2-(Methylazoxy)-2-propanol Acetate (5).—To 41 g (0.477 mole) of acetone methylhydrazone in 75 ml of methylene chloride was added slowly with stirring a solution of 218 g (0.5 mole) of lead tetraacetate in 550 ml of methylene chloride over a period of 2 hr. An exothermic reaction occurred and the reaction mixture was stirred an additional 6 hr. The reaction solution was then washed successively with three 200-ml portions of water, three 200-ml portions of 5% sodium bicarbonate, and three 200-ml portions of water. The methylene chloride solution was then dried over anhydrous sodium sulfate and filtered. The methylene chloride was removed from the solution under vacuum and the residue was distilled to give 37.2 g (55%) of 2-(methylazo)-1-propanol acetate (4); bp 60–65° (60 mm), n^{29}_{D} 1.4132.

The oxidation of 35 g (0.243 mole) of 4 in 100 ml of dry ether was carried out by the slow addition of 50 ml of 40% peracetic acid in acetic acid dissolved in 100 ml of dry ether with agitation. After stirring 3 hr the solution was washed with three 50-ml portions of water, three 50-ml portions of 5% sodium bicarbonate, and was dried over magnesium sulfate. The ether was evaporated from the solution after filtration and the residue was vacuum distilled to furnish 19 g (50%) of 2-(methylazoxy)-2-propanol acetate (5), bp 84–87° (20 mm), n^{28}_{D} 1.4362.

Anal. Calcd for $C_6H_{12}N_2O_3$: C, 44.98; H, 7.49; N, 17.49. Found: C, 45.06; H, 7.35; N, 17.70.

Peracetic Acid Oxidation of Isobutyraldehyde Methylhydrazone.—To 10 g (0.1 mole) of isobutyraldehyde methylhydrazone[11] in 50 ml of methylene chloride was slowly added with stirring 20 g of a 40% peracetic acid solution in acetic acid. The solution was allowed to stir for 3 hr after the addition was completed. The solution was then rinsed with water until the aqueous phase gave no reaction with sodium bicarbonate. The methylene chloride was then dried over anhydrous sodium sulfate, filtered, and vacuum concentrated. The concentrate was then evaporatively distilled to give 10.4 g (66%) of N′-acetylisobutyric acid methylhydrazide (6a), bp 75° (0.02 mm), n^{26}_{D} 1.4655, d^{25} 1.009, whose infrared spectrum showed an NH peak at 3.18 μ and two carbonyl peaks at 5.88 and 6.25 μ, respectively. The distillate slowly crystallized to a low-melting hydroscopic solid, which could be sublimed and kept crystalline under a dry nitrogen atmosphere or in a drybox.

Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.15; H, 8.92; N, 17.71. Found: C, 53.00; H, 9.13; N, 17.66.

Peracetic Acid Oxidation of Heptaldehyde Methylhydrazone.—To 14.2 g (0.1 mole) of heptaldehyde methylhydrazone[11] in 50 ml of anhydrous ethyl ether was slowly added 20 g of 40% peracetic acid in acetic acid with stirring. After 3 hr of additional stirring, the ether solution was washed with three 50-ml portions of water, three 50-ml portions of 10% sodium bicarbonate solution, and it was then dried over anhydrous sodium sulfate. Upon filtration of the drying agent, the solution was concentrated and 14 g of crude material was obtained. The distillation of this residue gave 11 g (55%) of N′-acetylheptanoic acid methylhydrazide (6b), bp 75° (0.1 mm), n^{25}_{D} 1.4580, d^{25} 0.901. An nmr spectrum of this material showed singlets at 11.75 ppm (NH), 3.05 (NCH_3), 1.97 ($NCOCH_3$), triplets at 2.25 (CH_2CO) and 0.90 ppm (CH_3), and a broad band at 1.35 ppm (CH_2) at the respectively integrated intensities of 1:3:3:3:3:8.

Anal. Calcd for $C_{10}H_{20}N_2O_2$: C, 59.97; H, 10.07; N, 13.99. Found: C, 59.87; H, 10.20; N, 14.26.

