

The reverse process has been shown to be very slow at 25°. ^{4,16}

In the present work V_{-1} has been shown to be appreciably smaller than V_2 and V_2 has been shown to be greater than V_1 which leads to

$$V_{\text{addition}} = V_1 = k_1[\text{R}_2\text{C}=\text{CR}_2][\text{HCl}]^2$$

The kinetic description of the reaction path does not describe the structure of the transition state nor the position of the hydrogen dichloride anion in it. These questions will be the subject of future studies in this area.

(16) Y. Pocker, *J. Chem. Soc.*, 1972 (1960).

The possibility has recently been raised that addition of acids to olefins might involve synchronous addition of proton and anion by two different molecules of acid. ^{17,18} On the basis of the evidence given in this paper such a process is not required in nitromethane solvent. The stereochemistry of addition and the definitive demonstration or exclusion of a carbonium ion intermediate are required prior to reaching any conclusion on this point. At present, the formation of an ion pair intermediate seems the simplest scheme which accords with all of the data presented in this paper.

(17) R. C. Fahey and M. R. Monahan, *Chem. Commun.*, 936 (1967).
(18) R. C. Fahey and D. J. Lee, *J. Am. Chem. Soc.*, **89**, 2780 (1967).

Kinetics and Mechanism of Addition of Acids to Olefins.

IV. The Addition of Hydrogen and Deuterium Chloride to 3-Methyl-1-butene, 3,3-Dimethyl-1-butene, 1-Methylcyclopentene, and 1-Methylcyclopentene-2,5,5- d_3 ¹

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Abstract: The addition of hydrogen and deuterium chloride to 3-methyl-1-butene, 3,3-dimethyl-1-butene, 1-methylcyclopentene, and 1-methylcyclopentene-2,5,5- d_3 has been studied in nitromethane at 25.0°. In the initial stages of the reaction, 3-methyl-1-butene is shown to form 40% normal addition product, 2-chloro-3-methylbutane, and 60% rearranged product, 2-chloro-2-methylbutane, while 3,3-dimethyl-1-butene is shown to form only 17% normal addition product, 2-chloro-3,3-dimethylbutane, and 83% rearranged product, 2-chloro-2,3-dimethylbutane. Hydrogen chloride catalyzes the rearrangement of 2-chloro-3-methylbutane but control experiments show that the rate of this Wagner-Meerwein rearrangement is too slow to account for the observed product ratio during the initial stages of the addition reaction. Under similar conditions the rearrangement of 2-chloro-3,3-dimethylbutane is very slow and can be neglected. The addition of deuterium chloride to 1-methylcyclopentene and of hydrogen chloride to 1-methylcyclopentene-3,5,5- d_3 is shown to lead to 96 ± 4% *trans*-addition product.

For the addition of hydrogen chloride to aliphatic alkenes in nitromethane, kinetics alone do not allow a distinction to be made between a one-step and a two-step process. ^{1b} Thus the rate law, $V = k_3[\text{alkene}][\text{HCl}]^2$, allows us to deduce the stoichiometric composition of the activated complex but does not provide any compelling evidence as to whether the reaction takes place in two discrete steps, with transfer of Cl^- from HCl_2^- to carbonium ion following the proton transfer from acid to alkene or as a concerted one-step process. For the addition of DCl and TCl to styrene³ the small but measurable incorporation of tracer into alkene which *accompanies* addition is best interpreted in terms of a two-step addition process. This test fails, how-

ever, in the case of simple aliphatic alkenes. Thus starting with the two isomeric olefins, 2-methyl-2-butene and 2-methyl-1-butene, in nitromethane we have shown (see preceding paper) that at 30% reaction neither olefin has been *measurably* converted to the other isomer in spite of the fact that the addition of a proton to either of these olefins leads to the same carbonium ion. This observation was also substantiated by showing that no H-D exchange occurs in either unreacted olefin during an essentially irreversible addition. These results made it necessary for us to apply more direct tests for the presence of carbonium ion intermediates. Consequently we have examined the addition of hydrogen chloride to 3-methyl-1-butene and 3,3-dimethyl-1-butene in nitromethane, since these are reactions which could provide a special piece of evidence for an ionic two-stage process, if accompanied by Wagner-Meerwein rearrangements.

Whitmore and Johnston⁴ have shown that the addition of HCl to 3-methyl-1-butene (neat) and 3,3-di-

(1) (a) This research was supported by a grant from the National Science Foundation. (b) Part III of this series: Y. Pocker, K. D. Stevens, and J. J. Champoux, *J. Am. Chem. Soc.*, **91**, 4199 (1969). (c) Taken from the Ph.D. Thesis of K. D. Stevens, University of Washington, 1966.

(2) Weyerhaeuser Research Fellow, 1963-1964; National Science Foundation Cooperative Research Fellow, 1964-1965.

(3) Y. Pocker, F. Naso, and G. Tocchi, *Proc. XIXth Intern. Congr. Pure Appl. Chem.*, **A1-42**, 45 (1963); Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p 50M.

