of 2-propanol in 92% acetic acid has been made by Wiberg and Schäfer.[17] In this case also the intermediate was identified as a chromate ester. Hence it is probable that the phenomenon is a fairly general one and that it will also be observed in other concentrated acid solutions.

Registry No.—Sulfuric acid, 7664-93-9; 2-propanol, 67-63-0; 2-propanol-2-*d*, 3972-26-7; 1,1,1-trifluoro-2-propanol, 374-01-6; 1,1,1-trifluoro-2-propanol-2-*d*, 13369-60-3; 1,1,1,3,3,3-hexafluoro-2-propanol, 920-66-1.

Acknowledgment.—The financial support of the National Research Council of Canada is gratefully acknowledged.

[17] K. B. Wiberg and H. Schäfer, *J. Am. Chem. Soc.*, **89**, 455 (1967).

Solvent Effects and Other Factors in Carbenic and Cationic π Cyclizations. I. The Δ^3-Cyclohexenecarboxaldehyde *p*-Toluenesulfonylhydrazone System[1a,b]

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The susceptibility of the decomposition of the tosylhydrazones of simple carbonyl compounds to changes in the proton-donating ability (protonicity) of the solvent have long been known,[2] but only recently has the mechanistic path of this reaction been explored in detail. The nature of the products in tosylhydrazone decomposition (and thus by inference the nature of the intermediates) has been found to depend on (1) the protonicity of the solvent,[2] (2) the concentration of the base,[3] and (3) the nature of the cation associated with the base.[4] In recent deuterium-labeling studies on the base-catalyzed decomposition of the tosylhydrazones of cyclopropanecarboxaldehyde[5] (I), norbornan-2-one (II),[6] and camphor[3b,4] (III), evidence has accumulated for the existence of two distinct paths involving a "carbenic" and a "cationic" intermediate in this reaction depending on the reaction conditions. Present evidence indicates that the observed products from tosylchydrazone decomposition arise from either a carbene or a diazonium salt, generated from an intermediate diazo compound. In the absence of a Lewis acid, there is no present evidence to support a carbonium ion as an intermediate in the protonic decomposition of tosylhydrazones.[4]

This investigation is concerned with the effect of the protonicity of the solvent and the concentration of base on the nature and numbers of products resulting from the base-catalyzed decomposition of Δ^3-cyclohexenecarboxaldehyde (IV). Compound IV was of special interest to us, as it represented an initial probe into the effect of geometry of a π-electronic center on the formation of intermediates in the Bamford–Stevens reaction, analogous to such interactions in cationic species produced by solvolysis.[7]

Results and Discussion

The relative amounts of products resulting from the alkaline decomposition of IV and its sodium salt in decalin, diglyme, and ethylene glycol with sodium bases is *independent* of the nature of the solvent and highly *insensitive* to the amount of base used. The over-all variation in the yields of the principal products was only slightly larger than the experimental error (±3%) over a wide range of base concentrations. The decomposition of IV under flash conditions yields a complex mixture of C_4H_{10} hydrocarbons in 60–85% yield. The principal reaction products were bicyclo[4.1.0]hept-2-ene (V) in 18–22% yield; 4-methylene-1-cyclohexene (VII) in 35–70% yield, and 1-methylcyclohexa-1,3-diene (VIII) in 15–30% yield. In addition to these, the reaction mixture also contained small amounts of bicyclo[4.1.0]hept-3-ene (VI), 1-methylcyclohexa-1,4-diene (IX), bicyclo[2.2.1]hept-2-ene (X), and a material tentatively identified as tricyclo[4.1.0.$0^{3,7}$]heptane (XI). Compounds X and XI accounted for less than 3% of the reaction mixture. Control experiments showed bicycloheptene V to be stable to the reaction conditions, but that as the concentration of base was increased the amounts of VIII and IX increased at the expense of diene VII.[8b] These reactions are described in Scheme 1.