Peracetic Acid Oxidation of Propionaldehyde Phenylhydrazone.—To 14.8 g (0.1 mole) of propionaldehyde phenylhydrazone in 100 ml of methylene chloride was added slowly with stirring at ice-bath temperature 20 g of a 40% peracetic acid solution in acetic acid. After the addition was completed, the solution was stirred for 3 hr. The solution was then rinsed with water until the aqueous phase gave no reaction with a bicarbonate solution. The methylene chloride was then dried over anhydrous sodium sulfate, filtered, and vacuum concentrated. The concentrate was subjected to an evaporative distillation whereby 8 g (49%) of N′-acetylpropionic acid phenylhydrazide (6c), bp 80° (0.04 mm), n^{26}_{D} 1.5342, d^{25} 1.175, was obtained. The infrared spectrum of this compound exhibited double carbonyl peaks at 5.8 and 5.95 μ and were identical with the infrared spectrum of material obtained in 75% yield by the action of acetic anhydride on N′-phenylpropionic acid hydrazide and which exhibited the same physical constants. The nmr spectrum of this material showed peaks at 0.92 (CH_3), 1.9 ($CH_3C{=}O$), 2.23 ($CH_2C{=}O$), and 7.13 ppm (C_6H_5) in ratios of 3:3:2:5, respectively.

Anal. Calcd for $C_{11}H_{14}N_2O_2$: N, 13.58. Found: N, 13.06.

Registry No.—**1a**, 13369-61-4; **1b**, 13369-62-5; **2a**, 13369-63-6; **2b**, 13369-64-7; **4**, 13369-65-8; **5**, 13395-57-8; **6a**, 13369-66-9; **6b**, 13369-67-0; **6c**, 13369-68-1; peracetic acid, 79-21-0; acetone methylhydrazone, 5771-02-8.

The Oxidation of Aliphatic Secondary Alcohols by Chromium(VI) in Concentrated Sulfuric Acid Solutions[1]

DONALD G. LEE AND ROSS STEWART

Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada

Received March 22, 1967

A study of the rates of oxidation of 2-propanol, 1,1,1-trifluoro-2-propanol, and 1,1,1,3,3,3-hexafluoro-2-propanol by chromium(VI) in concentrated sulfuric acid solutions has been made and the results have been explained on the basis of a chromate ester mechanism. When 1,1,1-trifluoro-2-propanol was oxidized in very concentrated acid solutions, a reaction intermediate (or a species in equilibrium with it) was observed spectrophotometrically and the primary kinetic hydrogen isotope effect was found to be markedly decreased. These results suggest that under strongly acid conditions the rate-determining step in the oxidation of this compound is ester formation.

There is good evidence that chromic acid oxidizes alcohols *via* a chromate ester which undergoes a rate-determining decomposition by cleavage at the α-carbon–hydrogen bond[2] (eq 1 and 2).

$$R_2CHOH + H_2CrO_4 \overset{\text{fast}}{\rightleftharpoons} R_2CHOCrO_2OH + H_2O \qquad (1)$$

$$R_2CHOCrO_2OH \xrightarrow{\text{slow}} R_2C{=}O + H_2CrO_3 \qquad (2)$$

We have previously reported kinetic results which indicate that the rate of oxidation of 2-propanol by chromium(VI) in aqueous acid is dependent not only on the acidity of the solution, but also on the identity of anions present.[3] The results were satisfactorily explained by assuming that the anions become intimately associated with the oxidant in moderately con-

---

(1) From part of the Ph.D. thesis of D. G. Lee, University of British Columbia, 1963. Presented at the 48th Conference of the Chemical Institute of Canada, Montreal, 1965.

(2) (a) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949); (b) R. Brownell, A. Leo, Y. W. Chang, and F. H. Westheimer, *J. Am. Chem. Soc.*, **82**, 406 (1960); (c) J. Roček, F. H. Westheimer, A. Eschenmoser, L. Moldovanyi, and J. Schreiber, *Helv. Chem. Acta*, **45**, 2554 (1962); (d) K. B. Wiberg in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, p 142 ff; (e) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, pp 37–48.

(3) D. G. Lee and R. Stewart, *J. Am. Chem. Soc.*, **86**, 3051 (1964).

centrated acid solutions. We now wish to report the results obtained from a kinetic study of the oxidation of several aliphatic alcohols in concentrated sulfuric acid solutions.

