	46	51
Ethylene glycol	32.3	43	I	21	4.2	58	17	13	7.4			
			II							1.1	53	46

[a] I or II (2.5 mmoles), 2.75 mmoles (1.1 equiv) of NaOMe, and 5 ml of solvent at reflux or 190–195° whichever is lower. [b] Yields and compositions determined *via* glpc using internal standard technique. Yields are probably higher in an "aprotic" solvent since much diazoalkane is swept over and does not "come off" the glpc column.

propane (MCP) formation decreases in a regular fashion, 36, 27, 18, and 4% in triethylcarbinol, ethyl Carbitol, 1,3-butanediol, and ethylene glycol, respectively, with a concomitant increase in the 1- and 2-butenes, 3.9, 5.9, 21.1, and 37.4% (Table I). Thus, triethylcarbinol [PE 8.61, $K_e < 0.2$] and methylisobutylcarbinol [PE 9.78, $K_e < 0.2$] are relatively weak proton donor solvents while 1,3-propanediol [PE 26.3, K_e = 12], diethylene glycol (DEG) [PE 18.8, K_e = 33], and ethylene glycol [PE 32.3, K_e = 43] are strong proton donors. Ethyl Carbitol [PE 7.45, K_e = 14.8] and 1,3-butanediol [PE 22.2] are intermediate in their ability to donate protons. On the basis of MCP formation triethylcarbinol appears to be as "aprotic" as diethyl Carbitol (DEC), a hydroxyl-free solvent. The use of "aprotic" alcohols for tosylhydrazone decompositions has preparative value since most of the reactions are homogeneous, the effect of impurities is minimized, and a great variation in reaction conditions and product work-up is possible.

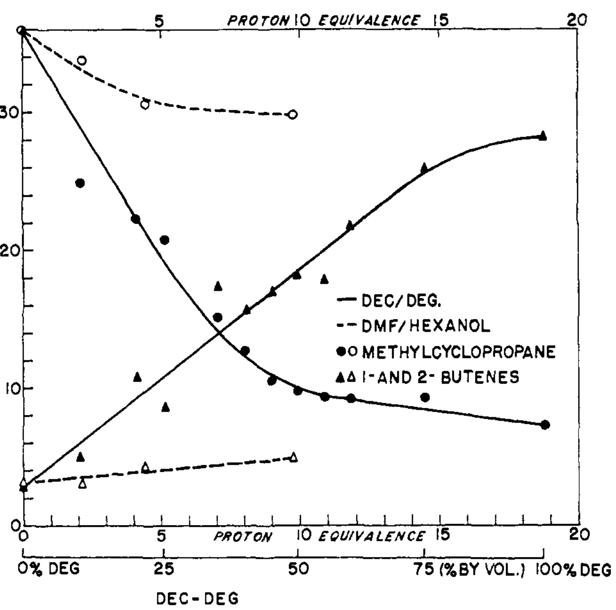
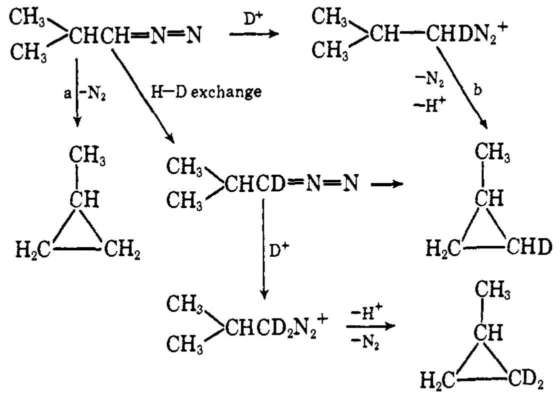


Figure 1. Percentage of methylcyclopropane and the butenes as a function of solvent composition.

The importance of K_e becomes apparent by comparing the relative amounts of MCP and the butenes formed in solvents of equal PE, *i.e.*, hexanol-DMF *vs.* DEG-DEC mixtures (Figure 1). For example, at PE 10, neat hexanol is significantly more "aprotic" (30% MCP) than DEG-DEC (50:50) (9% MCP).

Inasmuch as it has been shown that several cationic precursors afford cyclopropanes by intramolecular processes I was decomposed in ethylene glycol-d_2 in order to distinguish between the competitive carbenic (a) and cationic (b) routes[8] (Scheme I).

Scheme I



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(8) The extent of concomitant carbenic and cationic processes resulting from decomposition of I anion cannot be directly determined from product analysis since MCP and 2-methylpropene are formed *via* both.[3,7] For other examples of cationic and carbenic precursors leading to cyclopropanes see: J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 659 (1965); F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966); A. Nickon and N. H. Werstiuk, *ibid.*, **88**, 4543 (1966); R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *ibid.*, **89**, 1442 (1967).

Thus, decomposition of the sodium salt of I gave MCP containing d_0, d_1, and, unexpectedly, d_2 species (23, 55, and 22%, respectively). The occurrence of d_0 and d_1 products clearly shows that MCP is formed by competitive processes and the presence of d_2 products shows that hydrogen–deuterium exchange is also involved in these reactions.[9] Thus, in ethylene glycol-d_2 the extent of concomitant carbenic (<27%) and cationic (>73%) participation leading to MCP was estimated by comparing the deuterium contents of the MCP and 1-butene. However, the extent of carbenic and cationic pathways leading to all hydrocarbon products was approximately 0.035 and 0.96, respectively.