(4) (a) F. C. Whitmore and F. Johnston, *J. Am. Chem. Soc.*, **55**, 5020 (1933); (b) G. G. Ecke, N. C. Cook, and F. C. Whitmore, *ibid.*, **72**, 1511 (1950).

methyl-1-butene (neat) is always accompanied by various amounts of rearrangements. They tested the stability of the unrearranged products by heating them to 100° for 24 hr and found them to be stable under these conditions. Unfortunately, in view of the capacity of HCl to catalyze the ionization of similar alkyl halides in aprotic media⁵ this control experiment⁴ can no longer be regarded as definitive. Consequently, we have also reinvestigated the addition of HCl to 3-methyl-1-butene (neat) and 3,3-dimethyl-1-butene (neat) under strict kinetic control. The addition of deuterium chloride to *trans*-1-phenylpropene in nitromethane gives 55 ± 5% *cis*-addition product and 45 ± 5% *trans*-addition product.⁶ This result is consistent with a carbonium ion mechanism in which encumbrance or ion-pair formation is at a minimum. The lifetime and the freedom of benzyl-type carbonium ions is greater in nitromethane than that of ions produced from aliphatic olefins, and this fact makes the extension of the results obtained with 1-phenylpropene in nitromethane to aliphatic cases unwarranted.⁷ Consequently, in the present work we have also examined the stereochemistry of addition of deuterium chloride to methylcyclopentene and of hydrogen chloride to 1-methylcyclopentene-2,5,5-*d*₃.

Experimental Section

Materials. Eastman Spectro Grade nitromethane was purified as previously described.^{1b} 3-Methyl-1-butene (Columbia Organic Chemicals) was checked for purity by gas chromatography; there were no detectable impurities. 3,3-Dimethylbutene was purchased from the American Petroleum Institute and was guaranteed 99.98 mol %. 1-Methylcyclopentene (Aldrich Chemical Co.) was used without further purification after examining the purity by gas chromatography (A90P, 10 ft × 0.25 in. Dow Silicone 710, Carbowax 20M, and Ucon nonpolar, 50°, 50 cc/min He flow for all alkenes examined). 1-Methylcyclopentene-2,5,5-*d*₃ was prepared from the reaction of 1-methylcyclopentanol-2,2,5,5-*d*₄ and dideuteriooxalic acid. The alkene showed a trace analysis in the vinyl region on nmr analysis. The mass spectrum indicated 95% *d*₃ incorporation. The deuterated alcohol was prepared *via* the reaction of methylmagnesium bromide with cyclopentanone-2,2,5,5-*d*₄. The ketone was deuterated by repeated exchanges with 99.7% D₂O with Na₂CO₃ as catalyst. 1-Chloromethylcyclopentane was prepared from the reaction of 1-methylcyclopentanol and a twofold excess of Lucas reagent. The reaction was almost instantaneous and the chloride separated as an upper layer. 1-Chloromethylcyclopentane-2,2,5,5-*d*₄ was prepared in an analogous manner using deuterated alcohol. The rapidity of the reaction and the insolubility of the product prevented significant exchange of the α -protons as shown by the nmr spectrum. HCl and DCl were prepared as previously described.^{1b} Dimethyl sulfoxide was distilled from molecular sieves under reduced pressure. *t*-Butyl alcohol was used without further purification. Potassium *t*-butoxide was prepared by adding freshly cut potassium metal to refluxing *t*-butyl alcohol under a nitrogen atmosphere. 2-Chloro-2-methylbutane was prepared as previously described (preceding paper). 2-Chloro-3-methylbutane was prepared by the reaction of 3-methyl-2-butanol with triphenylphosphine dichloride in dimethylformamide.⁸ The material was distilled twice and the fraction boiling at 91–93° was collected (lit.⁹ bp 92.9–93.1°). The sample gave only one peak when subjected to gas chromatographic analysis on Silicone 710, Carbowax 20M, and Ucon nonpolar columns (all 10 ft × 0.25

in. at 50° and 50 cc/min of He flow). The nmr spectrum showed resonances at τ 8.98 (D), 8.58 (D), 8.42 (M), and 6.17 (M) with areas 6, 3, 1, and 1, respectively, yield 51% after two distillations. 2-Chloro-3,3-dimethylbutane was prepared by the reaction of 3,3-dimethyl-2-butanol with triphenylphosphine dichloride in dimethylformamide.⁸ This material, after removal of a formate impurity, was analyzed by gas chromatography in the same way as the previous compound with the difference that the column temperature was 70°. Again only one peak was observed. The boiling point was 112° (lit.¹⁰ bp 109.9° (737 mm)). The nmr spectrum was unambiguous with resonances at τ 9.01 (S), 8.58 (D), and 6.21 (Q) with areas 9, 3, and 1, respectively; yield after two distillations was 56%. 2-Chloro-2,3-dimethylbutane was prepared by allowing 3,3-dimethyl-2-butanol to react with a twofold excess of Lucas reagent. This material was distilled twice and the fraction boiling at 111–113° was collected. Analysis by gas chromatography was performed in the same manner as the previous compound and again only a single peak resulted. The nmr spectrum showed resonances at 8.95 (D), 8.50 (S), and ca. 8.38 (M) with areas 6, 6, and 1, respectively; yield after two distillations was 63%.

