[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE UNIVERSITY]

The Steric Course of Hydration of 1,2-Dimethylcyclohexene

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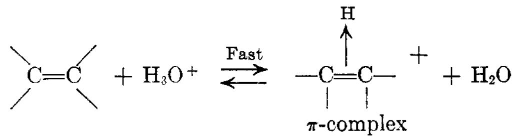
Hydration of 1,2-dimethylcyclohexene in aqueous nitric acid gives nearly equal amounts of *cis-* and *trans*-1,2-dimethylcyclohexanol. The result is consistent with any mechanism in which the product-determining step involves hydration of a carbonium ion.

Much information, both kinetic[3–12] and isotopic,[13] has been presented on the mechanism of the acid-catalyzed hydration of olefins to tertiary alcohols. On the basis of this evidence, Taft[8] proposed a mechanism for the hydration which involved both a π-complex and a classical carbonium ion, as shown in equations 1-3. Step 1, the protonation of the double bond to form the π-complex, and step 3, the conversion of the carbonium ion to to the alcohol, are considered to be relatively rapid; while step 2, the interconversion of the π-complex and the classical carbonium ion, is regarded as rate-determining.



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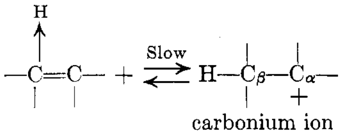
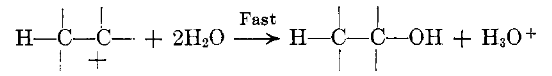


$$-\overset{\overset{H}{\uparrow}}{C}=C- + \overset{\text{Slow}}{\rightleftarrows} H-C_{\beta}-\underset{+}{C_{\alpha}}- \quad (2)$$



$$H-C-\underset{+}{C}- + 2H_2O \xrightarrow{\text{Fast}} H-C-C-OH + H_3O^+ \quad (3)$$

Further refinements by Taft have described the π-complex as nearly olefinic, with a trigonal, coplanar structure and the proton embedded in the electron cloud,[14] *i.e.*, a nonequivalent proton.[13] This is distinguished from both the bridged-hydrogen species[15] and the transition state of Equation 2, which resemble the π-complex in geometry but have more of the electronic character of carbonium ions.[16] Kinetic evidence indicates, but does not compel, the conclusion that the rate-determining step does not involve a proton transfer[13] and that no water is tightly bound to the system in the transition state.[10,11]

Such a mechanism would not be expected to be highly stereospecific if a planar carbonium ion is formed in reaction 2. Even if the lifetime of the cation were short in comparison with rotation about the C_{α}—C_{β} bond, the direction of approach of the water molecule should be determined largely by steric interactions with the substituents attached to C_{β}. Any steric preference introduced by such an effect would probably result in preferential *cis* addition.

Recently, work with several strong acids has shown a *trans* stereospecificity to the addition reaction. Thus, Hammond and Nevitt[17] have observed a clean, stereospecifically *trans* addition of hydrogen bromide to 1,2-dimethylcyclohexene; Hammond and Collins[18] have observed a similar *trans* stereospecificity with hydrogen chloride and 1,2-dimethylcyclopentene; Winstein and Holness[19] have observed a stereospecific attack of formic acid on 4-*t*-butylcyclohexene, and Schleyer[20] has observed a stereospecific proton addition in the reaction of 1-methylnorbornene with formic acid and with ethanolic hydrochloric acid. In each case, the stereospecificity observed was explained by direct attack of the anion on the π-complex or, at least, a sufficiently concerted opening of the complex, coupled with attack of the anion, to yield stereochemically pure product.

The current work on the hydration of 1,2-

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TABLE I

PRODUCT COMPOSITION IN HYDRATION OF 1,2-DIMETHYLCYCLOHEXENE

Run No.	Concn. Nitric Acid	Time, Days	Temp.	Alcohol		Recovered Alkene,[a] %	
				trans	*cis*	1,2-	2,3-
1	0.1M	1	50	52	48		
2	0.1M	7	50	64	36		
3	0.1M	30	50	58	42	89	11
4	0.1M	5	50	55	45		
5	1.0M	5	28	55	45	93	7

[a] Original mixture contained 85% 1,2-dimethylcyclohexene and 15% 2,3-dimethylcyclohexene.

dimethylcyclohexene was undertaken to resolve the question of the stereochemistry.

