64–66°, 70.5–71.5°). The solid was unstable at room temperature and decomposed in a few hours with liberation of hydrogen bromide. The material must be recrystallized and stored at ice temperature or below. Purified acenaphthylene deuteriobromide obtained by this procedure was used in the isomerization studies and dehydrobromination reactions described below.

The isomerization studies were conducted in a fashion very similar to that given above. A solution of purified bromide in methylene chloride was placed in the reaction flask and the required deuterium bromide distilled in. After the reaction interval the solvent and excess deuterium bromide were removed under vacuum as above. The fact that samples of the bromide submitted to the reaction conditions and worked up in this fashion showed no isomerization (expt. 19 and 20) demonstrates that no isomerization was taking place during isolation.

Experiments aimed at establishing the effect of deuterium bromide concentration on the stereochemistry of addition were carried out by preparing a solution of deuterium bromide in methylene chloride in the reaction flask and adding a concentrated solution of acenaphthylene in methylene chloride through the syringe cap. In this way the concentration of deuterium bromide remained between definite limits during the reaction. The work-up procedure described above was also used in these experiments.

When hydrogen bromide was added to equal amounts of acenaphthylene and styrene in methylene chloride the n.m.r. spectrum of the product showed, in addition to the peaks characteristic for 1-bromoacenaphthene, a doublet at high field (8.1 τ) and a quartet at low field (4.9 τ) characteristic of (2-bromoethyl)-benzene.

A procedure similar to that described by Hammond and Nevitt[6] was used for the additions carried out in deuterioacetic acid. A solution of deuterium bromide (2 *M*) in deuteroioacetic acid was prepared. A sample (2 ml.) of this solution was added to a solution of acenaphthylene (3.3 mmoles) in deuterioacetic acid (2.5 ml.) with shaking in a separatory funnel. After the reaction interval, ice-water and methylene chloride were added and the mixture agitated to quench the reaction. The organic layer was separated, dried over anhydrous sodium carbonate, and filtered. The solvent was removed on a rotary evaporator and the residue prepared for n.m.r. analysis as described above.

Dehydrobromination Experiments.—In a typical run 15 mmoles of purified acenaphthylene deuteriobromide was treated with a solution of potassium *tert*-butoxide in *tert*-butyl alcohol (25 ml. of 1 *M*). The mixture was stirred at 75° for 2 hr. The characteristic yellow color of acenaphthylene developed rapidly and solid potassium bromide separated from solution. The mixture was worked up by dumping into water and extracting twice with methylene chloride. The organic layer was separated, washed with dilute hydrochloric acid, and dried over anhydrous sodium carbonate. After filtration, the solvent was evaporated to give 80–90% crude yields of acenaphthylene. Sublimation gave yellow leaflets, m.p. 89–91°, which were submitted for mass spectral analysis.

Addition of Deuterium Chloride to Acenaphthylene.—The procedure used was similar to that described for addition of deuterium bromide. The reactions were run in saturated solutions of deuterium chloride in the solvent and saturation was maintained throughout the reaction by passing a slow stream of deuterium chloride into the reaction mixture. Runs in methylene chloride were worked up by evaporation of solvent and deuterium chloride under vacuum. Runs in deuterioacetic acid were worked up by pouring the reaction mixture into ice-water, extracting with methylene chloride, washing the organic layer with dilute sodium bicarbonate solution and drying over anhydrous magnesium sulfate. After filtration the solvent was evaporated. The products in these reactions were yellow oils which solidified only below 0°. N.m.r. spectra were obtained on neat samples of the product.

N.m.r. Analysis.—The samples for n.m.r. analysis were stored in Dry Ice until just before the spectra were run. No detectable isomerization occurred during the period required to complete the analysis. Details of the n.m.r. procedure and of the decoupling techniques employed will be given elsewhere. The ratio of *cis* to *trans* isomer was established from peak height measurements. Values obtained in this way compared well with estimates obtained from integrated intensity measurements. From 6 to 12 traces were obtained for each sample with field sweep in both directions. Average deviation in the measured values for a given sample was usually less than 1%; however, systematic errors due to incomplete resolution of the resonance lines probably reduces the absolute accuracy. It is thought that the analysis in most cases is reliable to ±2–3%. Spectra obtained from samples of the acenaphthylene deuteriochloride were essentially identical in pattern with those obtained from the bromide.

The % reaction was estimated from the relative intensity of the signal at 4.25 τ characteristic for the addition product and the signal at 3.08 τ characteristic for the C_1–H protons in the unreacted acenaphthylene. The values quoted for % reaction are probably only reliable to ±5–8%.