Mass spectra were obtained on a Consolidated Engineering Corporation Model 21-103 spectrometer. Analytical gas chromatography was carried out using a Wilkins Aerograph Hy-Fi 600 equipped with a flame ionization detector. Preparative-scale work was performed on an Aerograph A-90P. Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60 spectrometer. Temperature control was maintained with a Sargent Thermonitor Model S-PN-2770. The variation in temperature was ±0.02°.

Methods. The kinetics of addition were carried out as previously described (previous paper). The kinetics of the base-catalyzed dehydrohalogenation of 1-chloromethylcyclopentane and 1-chloromethylcyclopentane-2,2,5,5-*d*₄ were measured as follows: 15 ml of dimethyl sulfoxide was mixed with 7 ml of *t*-butyl alcohol containing the desired amount of potassium *t*-butoxide. Exactly 2 ml of this solution was removed, and the concentration of base was determined by titration with methanolic hydrogen chloride to a lacmoid end point. The solvent was 68% dimethyl sulfoxide and 32% *t*-butyl alcohol by volume. After thorough mixing, the solution was allowed to stand for at least 30 min in the thermostat. Alkyl chloride was then added by dropping a weighed amount in a very small beaker into the reaction vessel. Aliquots were removed, and the remaining base was titrated in ethanol at –78° with methanolic HCl to a lacmoid end point. When alkyl chloride was added to a solution containing no base, the amount of acid eliminated over a period equivalent to ten half-lives for the median base-catalyzed elimination corresponded to less than 1.3% reaction.

Reaction of 3-Methyl-1-butene with Hydrogen Chloride in Nitromethane. Detailed kinetics of addition to this olefin were not carried out as the rate was so low that under conditions leading to appreciable alkyl halide formation the reaction between hydrogen chloride and nitromethane became significant. The two possible products have been carefully characterized. A stock solution 3 *M* in 3-methyl-1-butene in nitromethane was prepared. Aliquots of this solution were acidified with hydrogen chloride in nitromethane resulting in solutions 1.5 *M* in olefin and 2 *M*, 1 *M*, and 0.5 *M* in acid, respectively. The course of each reaction was followed by gas chromatography (A-90P, 50 cc/min of He, 10 ft × 0.25 in. Carbowax 20M, 70°); retention times: 2-chloro-2-methylbutane, 2.85 min; 2-chloro-3-methylbutane, 3.07 min. At 1% reaction, *i.e.*, when the sum of alkyl halides corresponded to 1% reaction, the peaks were too small to allow unambiguous estimation of areas. The final areas (as obtained at 3 and 6% reaction) were in the ratio of 2-chloro-3-methylbutane:2-chloro-2-methylbutane 40:60.

Reaction of 3-Methyl-1-butene with Hydrogen Chloride. 3-Methyl-1-butene (0.50 ml, 0.046 mol) was placed in a vial sealed with a serum stopper, and the stopper was punctured with two needles. A source of hydrogen chloride was connected to one needle and the slow flow of gas started. At the same time, the bottom of the vial was cooled in liquid nitrogen. When an amount of solid hydrogen chloride about equal to the alkene had accumulated, the vial was placed in Dry Ice and the excess hydrogen chloride allowed to boil off. The vial was warmed to 0° and the reaction mixture analyzed periodically on the gas chromatograph (same conditions as previous experiment). Two products were formed in the ratio 60:40. These products had the same reten-

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(6) Y. Pocker, Y. V. S. Devi, F. Naso, and K. D. Stevens, *Proc. Intern. Symp. Solvation Phenomena*, 1, 27 (1963); also Y. Pocker and F. Naso, unpublished observations.

(7) (a) G. S. Hammond and T. D. Nevitt, *J. Am. Chem. Soc.*, **86**, 5035 (1964); (b) R. C. Fahey and R. A. Smith, *ibid.*, **86**, 5035 (1964); (c) M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2245, 2248, 3645 (1963).

(8) G. A. Wiley, R. L. Hershkovitz, B. M. Rein, and B. C. Chung, *ibid.*, **86**, 964 (1964).

(9) F. C. Whitmore and F. Johnston, *ibid.*, **60**, 2265 (1938).

(10) F. C. Whitmore, H. I. Bernstein, and L. W. Mixon, *ibid.*, **60**, 2539 (1938).