It is well known that the rate of oxidation of many organic compounds by chromium(VI) in sulfuric acid media is maximal in solutions containing 60–75% H_2SO_4 by weight.[4-6] Pungor and Trompler claim that an explanation for the occurrence of a maximum in the rate–acidity plot for the oxidation of methanol, ethanol, and formic acid at 73% H_2SO_4 may lie in a consideration of the stability of chromium(VI) in various solutions of sulfuric acid. However, a more likely explanation is that either the alcohol or the chromium(VI) species becomes protonated at this acidity.[4-7] Since the kinetics of the reaction indicate the inclusion of one proton in the transition state, protonation of either of the reactants would result in a change of slope from unity to zero in the rate–acidity plot. If it is the oxidant which accepts a proton, the rates of reaction of all compounds should become maximal at the same acidity, if indeed protonation of the oxidant can cause a rate maximum of any sort. (The oxidizing power of most oxidants is increased by protonation). On the other hand an explanation on the basis of alcohol protonation demands that the point of slope change vary with the pK_{BH^+} of the reductants.

This investigation was undertaken to examine these possibilities by studying the rates of oxidation of 2-propanol, 1,1,1-trifluoro-2-propanol, and 1,1,1,3,3,3-hexafluoro-2-propanol in solutions of varying sulfuric acid concentrations. Substitution of a trifluoromethyl group for an α-methyl group usually lowers pK values of alcohols by about 4 units.[8-11] Hence it was expected that these alcohols would protonate at widely different acidities and that it would be readily apparent whether or not there was a correlation between the point of slope change and the pK_{BH^+} of the alcohols undergoing oxidation.

Experimental Section

The protioalcohols used in this investigation were obtained commercially with the exception of 1,1,1,3,3,3-hexafluoro-2-propanol which was kindly supplied by Dr. S. Andreades of E. I. du Pont de Nemours and Co. The deuterioalcohols were all prepared through reduction of the corresponding ketones with lithium aluminum deuteride.[12,13] All alcohols were purified by gas chromatography.

The rates of oxidation were followed spectrophotometrically using a Beckman DU spectrophotometer as previously described.[3] Pseudo-first-order rate constants were obtained from a plot of log absorbance at 349 mμ against time and converted to second-order rate constants through division by the alcohol concentration. Good straight lines up to about 80% of the reaction were obtained in all runs except those for the oxidation of 1,1,1-trifluoro-2-propanol in greater than 60% H_2SO_4. As indicated in Figure 1, the initial decrease in absorbance is slow in 76–86% H_2SO_4 and actually passed through a maximum in 64–70% H_2SO_4.

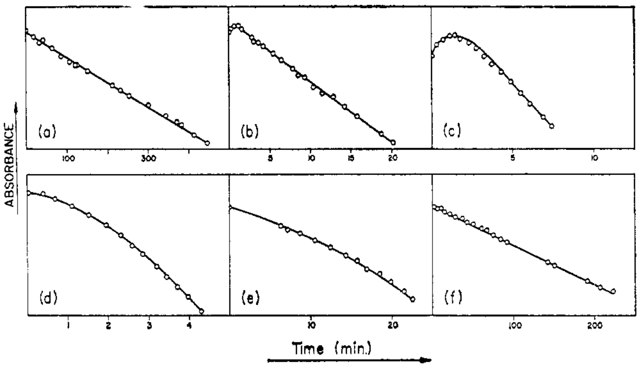


Figure 1.—Chromic acid oxidation of 1,1,1-trifluoro-2-propanol in aqueous sulfuric acid at 25°: (a) 57.6% H_2SO_4, $k_H/k_D = 10.5$; (b) 63.6% H_2SO_4; (c) 68.5% H_2SO_4, $k_H/k_D = 5.99$; (d) 76.4% H_2SO_4, $k_H/k_D = 5.7$; (e) 85.7% H_2SO_4; (f) 95.3% H_2SO_4, $k_H/k_D = 1.3$.

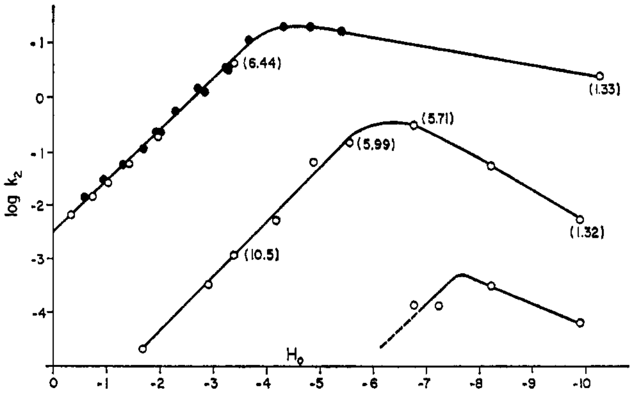


Figure 2.—Rate–acidity plot for the oxidation of 2-propanol, 1,1,1-trifluoro-2-propanol, and 1,1,1,3,3,3-hexafluoro-2-propanol (top to bottom). Primary deuterium isotope effects are indicated in parentheses; rate constants were determined spectrophotometrically (○) and polarographically[4] (●).