RESULTS AND DISCUSSION

Table I lists the relative amounts of the *cis-* and *trans*-1,2-dimethylcyclohexanols formed in the hydration experiments. Although the total conversion to alcohols was small (less than 10% of the total sample analyzed), with virtually all of the rest of the material being unchanged olefin, the percentages observed for the *cis-* and *trans*-alcohols indicate nearly equal amounts of each isomer in both 0.1M and 1.0M nitric acid solutions. The composition of the remaining olefin is also noted. Thus, it is seen that the olefin composition changes little from its original value (85% 1,2-dimethylcyclohexene) in the more dilute acid, while some isomerization is detectable in the more concentrated acid solution. The actual equilibrium mixture contains even greater amounts of the symmetrical alkene.

To determine if equilibration of the *cis-* and *trans*-1,2-dimethylcyclohexanols were causing the near equivalence of the isomeric composition in the hydration experiments, several different alcohol mixtures were subjected to similar treatment. Results are given in Table II and indicate that, within experimental error, no (dilute) acid-catalyzed isomerization was taking place.

TABLE II

EQUILIBRATION STUDIES WITH 1,2-DIMETHYLCYCLOHEXANOLS IN 0.1M NITRIC ACID

Run No.	% Composition				Time, Days
	Starting Material		Recovered Material		
	trans	*cis*	*trans*	*cis*	
1	100	0	100	0	1
2	100	0	100	0	1
3	43	57	48	52	1
4	43	57	42	58	1
5	27	73	23	77	3
6	27	73	26	74	1

As the nearly equivalent amounts of *cis-* and *trans*-1,2-dimethylcyclohexanol found in the hydration of 1,2-dimethylcyclohexane are not the result of an isomerization of a stereospecifically formed alcohol but rather are the actual results of the hydration itself, the results are in agreement with any mechanism, including that of Taft,[8] in which the product determining step involves hydration of an open carbonium ion.[21]

As the stereochemical course of hydration is different from that observed in addition of certain acids in organic solvents, there must be some mechanistic differences. However, the variations suggested are both small and of a character which might be anticipated. Both types of reaction can be reasonably formulated as involving complexes between an alkene and a proton (or molecular acid). If it is granted that such complexes maintain their integrity and react directly with a nucleophile in organic solvents, one could hardly devise conditions more favorable for allowing the complexes to isomerize to a carbonium ion than those obtaining in the hydration studies. The reaction is carried on in a medium (water) of high dielectric constant with a good capacity for specific solvation of cations, and the nucleophile (water) ultimately involved in the reaction is less reactive than those involved in most of the stereo-specific reactions.

The fact that two electrophilic addition reactions, hydrogen bromide adition and hydration, with a single substrate, 1,2-dimethylcyclohexene, give different stereochemical results indicates that predictions of the stereochemistry of such reactions will probably be unsafe unless they are based upon very close analogies. Similar pessimism is probably also warranted concerning other problems, such as prediction of the likelihood of molecular rearrangements in the course of addition reactions.

EXPERIMENTAL

Materials. cis- and trans-1,2-Dimethylcyclohexanol were prepared by the method of Nevitt and Hammond.[22] Physical constants were: *cis*-alcohol, b.p. 78.9–79.6° at 25 mm.

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[21] A referee has suggested that, if the rate of hydration of 2,3-dimethylcyclohexene is much faster than that of the 1,2-isomer, most of the alcohols could come from that compound and mixtures could be produced by concerted, *trans*-addition. We agree, but feel that this is unlikely in view of the usual reactivity relationships among variously substituted alkenes.

[22] T. D. Nevitt and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 4124 (1954).

(lit.,[22] b.p. 95.7 at 53 mm.) and *trans*-alcohol, b.p. 72.4–72.9° at 25 mm. (lit.,[22] b.p. 86.8° at 52 mm.).