Table I

Compound	Vpc ^a retn time	Nmr peaks		Reaction with AgNO ₃ ^b
		Position, τ	Area	
Me ₃ C·CHCl·Me	~2.95	6.21 (Q) 8.58 (D) 9.01 (S)	1 3 9	Slow
Me ₂ CClCHMe ₂	~2.95	~8.38 (M) 8.50 (S) 8.95 (D)	1 6 6	Fast
Prodt of reaction Me ₃ C·CH=CH ₂ + HCl (in MeNO ₂)	~2.95	6.21 (Q) ~8.38 (M) 8.50-8.58 8.95-9.01	~1/6 ~5/6 5.5 6.5	Slow component (17%) Fast component (83%)
Prodt of reaction Me ₃ C·CH=CH ₂ + HCl (in MeNO ₂) after treatment with alcoholic AgNO ₃	~2.95	6.21 (Q) 8.58 (D) 9.01 (S)	1 3 9	Slow
Prodt of reaction Me ₃ C·CH=CH ₂ + HCl (no solvent)	~2.95	6.21 (Q) ~8.38 (M) 8.50-8.58 8.95-9.01	0.5 0.5 4.5 7.5	Slow component (50%) Fast component (50%)
Prodt of reaction Me ₃ C·CH=CH ₂ + HCl (no solvent) after treatment with alcoholic AgNO ₃	~2.95	6.21 (Q) 8.58 (D) 9.01 (S)	1 3 9	Slow

^a Minutes from N₂ peak (6 ft × 1/8 in. Carbowax 20M, 50°, 20 cc/min of N₂, Hy-Fi). ^b Reaction with cold alcoholic silver nitrate.
^c Area corresponding to the lone proton in the mixture of the two isomeric chlorides.

tion times as 2-chloro-2-methylbutane and 2-chloro-3-methylbutane, respectively.

Reaction of 2-Chloro-3-methylbutane with Hydrogen Chloride in Nitromethane. Authentic 2-chloro-3-methylbutane (0.05 ml, 0.0041 mol) was dissolved in 0.45 ml of nitromethane which was 0.8 M in hydrogen chloride. This solution was analyzed periodically for chloride composition by gas chromatography. After 3 days at 25.0°, only 7 ± 0.5% of the chloride had rearranged to 2-chloro-2-methylbutane as shown by the areas of the peaks obtained on gas chromatographic analysis (same conditions as previous experiment).

Reaction of 3,3-Dimethylbutene with Hydrogen Chloride in Nitromethane. 3,3-Dimethylbutene (0.68 ml, 0.053 mol) and 4.32 ml of nitromethane, 0.91 M in hydrogen chloride, were introduced into a vial sealed with a serum stopper and mixed well. The course of reaction was initially followed on the gas chromatograph (6 ft × 1/8 in. Carbowax 20M, 50°, 20 cc/min of N₂, Hy-Fi). Only one new peak was observed during the entire reaction. However, since the two chlorides, 2-chloro-3,3-dimethylbutane and 2-chloro-2,3-dimethylbutane were not separable on the above vpc column,¹¹ the magnitude of this peak as a function of time did not permit any product resolution but was merely a measure of the over-all reaction rate. Parallel measurements were carried out by quenching aliquot portions of the reaction mixture in cold acetone and titrating against standard sodium methoxide using lacmoid indicator. The proportion of tertiary chloride, 2-chloro-2,3-dimethylbutane, in the product mixture was 83 ± 2%. This was determined by removing hydrogen chloride from aliquot portions of the reaction mixture under reduced pressure, quenching the residual solutions with cold alcoholic silver nitrate and back-titrating against standardized potassium chloride. Control experiments have confirmed (a) the relatively low reactivity of cold alcoholic silver nitrate toward 2-chloro-3,3-dimethylbutane, and (b) the general validity of the silver nitrate procedure as an analytical method for the quantitative determination and removal of a tertiary alkyl chloride from mixtures containing isomeric tertiary and secondary alkyl chlorides.¹²

The product fraction from a scaled up reaction mixture was isolated by preparative gas chromatography (20 ft × 3/8 in. Carbowax Prep, 80°, A-90P, 50 cc/min of He). The isolated fraction, although showing only one vpc peak,¹¹ proved on treatment with alcoholic silver nitrate to be a mixture of two chlorides, the unrearranged adduct, 2-chloro-3,3-dimethylbutane (17%), and the rearranged adduct, 2-chloro-2,3-dimethylbutane (83%). Thus, on treating the fraction isolated from the scaled up experiment with

alcoholic silver nitrate, rapid precipitation of AgCl occurred accounting for 83% of the total product. The relatively unreactive chloride, amounting to ca. 17% of the material balance, proved after chromatographic purification to be identical with an authentic sample of 2-chloro-3,3-dimethylbutane. The results are summarized in Table I.