The reaction products were identified by means of quantitative hydrogenation, spectroscopic analysis, and by comparison of recovered materials with authentic standards. When the crude reaction mixtures were hydrogenated over 5% Pd–C, the only products found were methylcyclohexane (XII) (75 ± 2% yield), bicyclo[4.1.0]heptane (XIII) (23 ± 1% yield), and bicyclo[2.2.1]heptane (XIV) (2% yield), confirming the invariance of the ratio of 2:3 insertion over the reaction range. Moore has reported the conversion of the tricyclic XI to bicycloheptane XIV by catalytic hydrogenation with Pd–C.[9]

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(1) (a) Partial support by the National Aeronautics and Space Administration under Grant NsG-518 is gratefully acknowledged. (b) Presented before the Division of Organic Chemistry at the 152nd meeting of the American Chemical Society, New York, N. Y., Sept 1966. (c) Support by a grant from the National Science Foundation as a summer fellow is gratefully acknowledged.

(2) (a) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952). (b) J. W. Powell and M. C. Whitney, *Tetrahedron*, **7**, 305 (1959). (c) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); **82**, 1002 (1960).

(3) (a) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **87**, 659 (1965); J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *ibid.*, **87**, 661 (1965). (b) R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Am. Chem. Soc.*, **89**, 1442 (1967).

(4) R. H. Shapiro, *Tetrahedron Letters*, 3401 (1966).

(5) K. B. Wiberg and H. M. Lavanish, *J. Am. Chem. Soc.*, **88**, 5272 (1966); F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966).

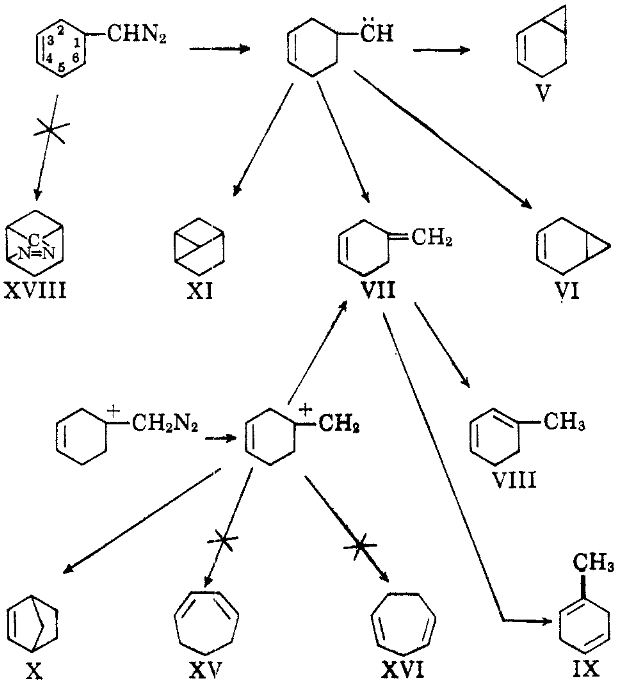
(6) A. Nickon and N. H. Werstiuk, *ibid.*, **88**, 4543 (1966).

(7) (a) G. Le Ny, *Compt. Rend.*, **251**, 1526 (1960); (b) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961); (c) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); (d) S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961); (e) M. Hanack and W. Kaiser, *Angew. Chem. Intern. Ed. Engl.*, **3**, 583 (1964).

(8) (a) Although compounds VIII and IX contained deuterium, these materials resulted from the reaction of VII with base in the presence of D_2O; therefore the deuterium content is most probably due to a secondary isomerization process. (b) We are examining the reactions in this system as part of another study.

(9) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); W. R. Moore, H. R. Ward, and R. F. Merrit, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

SCHEME I



No cycloheptadienes (XV, XVI) were found as reaction products in the decomposition of IV as evidenced by the absence of cycloheptane (XVII) among the hydrogenation products. This is in contrast to the work of Kuh,[10] who reported that ring enlarged products predominate in the solvolysis of the esters having the Δ^3-cyclohexenylcarbinyl structure. The decomposition of IV did not result in pyrazoline formation (XVIII), although Schwartz reported the formation of 8,9-diazatricyclo[5.3.0.0^{4,10}]dec-8-ene[11] (XX) as the principal product in the decomposition of Δ^4-cycloheptenecarboxaldehyde tosylhydrazone (XIX) with 1 equiv of base in diglyme.[12] The ratio of norcarenes V and VI can be rationalized by Kirmse's observation that the transition state for intramolecular carbene insertion requires an eclipsed conformation for the carbene carbon atom and the carbon-hydrogen bond,[13] resulting in, according to Dreiding Models, an unfavorable conformation for insertion into the C_6–H bond of IV.