Similar results were obtained when 2,2-dimethylpropanal tosylhydrazone (II) anion was decomposed in that the formation of 1,1-dimethylcyclopropane decreased and 2-methyl-1-butene increased[7] with increasing solvent protonicity (Table I). Since the neopentyl cation or diazonium ion affords dimethylcyclopropane to only a minor extent (<1%) while it is a major product (>95%) from *t*-butylcarbene the extent of concomitant carbenic and cationic modes of decomposition occurring in various solvents can be directly determined by product analysis.[10] Thus, for example, in diethyl Carbitol, the carbenoid fraction is 0.98, in hexanol 0.89, in ethyl Cellosolve 0.50, and in ethylene glycol 0.02.[11]

[9] A small portion of the d_0 product comes from protonation with protium in the solvent, protium formed in neutralization of the tosylhydrazone, and protium generated *via* the processes outlined in Scheme I.

[10] The carbenoid fraction is the amount of dimethylcyclopropane plus that portion of 2-methyl-2-butene arising *via* the carbenoid route. The latter is estimated (by difference) from the cationic ratio (2-methyl-1-butene/2-methyl-2-butene, ~1.1–1.25) which was obtained by solvolysis of neopentyl tosylate or diazotization of neopentylamine at conditions comparable to the tosylhydrazone decomposition reaction conditions. For results of thermolysis of diazoneohexane in various solvents see W. Kirmse and K. Horn, *Chem. Ber.*, **100**, 2698 (1967).

[11] (a) Diazoalkanes derived from I and II respond similarly to protonicity in the solvents studied; with more highly hindered diazo compounds the ability of a given protic solvent to effect cationic decomposition is considerably lessened. Lowering the reaction temperature or the amount of base in a proton-donor solvent enhances decomposition of a tosylhydrazone by a cationic route. (b) Cationic decomposition of a diazo compound generated *in situ* may be frequently effected in aprotic solvents by using insufficient base to neutralize the parent tosylhydrazone. The protonicity of such systems is controlled by the stoichiometric ratio of the base and the tosylhydrazone.

[12] NASA Fellow, 1963–1966.

John H. Bayless,[12] Lester Friedman
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Francis B. Cook, Harold Shechter
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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Reexamination of the Reactions of Triethyl- and Trimethylboron with Sodium and Potassium in Liquid Ammonia

Sir:

Smith and Kraus[1] reported that trimethylboron is quantitatively reduced by sodium in liquid ammonia according to the equation

$$(CH_3)_3B + NH_3 + Na \longrightarrow (CH_3)_3BNH_2Na + 0.5H_2 \quad (1)$$

These investigators suggested that the metal replaces a hydrogen in the coordination compound $(CH_3)_3BNH_3$. Later, Holliday and Thompson[2] mixed trimethylboron with potassium metal in liquid ammonia and obtained the salt $(CH_3)_3BNH_2K$ and approximately 0.5 mole of hydrogen gas per g-atom of potassium metal upon complete decolorization of the solution.

The object of the present study was to suggest a mechanism for the reaction

$$R_3B + NH_3 + M \longrightarrow R_3BNH_2M + 0.5H_2 \quad (2)$$

where R = methyl or ethyl and M = sodium or potassium. The reactions of trimethyl- and triethylboron with sodium and potassium in liquid ammonia were studied conductometrically in a closed system. Either a high-precision ac bridge, similar to that described elsewhere,[3] or a Wayne Kerr Universal bridge B221A was used in conductance measurements. The conductance measurements were made in a Pyrex vessel which had pinpoint tungsten or platinum electrodes sealed into a side arm and a calibrated bulb for volume determination. Triethylboron (K and K Laboratories, Inc.) was first degassed by two high-vacuum distillations and then distilled onto a sodium mirror. Next it was distilled off the sodium into a tared tube containing a break-seal. Trimethylboron was prepared following the procedure described by Brown.[4] Trimethylboron was also distilled off a sodium mirror and stored in glass ampoules on the high-vacuum line. The freezing points of both triethyl- and trimethylboron agreed with reported values.[5] Using the ideal gas law, a molecular weight of 58 was obtained for trimethylboron. Ammonia (Matheson) was purified by a method described elsewhere.[6]

A run consisted of distilling sodium or potassium metal from another side arm into the reaction vessel which had been previously evacuated to pressures of less than 5×10^{-6} torr after flaming. The ammonia was then distilled into the reaction vessel. In the case of triethylboron studies, the reaction vessel was removed from the high-vacuum line, transferred to a refrigerated bath at $-34°$, and allowed to come to thermal equilibrium. The initial resistance of the solution was measured, and then the break-seal containing the triethylboron was broken with a glass-encased magnet. The resistance was subsequently followed with time. When trimethylboron was used, the frozen metal–ammonia solution with trimethylboron condensed on its surface was transferred directly to the bath, thawed, agitated, and allowed to reach thermal equilibrium. The resistance was then followed as a function of time. In all runs the concentration of alkali metal was less than that of the alkylboron so that the end of the reaction could be determined visually by the disappearance of the blue color. Finally, the metal concentrations were determined by addition of ammonium bromide to the metal solution which resulted in the reaction

$$NH_4^+ + M \longrightarrow NH_3 + M^+ + 0.5H_2 \quad (3)$$

The total hydrogen evolved was pumped into the gas buret, and its volume and pressure were measured.

The results of this study are summarized in Table I.

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[1] J. E. Smith and C. A. Kraus, *J. Am. Chem. Soc.*, **73**, 2751 (1951).

[2] A. K. Holliday and N. R. Thompson, *J. Chem. Soc.*, 2695 (1960).

[3] G. E. Smith, Ph.D. Thesis, Michigan State University, 1963.

[4] H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945).

[5] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 50.

[6] D. F. Burow and J. J. Lagowski in "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 125.