Reaction of 3,3-Dimethylbutene with Hydrogen Chloride. 3,3-Dimethylbutene (0.1 ml, 0.0077 mol) was placed in the bottom of a small vial. Hydrogen chloride was collected as described for the reaction with 3-methyl-1-butene. After the amount of solid hydrogen chloride collected was visibly greater than the amount of alkene, the flask was warmed to -78°. Excess hydrogen chloride boiled off, and when the evolution of gas had ceased, the vial was warmed to 0° and the course of the reaction followed by gas chromatography (6 ft × 1/8 in. Carbowax 20M, 50°, 20 cc/min of N₂, Hy-Fi). A single new peak appeared during the reaction which proved in fact to arise from the difficultly separable mixture¹¹ of the two isomeric chlorides (Table I), the unrearranged, 2-chloro-3,3-dimethylbutane (50%) and the rearranged, 2-chloro-2,3-dimethylbutane (50%). In a control experiment, equimolar amounts of the authentic chlorides were dissolved in nitromethane and the resulting solution was shown to behave in the same manner with respect to vpc retention time, nmr spectral analysis, and alcoholic AgNO₃ treatment as the product mixture isolated from the above experiment.

Reaction of 2-Chloro-3,3-dimethylbutane with HCl in CH₃NO₂. Authentic 2-chloro-3,3-dimethylbutane (0.10 ml, 0.00073 mol) was dissolved in 0.90 ml of nitromethane which was 0.9 M in HCl. At various intervals solution aliquots were withdrawn and after being freed of HCl were analyzed for the presence of 2-chloro-2,3-dimethylbutane with cold alcoholic AgNO₃. Only a small change occurred over a period of 3 days.

Reaction of 1-Methylcyclopentene with Deuterium Chloride in Nitromethane. 1-Methylcyclopentene (4.1 g, 0.05 mol) was placed in a 50-ml volumetric flask and the solution made up to volume with 0.90 M deuterium chloride in nitromethane. This resulted in a solution 1.0 M in alkene and 0.80 M in deuterium chloride. After 4 hr a small sample that had been saved had an acid concentration less than 0.0002 M. The bulk of the reaction solution was distilled after 50% reaction at 140 mm and the first fraction was found to contain the product. Isolation of the product was achieved on a 0.5-in. Carbowax column at 90° (A-90P, 50 cc/min of He). The isolated product (0.5 ml) was added to 3 ml of dimethyl sulfoxide and to this solution was added 2 ml of *t*-butyl alcohol saturated with potassium *t*-butoxide. The reaction mixture was allowed to stand for 5 min and then distilled until all of the alkene fraction had been collected. The sample collected was submitted twice for mass spectral analysis. A reaction that was stopped after 20% reaction gave the same results. Analysis by gas chromatography showed only one product peak (A90P, 10 ft × 0.25 in. Carbowax 20M,

(11) We are grateful to Dr. R. C. Fahey for informing us that 2-chloro-3,3-dimethylbutane is not separable from 2-chloro-2,3-dimethylbutane on packed vpc columns up to 25 ft in length and that these compounds could only be adequately resolved on a 300-ft capillary column.

(12) Y. Focker and J. H. Wong, unpublished observations.

50°, 50 cc/min of He). The retention time was identical with that of 1-methylcyclopentene, 3.65 min.

Reaction of 1-Methylcyclopentene-2,5,5-*d*₃ with Hydrogen Chloride in Nitromethane. This reaction was carried out in the same manner as the addition of deuterium chloride to the undeuterated alkene. Quantities used were 0.43 g (0.005 mol) of alkene and 4.5 ml of nitromethane 0.90 *M* in hydrogen chloride. Work-up was carried out as in the previous case. The gas chromatogram again showed only one product peak (same conditions as previous compound). The mass spectrum was obtained as before. In both cases just described an attempt was made to obtain a mass spectrum of the product isolated before reaction with base. It was never possible to obtain a parent peak for the chlorides.

Results

I. Addition of Hydrogen Chloride to 3-Methyl-1-butene and 3,3-Dimethyl-1-butene in Nitromethane and in the Absence of Solvent. The addition of hydrogen chloride to 3-methyl-1-butene is very slow and the hydrogen chloride catalyzed decomposition of the solvent becomes progressively significant. Consequently, analysis of reaction mixtures had to be carried out at low percentage conversion.

Nitromethane solutions 0.1 *M* in 3-methyl-1-butene and 0.05 *M* in hydrogen chloride were analyzed by gas chromatography over a period of a week and the chromatograms compared to those obtained using olefin 1.5 *M* and acid *ca.* 1 *M*. Both sets of chromatograms gave the same peaks. Thus it was possible to obtain larger peaks during shorter reaction times using high reactant concentrations. From the time that the product peaks could be analyzed with consistent precision, *i.e.*, at *ca.* 3% reaction, the ratio of 2-chloro-2-methylbutane to 2-chloro-3-methylbutane was about 2:1. This value decreased to 1.4:1 during a period of 3 days. The analysis of these mixtures was as described below. The retention times of the products were compared to authentic samples of both chlorides run under conditions as close to identical as possible, *i.e.*, one right after another. The chromatogram of the reaction mixture was also compared to those obtained by adding authentic chloride samples to a reaction aliquot.

As a comparison to earlier work⁴ the reaction of hydrogen chloride with 3-methyl-1-butene was carried out in the absence of solvent. The results were in essential agreement with those obtained by Whitmore. Two products were obtained and identified by gas chromatography as 2-chloro-3-methylbutane and 2-chloro-2-methylbutane in the ratio 40:60.