Since no pyrazolines were identified in the reaction mixtures and tricycloheptane XI constituted only 1–2% of the reaction mixture, it is unlikely that any great amount of double-bond participation took place in the decomposition of IV. This is strongly supported by the work of Kuh[10] which showed the absence of any products indicative of double-bond participation in the solvolysis of the esters of the Δ^3-cyclohexylcarbinyl system.

When the decomposition of IV was carried out in ethylene glycol enriched with D_2O, analysis of recovered methylenecyclohexene VII and bicycloheptene V showed them to contain negligible amounts of deuterium.[8a] This can be compared with the incorporation of appreciable amounts of deuterium in the products of the decomposition of the tosylhydrazones in the cyclopropylcarbinyl and norbornyl systems under similar reaction conditions.[5,6]

Of the intermediates possible in the base-catalyzed decomposition of carbonyl tosylhydrazones, our experimental results are consistent only with a carbene or diazo compound. A cationic intermediate (either a diazonium salt or a carbonium ion) is unlikely on the basis of the deuteration experiments, the absence of ring expanded products, and the constancy of the ratios of bicyclo[4.1.0]heptenes to products related to methylcyclohexane. A Lewis acid complexed carbene can be eliminated, since the reaction was carried out exclusively in sodium ion bases. With the exception of a trace of bicyclo[2.2.1[hept-2-ene (XII),[14] all of the reaction products can be accounted for by either a carbene intermediate or by the reaction with synchronous elimination of an extremely short-lived diazo compound. Both intermediates are consistent with the deuteration results and our experimental results do not clearly distinguish between them.

In conclusion, it would appear that those systems in which facile intramolecular cyclizations do not occur in solvolysis reactions show an absence of double-bond participation in carbenic reactions. The Δ^3-cyclohexenyl system is further unique in that it is surprisingly insensitive to a wide variation in reaction conditions.

Experimental Section[15]

Preparation of Δ^3-Cyclohexenecarboxaldehyde Tosylhydrazone (IV).—*p*-Toluenesulfonylhydrazide[16] (18.6 g, 0.1 mole) was dissolved in 100 ml of 95% ethanol at 50°. Δ^3-Cyclohexenecarboxaldehyde (11.0 g, 0.1 mole, 11.5 ml) was added to this solution over a 20-min period, followed by cooling to room temperature. Water (50 ml) was added to the reaction mixture and the heterogeneous mixture was cooled overnight at −15° to complete precipitation. The product was filtered and the crude product was recrystallized once from aqueous ethanol (1:1) to result in a white crystalline product: mp 79–80°; yield 85%; infrared analysis ($CHCl_3$), 3200, 3010, 2900, 2830, 1590, 1420, 1340, 1300, 1150, 1080, 1010, 920, and 800 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O_2N_2S$: C, 68.48; H, 5.08. Found: C, 68.30; H, 5.38.

Decomposition of III.—The decomposition of III was carried out by the procedure of Closs[17] and Kirmse[13] in decalin, diglyme, or ethylene glycol solvent. The reaction products (methanol and C_7H_{10} hydrocarbons along with some solvent) were distilled on a short Vigreaux column and the fraction boiling between 50 and 160° was partitioned beween ice water and purified pentane. The pentane solution was dried over magnesium sulfate and analyzed by gas chromatography. A portion of the pentane solution was hydrogenated at room temperature with 5% palladium on charcoal and analyzed by gas chromatography to determine the ratios of isomeric ring structures. The decomposition of the sodium salt of III, prepared by the method of Cristol,[18] was carried out in an analogous fashion with the omission of the sodium methoxide catalyst.

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(10) A. D. Kuh, Ph.D. Thesis, Cornell University, 1965.

(11) This name is more in accord with IUPAC nomenclature rules than is 2,3-diazatricyclo[3.3.2.0^{2,6}]dec-2-ene.