Results

The rate constants obtained in this investigation are presented in Tables I, II, and III and plotted in Figure 2 against the H_0 acidity function.[14,15] (The results obtained by Roček and Krupička[4] from a polarographic study of the rate of oxidation of 2-propanol in sulfuric acid solutions of varying concentrations are included as closed circles for comparison purposes.)

Discussion

As Figure 2 indicates, the acidity at which the rate–acidity plot crests is certainly dependent on the identity of the alcohol undergoing oxidation and hence the change in slope cannot be due to protonation of the chromium species. Such an explanation would require that the plots all crest at the same acidity. On the other hand the distance from crest to crest is not nearly so great as would be predicted from the pK_a values of the alcohols. In light of these results it would seem

---

(4) J. Roček and J. Krupička, *Coll. Czech. Chem. Comm.*, **23**, 2068 (1958).

(5) E. Pungor and J. Trompler, *J. Inorg. Nucl. Chem.*, **5**, 123 (1957).

(6) H. C. S. Snethlage, *Rec. trav. Chem.*, **60**, 877 (1941).

(7) F. Mareš and J. Roček, *Coll. Czech. Chem. Commun.*, **26**, 2389 (1961).

(8) R. N. Haszeldine, *J. Chem. Soc.*, 1757 (1953).

(9) The preceding reference gives the pK_a values of the alcohols whereas this work is concerned with the pK_{BH^+} values, only one of which is known with exactness.[10] However, it is known that a fairly good correlation exists between pK_a and pK_{BH^+} values for a number of compounds[11] and it seems reasonable to assume that the pK_{BH^+} values of these alcohols would vary by approximately the same amount as the corresponding pK_a values.

(10) R. E. Weston, Jr., S. Ehrenson, and K. Heinzinger, *J. Am. Chem. Soc.*, **89**, 481 (1967).

(11) R. Stewart and J. P. O'Donnell, *Can. J. Chem.*, **42**, 1694 (1964); R. Stewart and D. Dolman, *ibid.*, **45**, 925 (1967).

(12) A. Leo and F. W. Westheimer, *J. Am. Chem. Soc.*, **74**, 4383 (1952).

(13) R. Stewart and D. G. Lee, *Can. J. Chem.*, **42**, 439 (1964).

(14) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(15) M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963).

TABLE I

OXIDATION OF $CH_3CROHCH_3$ IN SULFURIC ACID SOLUTIONS AT 25°

R	H_2SO_4, %	[Cr(VI)] × 10^3 *M*	[Alcohol], *M*	k_2, l. mole^{-1} sec^{-1}	k_H/k_D
H	5.29	4.10	0.129	0.0023	
H	10.6	4.23	0.129	0.00636	
H	16.0	4.13	0.129	0.0145	
H	20.2	4.13	0.129	0.0261	
H	25.8	4.10	0.129	0.0595	
H	33.4	3.42	0.0409	0.179	
H	50.1	1.03	0.0131	4.21	
H	50.1	1.03	0.0131	4.26	
H	50.1	1.03	0.0131	4.06	
D	50.1	1.03	0.0343	0.683	6.27
D	50.1	1.03	0.0214	0.673	
D	50.1	1.03	0.0103	0.626	
H	97.3	0.0515	0.00964	2.39	
H	97.3	0.0515	0.01326	2.86	
H	97.3	0.0515	0.01820	2.63	
D	97.3	0.0515	0.00888	1.89	1.33
D	97.3	0.0515	0.0169	2.04	

TABLE II

OXIDATION OF $CF_3CROHCH_3$ BY CHROMIUM(VI) IN SULFURIC ACID SOLUTIONS AT 25.0°

R	H_2SO_4, %	[Cr(VI)] × 10^4 *M*	[Alcohol] × 10^3 *M*	k_2, l. mole^{-1} sec^{-1}	k_H/k_D
H	29.4	10.3	36.5	0.000021	
H	45.7	12.4	22.0	0.000335	
H	50.1	10.3	74.4	0.00122	
H	50.1	10.3	37.2	0.00113	
H	50.1	10.3	37.4	0.00116	
D	50.1	10.3	36.9	0.000110	10.54
D	50.1	10.3	78.0	0.000112	
H	57.6	10.3	11.0	0.00515	
H	63.6	6.18	22.8	0.0619	
H	68.5	6.18	34.4	0.195	
H	68.5	6.18	10.8	0.126	
H	68.5	6.18	23.2	0.182	
D	68.5	6.18	33.5	0.0281	5.99
H	76.4	6.18	36.2	0.293	
D	76.4	6.18	38.3	0.0516	5.71
H	85.7	6.18	22.4	0.0518	
H	95.3	6.15	17.5	0.00635	
H	95.3	6.15	18.2	0.00515	
D	95.3	6.15	70.9	0.00540	1.32
D	95.3	6.15	37.7	0.00332	