The reaction of 2-chloro-3-methylbutane with hydrogen chloride in nitromethane was examined under the same conditions as the addition of the acid to 3-methyl-1-butene. This study showed that hydrogen chloride is a fairly powerful catalyst for the rearrangement of 2-chloro-3-methylbutane to 2-chloro-2-methylbutane. Approximately 7% rearrangement occurred in a period of 3 days. Although 2-chloro-3-methylbutane rearranges to 2-chloro-2-methylbutane under the influence of hydrogen chloride, this pathway cannot account for all of the rearranged chloride obtained in the initial stages of the addition of hydrogen chloride to 3-methyl-1-butene. Rearrangement is probably a major cause of the change in product composition.

In the same manner as described for 3-methyl-1-butene, the addition of hydrogen chloride to 3,3-dimethylbutene was followed both by gas chromatography and rate of acid disappearance. The olefin was 1.0 *M* and the acid 0.78 *M*. Two components were detected

during the course of the reaction (Table I) and were identified as 2-chloro-3,3-dimethylbutane (17%) and 2-chloro-2,3-dimethylbutane (83%). The reaction was allowed to continue to completion and the product mixture isolated using preparative gas chromatography. The nmr spectrum was identical with that of a mixture made up of authentic 2-chloro-2,3-dimethylbutane (⁵/₆) and 2-chloro-3,3-dimethylbutane (¹/₆). Treatment with cold alcoholic AgNO₃ removed the reactive component, 2-chloro-2,3-dimethylbutane, but left the unreactive component, 2-chloro-3,3-dimethylbutane, essentially intact.

The addition was repeated in the absence of solvent. The two isomeric chlorides again appeared as a single peak on the vpc but were separated by treatment with cold alcoholic AgNO₃ (Table I). The addition of hydrogen chloride to 3,3-dimethyl-1-butene was shown to give both unrearranged chloride, Me₃C·CHCl·Me (50%), and rearranged chloride, Me₂CCl·CHMe (50%). An nmr spectrum of a solution containing authentic 2-chloro-2,3-dimethylbutane and 2-chloro-3,3-dimethylbutane in the ratio 1:1 showed the same spectrum, within the accuracy limits of the experiment, as the product mixture isolated from the addition experiment.

Experiments were carried out to test whether the addition of hydrogen chloride to 3,3-dimethylbutene produces first 2-chloro-3,3-dimethylbutane which then rearranges to the more stable 2-chloro-2,3-dimethylbutane more rapidly than addition takes place. An authentic sample of 2-chloro-3,3-dimethylbutane was dissolved in nitromethane containing an equivalent amount of hydrogen chloride and aliquots were periodically analyzed, after HCl removal, using cold alcoholic AgNO₃. Only a small change could be detected in the composition of the reaction solution indicating that within the limits of detection little or no 2-chloro-2,3-dimethylbutane could be obtained *via* 2-chloro-3,3-dimethylbutane and it has to be formed during the addition process (kinetic control).

II. The Addition of Hydrogen Chloride and Deuterium Chloride to 1-Methylcyclopentene in Nitromethane. 1-Methylcyclopentene was chosen as the compound best suited for our stereochemical studies. Prior to undertaking these, we felt it necessary to confirm that the kinetics of addition of hydrogen chloride are strictly first order in olefin and second order in acid as observed in previous cases examined.

Table II presents the data obtained with hydrogen chloride and Table III the data for deuterium chloride. The isotope effect is $k_H/k_D = 0.61$.

Table II. Initial Second- and Third-Order Rate Coefficients. Addition of Hydrogen Chloride to 1-Methylcyclopentene at 25.0°

[Olefin], <i>M</i>	[Acid], <i>M</i>	10 ³ <i>k</i> ₂ , ^a <i>M</i> ⁻¹ sec ⁻¹	<i>k</i> ₃ , <i>M</i> ⁻² sec ⁻¹
0.0205	0.0550	44.5	0.809
0.0109	0.0183	14.0	0.763
0.00513	0.0116	9.85	0.850
0.00456	0.0321	26.5	0.826
0.00524	0.0234	18.4	0.787

^a Possible variation in *k*₂ due to error in determining initial slopes is about ±3%.

Kinetics and Isotope Effects in the Dehydrohalogenation of 1-Chloromethylcyclopentane and 1-Chloromethyl-

Table III. Initial Second- and Third-Order Rate Coefficients. Addition of Deuterium Chloride to 1-Methylcyclopentene at 25.0°

[Olefin], <i>M</i>	[Acid], <i>M</i>	$10^3 k_2,^a M^{-1} \text{sec}^{-1}$	$k_3, M^{-2} \text{sec}^{-1}$
0.00490	0.0373	49.2	1.32
0.00593	0.0128	17.1	1.33
0.00464	0.00856	11.0	1.29
0.00821	0.0244	32.0	1.31
0.00636	0.0129	17.4	1.35

^a Possible variation in k_2 due to error in measurement of initial slopes is about $\pm 2\%$.

cyclopentane-2,2,5,5- d_4 . The analysis of the addition product obtained when hydrogen chloride is added to 1-methylcyclopentene required a detailed knowledge of the kinetics and the isotope effect associated with the dehydrohalogenation of 1-chloromethylcyclopentane. Thus the rate of elimination of hydrogen chloride from 1-chloromethylcyclopentane using *t*-butoxide as base was measured in 68% dimethyl sulfoxide–32% *t*-butyl alcohol solvent by measuring the rate of formation of acid. The results are given in Table IV.