(12) M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

(13) W. Kirmse and G. Wachterhauser, *Tetrahedron*, **22**, 63 (1966).

(14) The possible thermal isomerization of compound XI to X under the reaction conditions is a possible source of X, but we have been unable to obtain enough XI to test this hypothesis.

(15) Melting points were determined on a Mel-Temp apparatus and are corrected. Infrared spectra were recorded on a Beckman Model IR-8, either as 5% solutions in carbon tetrachloride or as Nujol mulls. Nmr spectra were measured at 60 Mc/sec on a Varian Associates A-60 spectrometer using carbon tetrachloride as solvent and tetramethylsilane (δ 0.0 ppm) as internal standard. Gas chromatographic analyses were performed with helium as the carrier gas on a Varian–Wilkens Aerograph Model 700 Autoprep on tricresyl phosphate columns. Areas under the peaks were measured with the aid of a Keuffel and Esser Co. planimeter.

(16) L. Friedman and R. Little, *Org. Syn.*, **40**, 93 (1960).

(17) G. L. Closs, L. C. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **86**, 3796 (1964).

(18) S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963).

Identification of the Reaction Products.—The reaction products were separated by preparative vapor phase chromatography and the structure of the carbon skeletons were confirmed by quantitative hydrogenation in ethanol with 5% Pd–C catalyst. Bicyclo[4.1.0]hept-3-ene (VII),[19] 1-methylcyclohexa-1,4-diene (XII),[21,22] bicyclo[2.2.1]hept-2-ene (XII),[23] and bicyclo[4.1.0]hept-3-ene (XIII)[20,24] were identical with authentic samples.

4-Methylene-1-cyclohexene (VII)[25,26] showed an nmr br singlet (4 H)[27] at 2.1 ppm (allylic CH_2), br singlet (2 H) at 2.7 (double allylic CH_2), br singlet (2 H) at 4.7 (exocyclic CH_2), and a singlet (2 H) at 5.6 (vinyl); infrared bands (CCl_4) at 3062, 3020, 2980, 2930, 2900, 2838, 2085, 1650, 1430, 1414, 880, and 642 cm^{-1}; catalytic hydrogenation (4.0 equiv of hydrogen) to methylcyclohexane.

1-Methylcyclohexa-1,3-diene (VIII)[28] showed an nmr poorly resolved doublet (3 H) at 1.8 ppm (CH_3), br singlet (4 H) at 2.1 (allylic CH_2), br multiplet (3 H) at 5.6–5.8 (vinyl); infrared bands (CCl_4) at 3040, 2970, 2930, 2870, 2830, 1630, 1595, 1485, 1375, 880, and 680 cm^{-1}; catalytic hydrogenation (3.9 equiv of hydrogen) to methylcyclohexane.

Tricyclo[4.1.0.0^{3,7}]heptane (XI)[9] showed an nmr complex spectra containing no vinyl hydrogens; infrared bands (CCl_4) at 3068, 3039, and 2971 cm^{-1}; catalytic hydrogenation (1.9 equiv of hydrogen) to bicyclo[2.2.1]heptane.

Analysis of Deuterated Reaction Mixtures.—Recovered bicyclo[4.1.0]hept-2-ene and 4-methylene-1-cyclohexene from reaction mixtures containing D_2O were spectrally identical with authentic samples and did not contain a C–D stretching band at about 2100 cm^{-1} in the infrared spectrum.[29]

Registry No.—IV, 13428-09-6; VII, 13407-18-6; VIII, 1489-56-1; XI, 279-18-5.

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[19] An authentic sample of bicyclo[4.1.0]hept-2-ene was prepared by the Simmons–Smith synthesis from cyclohexa-1,3-diene[20] (Columbia Organic Chemicals Co., Columbia, S. C.).

[20] H. E. Simmons and R. D. Smith, *Org. Syn.*, **41**, 72 (1961).

[21] We would like to gratefully acknowledge a generous sample of 1-methylcyclohexa-1,4-diene from Columbia Chemicals Co.

[22] An authentic sample of XI was obtained from Columbia Chemicals, Co.

[23] An authentic sample of XII was obtained from the Matheson Co.