TABLE III

OXIDATION OF 1,1,1,3,3,3-HEXAFLUORO-2-PROPANOL IN SULFURIC ACID SOLUTIONS AT 25°

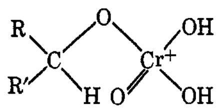
H_2SO_4, %	[Cr(VI)] × 10^4 *M*	[Alcohol] × 10^2 *M*	k_2, l. mole^{-1} sec^{-1}
76.4	6.18	3.18	0.000140
79.4	6.18	3.38	0.000134
85.7	4.12	2.96	0.000314
95.3	61.8	3.22	0.0000628

that the best explanation for the observed change in slope of the rate *vs.* acidity plots lies in a chromate ester protonation step (eq 3). Variations in the alkyl groups

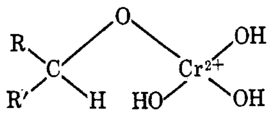
$$RR'CHOCrO_3H + H^+ \rightleftarrows RR'CHOCrO_3H_2^+ \qquad (3)$$

would cause smaller changes in the pK_{BH^+} values of the chromate esters than they would in the corresponding alcohols.

Such a suggestion is readily compatible with the previously proposed cyclic mechanism for this reaction.[2c,3,13] Thus the rate law in 5–70% sulfuric acid is $v = k[\text{alcohol}][H_2CrO_4]h_0$, indicating the presence of one proton in the transition state. Since it is well established that a chromate ester is an intermediate in this reaction,[2] the species participating in the rate-determining step would be



and as long as the reaction was carried out below the pK_{BH^+} of the ester the rate would be first order in h_0. However at acidities above the pK_{BH^+} the rate would show a zero-order dependence on h_0. Further protonation would lead to formation of a diprotonated species



which would be less likely to contribute *via* the cyclic mechanism since there are no unprotonated oxygen atoms available for participation in the hydrogen-transfer step. Hence one might observe first a leveling and then a drop in the plot of log k_2 *vs.* H_0.

Two very interesting, though somewhat unexpected, observations were made during the oxidation of 1,1,1-trifluoro-2-propanol. First, in solutions containing greater than 60% H_2SO_4 a reaction intermediate could be detected spectrophotometrically. Second, the primary deuterium isotope effect decreases gradually from a value of 10.5 in 57.6% H_2SO_4 to a value of 1.3 in 95.3% H_2SO_4. The implications of the above results are that the ester-forming step becomes rate determining in concentrated sulfuric acid solutions. That is, in 5–60% H_2SO_4 carbon–hydrogen bond cleavage is much slower than the rate of ester formation. However, in 60–80% H_2SO_4, ester formation and carbon–hydrogen bond cleavage occur at similar rates (note the rate plots in Figure 1b and c which suggest that an intermediate is accumulating and the decrease in the magnitude of the kinetic isotope effects) and in 95.3% H_2SO_4 ester formation is so slow that the kinetic isotope effect all but disappears.

Ester formation has also been found to be rate determining when sterically hindered alcohols are oxidized.[2c,16] These alcohols present a steric block which decreases the ease of ester formation until it becomes the slow step in the mechanism. It is possible under the conditions of the present investigation that the barrier presented to ester formation is an electrostatic one (*i.e.*, in very concentrated sulfuric acid solutions both the oxidant and the alcohol would probably bear positive charges and experience a mutual repulsion which would decrease the probability of ester formation), or it is possible that some entirely different mechanism prevails under these conditions.

During the interval between the completion of the work herein described and the submission of this paper, another report describing a similar spectrophotometric detection of an intermediate during the oxidation

---

(16) N. D. Heindel, E. S. Hanrahan, and R. J. Sinkovitz, *J. Org. Chem.*, **31**, 2019 (1966).

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]

Harry Babad, Wilton Flemon,[1c] and James B. Wood, III

Department of Chemistry, University of Denver, Denver, Colorado 80210

Received January 10, 1967

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]

---

[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).