Table IV. Rate Coefficients. Base-Catalyzed Elimination of Hydrogen Chloride from 1-Chloromethylcyclopentane at 25.0°

[<i>t</i> -BuOK], <i>M</i>	[RCl], <i>M</i>	$10^3 k_2, M^{-1} \text{sec}^{-1}$
0.0462	0.0295	8.59
0.0701	0.0429	7.96
0.0941	0.0290	8.35
0.117	0.0449	9.93
0.140	0.0474	11.4

In the same manner as described above for the undeuterated chloride and under the same conditions, the rate of elimination of deuterium chloride from 1-chloromethylcyclopentane-2,2,5,5- d_4 was measured. The data are presented in Table V along with k_H/k_D at various concentrations of base.

Table V. Rate Coefficients. Base-Catalyzed Elimination of Deuterium Chloride from 1-Chloromethylcyclopentane-2,2,5,5- d_4 at 25.0°

[<i>t</i> -BuOK], <i>M</i>	[RCl], <i>M</i>	$10^3 k_2, M^{-1} \text{sec}^{-1}$	k_H/k_D^a
0.0475	0.0444	3.02	2.84
0.0706	0.0439	2.94	2.71
0.0949	0.0437	3.11	2.68
0.119	0.0460	3.77	2.63
0.143	0.0440	4.11	2.77

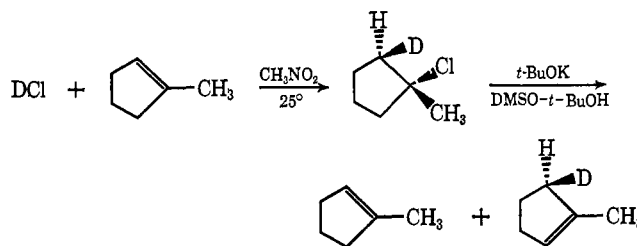
^a Corrected for amount of nondeuterated material in sample.

In an experiment in which no base was added the amount of acid liberated after a period equivalent to ten half-lives for 0.07 *M* base was measured. The acid present corresponded to less than 1.3% reaction. Thus there is essentially no uncatalyzed reaction concurrent with the base-catalyzed process, *i.e.*, the reaction is E2.

A solution was prepared that contained equal amounts of the deuterated and undeuterated chlorides and one half of the base necessary to effect complete elimination. The olefins were removed and analyzed by mass spectrometry. The results led to an isotope effect of 2.6 of the elimination. The average k_H/k_D

from all experiments was 2.7 and this value was used in the treatment of all later data.

III. The Stereochemistry of Addition. Deuterium chloride was allowed to react with 1-methylcyclopentene in nitromethane to an extent of 50%. The product was isolated and treated with base under the same conditions as were used in the kinetic studies. The olefin was collected and then analyzed by mass spectrometry. The reaction scheme and the stereochemical conclusion reached are shown below.



With k_H/k_D 2.7, the results shown in Table VI would be predicted. The mode of addition is consequently *trans* $96 \pm 3\%$ of the time. The sequence of reactions described above was repeated using hydrogen chloride and 1-methylcyclopentene-2,5,5- d_3 .

Table VI

Mode of addn/mode of elim	, %	, %
<i>trans/trans</i>	73	27
<i>cis/trans</i>	100	0
Obsd intensities ^a	250.1	84.3
Percentage composition	75	25

^a Corrected for per cent H in DCl.

With $k_H/k_D = 2.7$ and 1-methylcyclopentene-2,5,5- d_3 95% isotopically pure (5% H random on 2 and 5 positions), the results shown in Table VII would be pre-

Table VII

Mode of addn/ mode of elim	% mass 83 (1 D)	% mass 84 (2 D)	% mass 85 (3 D)
<i>trans/trans</i>	1.35	20.3	69.4
<i>cis/trans</i>	2.56	97.4	
Obsd intensities ^a		137.3	276.8
Percentage composition	1.41	32.7	65.9

^a Corrected for isotopic composition of starting material.

dicted. This corresponds to $95 \pm 4\%$ *trans* addition. Following Shiner, the secondary deuterium isotope effect observed in bimolecular eliminations is very small and can be neglected.¹³

It should also be noted here that a reaction path *via* methylenecyclopentane is excluded by the observation of only one alkene product on gas chromatographic analysis coupled with the fact that the isomerization of methylenecyclopentane by potassium *t*-butoxide in DMSO is *at least* 26 times slower than the elimination.¹⁴ Under the conditions employed in the present investi-

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(14) A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962).

gation, such an isomerization should be further slowed down relative to the elimination process.