[24] S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

[25] W. J. Bailey, R. Barclay, Jr., and R. A. Baylouny, *ibid.*, **78**, 2804 (1956).

[26] An authentic sample of IX was prepared by the pyrolysis of Δ^3-cyclohexenylcarbinyl acetate prepared from Δ^3-cyclohexenecarboxaldehyde by reduction with borohydride followed by acetylation with acetic anhydride.

[27] The integrated peak heights reported below were within 0.1 proton intensity of the predicted theoretical height.

[28] A. Mondrous, P. Potin, and R. Wylde-Lachazette, *Bull. Soc. Chim. France*, 1549 (1962).

[29] R. T. Coneley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, 1966, pp 26, 280.

Nucleophilic Opening of the Oxirane Ring of 1-Methyl-4-phenyl-3,4-epoxypiperidine

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The opening of the oxirane ring of 1-methyl-4-phenyl-3,4-epoxypiperidine (1) by reduction with lithium aluminum hydride or diborane occurs by a displacement at the 4 position to give *cis*-1-methyl-4-phenyl-3-piperidinol. The reaction of 1 with Grignard or lithium reagents gives an elimination reaction at room temperature to form 1-methyl-4-phenyl-1,2,3,6-tetrahydro-3-pyridinol, although at higher temperatures addition does occur. The reaction pathways are considered.

The reaction of 1-methyl-4-phenyl-3,4-epoxypiperidine (**1**) with lithium aluminum hydride to give *cis*-1-methyl-4-phenyl-3-piperidinol (**2**)[2] was highly unexpected in view of the direction of ring opening of epoxides reported previously.[3] From the reduction in ether there was no evidence for the formation of the expected product, 1-methyl-4-phenyl-4-piperidinol (**3**). In view of the unusual reactivity of **1**, a study of its properties was made.

The conversion of **1** to **2** could occur by either of two pathways (Scheme I). The usual ring opening of the epoxide occurs by a nucleophilic displacement on carbon and such a sequence at the C-4 position is represented by path A. An alternative pathway, B, in which a pinacollike rearrangement occurred, owing to a Lewis acid activity of the lithium aluminum hydride or an impurity, to give 1-methyl-4-phenyl-3-piperidone (**4**) would provide a plausible explanation for the unusual direction of ring opening.[3] The latter route, B, was disfavored since the reduction of **4** with lithium aluminum hydride had been shown to give both *cis*- and *trans*-1-methyl-4-phenyl-3-piperidinol;[2] this reaction sequence was completely eliminated by showing that the product of reduction of **1** with lithium aluminum deuteride was 1-methyl-4-phenyl-3-piperidinol-d_4 (**2**-d_4). The product of the reaction of **1** with lithium aluminum deuteride was shown by gas phase chromatography to be homogeneous and to have a retention time identical with that of unlabeled **2**. A comparison of the nmr spectra of **2** and **2**-d_4 showed that the integrated intensities of the signals (τ 6.20) for the carbinol protons at position C-3 were identical. Thus the pro-

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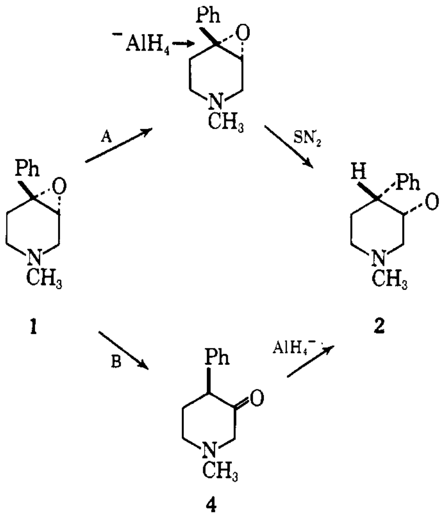

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[1] This research represents a portion of the thesis of W. E. Krueger presented to the Graduate Faculty of the University of New Hampshire in partial fulfillment of the requirements of the Ph.D. degree.

[2] R. E. Lyle and W. H. Krueger, *J. Org. Chem.*, **30**, 394 (1965).

[3] E. L. Eliel, *J. Am. Chem. Soc.*, **80**, 1744 (1958), and previous papers in this series; J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 435 (1967).