1,2-Dimethylcyclohexene was prepared by dehydration of the mixed alcohols by heating the mixture with iodine. The distilled olefin, b.p. 136.0–136.1° at 735 mm. (lit.,[17] b.p. 135.4–135.9°) was shown to contain 85% 1,2-dimethylcyclohexene and 15% 2,3-dimethylcyclohexene by gas chromatographic analysis on a 6-foot column using Apiezon L grease as the liquid phase. The olefin peaks were distinct and well separated. Calculation was by triangulation,[23] and the results are reproducible to ±2%. The infrared spectrum of this sample was identical with that obtained by the previous workers.[17]

Procedure. For the hydration experiments, 15 ml. of aqueous nitric acid (1.0 or 0.1*M*) was placed in a small flask and 1 g. of 1,2-dimethylcyclohexene added. The flask was fitted with a condenser and magnetic stirring bar and placed in a constant temperature bath (28° or 50°) where the solution was stirred for periods varying from 1 to 30 days. At the end of these intervals, the sample was extracted with pentane. The pentane solution was washed with water and sodium bicarbonate solution and dried briefly over anhydrous calcium sulfate. The pentane was then removed by distillation, and the products were analyzed by gas chromatography at 150° on a 6-foot column with Apiezon L grease as the liquid phase. The *cis*- and *trans*-alcohol peaks showed some overlapping but calculation (by triangulation)[22] of the amounts present was possible. However, because of this overlapping, the results are probably accurate only to ±3–4%.

For the equilibration experiments, 1 g. of an alcohol mixture of known composition was placed in 15 ml. of 0.1*M* nitric acid solution. Further treatment was identical with that of the hydration experiments.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MONTANA STATE UNIVERSITY]

Addition of Nucleophilic Reagents to *o*- and *p*-Cyanostyrene

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A new improved synthesis of *o*-cyanostyrene was developed. Reactions of a variety of amines and thiols with both *o*- and *p*-cyanostyrene were carried out and the yields were compared to those of similar reactions previously performed with α-cyanostyrene[3] and 2,4-pentadienenitrile.[2] Results indicate a considerable diminishing of the electron-withdrawing effect of the cyano group when passed through the benzene ring conjugation.

o-Cyanostyrene and *p*-cyanostyrene may be considered to be vinylogs of acrylonitrile. Vinylogs are related compounds of the type formula $A(CH{=}CH)_nB$, in which the groups A and B are linked through one or more conjugated vinylene groups. An empirical rule developed by Angeli[1] has been useful in correlating the relations observed in reactions of certain vinylogs. It states that substituent groups situated *ortho* or *para* to each other on a benzene nucleus behave qualitatively as though they were joined directly. Accordingly, it would be predicted that *o*-cyanostyrene might correspond closely to the open chain vinylog, 2, 4-pentadienenitrile ($CH_2{=}CH{-}CH{=}CH{-}CN$), of acrylonitrile—one conjugated vinylene group being part of the benzene ring.

Compounds which contain an alkene linkage directly connected to a highly electron-withdrawing group, or conjugated with it through other vinylene linkages, react by addition across the alkene linkage with nucleophilic reagents which contain labile hydrogen atoms—for example, with primary and secondary amines, thiols, and phenols. Thus, reactions of this type have been carried out with 2,4-pentadienenitrile[2] and atroponitrile[3] (α-cyanostyrene), and the results have been compared with the familiar cyanoethylation reactions of acrylonitrile. It was of interest, therefore, to study the addition of nucleophilic reagents to *o*-cyanostyrene and *p*-cyanostyrene and to determine whether the electron-withdrawing effect of the cyano group upon the alkene linkage is diminished when passed through the benzene ring conjugation.

o-Cyanostyrene has been prepared by Marvel and Hein[4] by the decarboxylation of *o*-cyanocinnamic acid following a sequence of reactions starting with *o*-tolunitrile. The compound has also been reported as prepared in a British patent to the Wingfoot Corporation[5] by direct chlorination of *o*-ethylbenzonitrile, followed by pyrolysis of the chloroethyl derivative to give *o*-cyanostyrene. It was impossible to duplicate the latter procedure in this investigation. The over-all yield in method

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