Discussion

We have previously shown that the reaction of olefins with hydrogen chloride in nitromethane follows third-order kinetics, *i.e.*, $V = k_3[\text{olefin}][\text{HCl}]^2$. The available data were sufficient to demonstrate that the rate-determining step was the transfer of a proton from acid to olefin and that molecular acid was the proton donor. It was tacitly assumed that the addition of hydrogen chloride to aliphatic olefins proceeds *via* a carbonium ion intermediate, though the data did not *require* such a path.

We now wish to show that in intimately related systems an electron-deficient intermediate is required to explain the products formed during the kinetically controlled portion of the reaction. The addition of hydrogen chloride to 3-methyl-1-butene and 3,3-dimethyl-1-butene was carried out neat (Whitmore's conditions) and in nitromethane (the conditions used in the work described previously). 3-Methyl-1-butene gives almost equal amounts of secondary and tertiary (rearranged) chloride both in the absence of solvent and in nitromethane, while 3,3-dimethyl-1-butene gives equal amounts of secondary and tertiary chloride in the absence of solvent but only 17% of the unrearranged secondary chloride in nitromethane. The rearrangement of 2-chloro-3-methylbutane to 2-chloro-2-methylbutane under the reaction conditions is far too slow to account for more than slight variations in the product ratio, while in the case of 2-chloro-3,3-dimethylbutane, little or no rearrangement could be observed under the reaction conditions. Thus rearrangement occurs concurrently with addition and not subsequent to it. The most direct explanation of these results is that addition proceeds *via* an intermediate containing a carbon atom with an incomplete octet (*i.e.*, a carbonium ion) which, under suitable conditions, may rearrange rapidly to a more stable carbonium ion. Addition of a proton to the olefins in question would lead to such a situation as both 3-methyl-1-butene and 3,3-dimethyl-1-butene would form secondary carbonium ions adjacent to tertiary centers, and in the latter case the ion is also a neopentyl ion. The degree of freedom of the carbonium ion is not defined by these results as the relative position of the HCl_2^- group during product formation is not available. The observed salt effects and the occurrence of exclusive 1,2 addition to isoprene strongly suggest that the first intermediate is, in fact, a carbonium ion pair with hydrogen dichloride.^{1b} Presumably the formation of the hydrogen dichloride ion is a consequence of hydrogen bonding to the developing chloride ion during proton addition. Thus the position normally occupied by solvent in protic media is assumed by hydrogen chloride in nitromethane (and probably in any less polar aprotic solvent).

The kinetics of addition of hydrogen chloride to 1-methylcyclopentene were studied in order to show that the reaction obeyed the same rate law. This is a necessary requirement if the stereochemistry of addition to 1-methylcyclopentene is to have any general significance. Examination of Table I shows that the addition does follow the expression $V = k_3[\text{olefin}][\text{HCl}]^2$ as has been observed in all of our studies. Before consideration of the results of the present stereochemical experiments, it is profitable to mention prior constraints on the mechanism imposed by previous experiments. The observance of Wagner-Meerwein rearrangements concurrent with addition rules out a concerted addition as a general pathway and also makes the postulation of attack of HCl_2^- on a π complex unattractive. Free carbonium ions are incompatible with the observation that the addition to dienes leads to 1,2 addition exclusively under kinetic control (previous paper). The observed stereochemical results indicate that the addition of hydrogen chloride to 1-methylcyclopentene proceeds to give $96 \pm 4\%$ *trans* addition. It is tempting to claim that the side of proton attack is blocked for the subsequent addition of chloride, but examination of molecular models of the carbonium ion (in contrast to those of the π complex) indicates that this is not the case, unless one also considers the rapid attack by the optimally positioned HCl_2^- ion of the tight ion-pair intermediate.

Account must be taken of the fact that the formation of the intermediate is rate determining since there is no isomer interconversion or deuterium incorporation accompanying addition. Recently Fahey has suggested that *trans* addition to cyclohexene in acetic acid may proceed *via* a termolecular path.¹⁵ He found that at higher concentrations the amount of *trans* chloride and the amount of reaction *via* a termolecular pathway increased simultaneously. He also observed a second-order process leading to *cis* chloride. In nitromethane, such a second-order component has been detected using very low concentrations of hydrogen chloride. Additionally, in the reverse reaction, there is a measurable component of elimination which is first-order in alkyl chloride but zero order in hydrogen chloride.¹⁶ In the present case, formation of *trans* chloride would not require any change in the observed stoichiometry since product formation follows the rate-determining proton-transfer step. Examination of molecular models shows that *cis* addition by donation of a chloride from the linear hydrogen dichloride ion¹⁷ is not always a process that would be easily accomplished, while *trans* attack is indeed considerably more favorable from an orientation point of view.

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