Acknowledgment.—We are most grateful to Dr. Seymour Meyerson of the American Oil Company, Whiting, Ind., for the mass spectral analyses of acenaphthylene samples.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Electrophilic Addition to Olefins. II.[1] Addition of Deuterium Halides to Indene; the Mechanism of Addition[2]

BY MICHAEL J. S. DEWAR AND ROBERT C. FAHEY[3]

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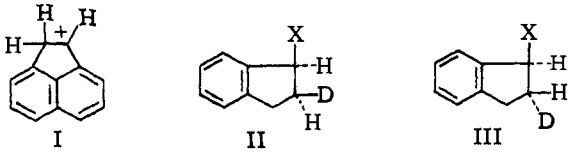
Addition of deuterium bromide to indene in methylene chloride or pentane at −78° gives 1-bromo-2-deuterioindane containing 80% of the *cis* adduct. A mechanism involving intermediate carbonium ion pairs is suggested to account for the available experimental evidence for the polar addition of hydrogen halides to olefins.

Introduction

In the preceding paper[1] we reported that polar addition of hydrogen bromide or hydrogen chloride to acenaphthylene involves *cis*-addition predominantly, an unexpected result since previous work had suggested that hydrogen halides add *trans* to olefins. Acenaphthylene is, however, a rather special case. Protonation of acenaphthylene to a classical carbonium ion (I) will be strongly favored both by the large mesomeric stabilization of (I) and by relief of strain in the five-membered ring. It is therefore conceivable that addition of hydrogen halides to acenaphthylene may take place by a classical carbonium ion mechanism leading to *cis*-addition, whereas addition to "normal" olefins may take place *trans* by a π-complex mechanism. We therefore decided to study the addition of hydrogen halides to olefins of a more conventional type.



I II III

One advantage of acenaphthylene was the absence of complications due to possible conformational effects. Owing to the rigid planarity of the five-membered ring, the classical ion I has a plan of symmetry and the two sides of the carbonium carbon are therefore equally open to attack by anions. The same situation should

(1) Part I: M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245 (1963).

(2) This work, which has been supported by a grant from the National Science Foundation, was presented at the 144th National Meeting of the American Chemical Society at Los Angeles, Calif., April, 1963.

(3) National Science Foundation Predoctoral Fellow.

hold in indene which therefore seemed the obvious choice for further study. Here the strain is less than in acenaphthylene, and a possible intermediate carbonium ion would be less stabilized (being a benzyl ion instead of an α-naphthylmethyl ion); the balance between a carbonium ion intermediate and an isomeric π-complex should be less biased in favor of the former.

Hydrogen bromide[4] and hydrogen chloride[5] are known to add easily to indene giving the polar adducts 1-bromo- and 1-chloroindane, respectively. The stereochemistry of addition can be studied by using deuterium halides in which case the products from *cis* (II) and *trans* (III) addition are distinguishable.

Results

The dehydrobromination method employed in part I[1] could not be used to establish the stereochemistry of addition in the case of indene. Attempts to eliminate hydrogen bromide from 1-bromoindane with base under various conditions all failed to give appreciable yields of indene. Fortunately the *cis* and *trans* isomers could be distinguished by the fine structure of the n.m.r. resonance line for the C_1–H proton in the addition product. The signal occurs as a doublet due to a coupling with the C_2–H proton, and this coupling is larger in the *cis* isomer than in the *trans* isomer.

A typical trace of the C_1–H proton resonance signal obtained from the addition product of deuterium bromide with indene is shown in Fig. 1A. The strong outer lines are assigned to the *cis* isomer and the weaker inner lines to the *trans* isomer, in accord with the previously established trends for variation of vicinal coupling constants with dihedral angle.[1,6] When the addition product was isomerized with lithium bromide in acetone, the recovered indene deuteriobromide gave the resonance pattern shown in Fig. 1B. The outer and inner lines are of nearly equal intensity, corresponding to equal amounts of the *cis* and *trans* isomers.

The addition of deuterium bromide to indene was carried out at −78° in methylene chloride and in pentane. The stereochemistry of the addition was established from peak height measurements on the n.m.r. spectra of the products. The results are shown in Table I. The values for *cis*-addition were generally reproducible to ±2%; however, because of systematic errors arising from incomplete resolution of the resonance lines, all of the values shown may be high or low by as much as 5%.

TABLE I

STEREOCHEMISTRY OF ADDITION OF DEUTERIUM BROMIDE TO INDENE

Solvent	Temp., °C.	Time, min.	% *cis*-addition
CH_2Cl_2	−78	10	81
		30	78
		40	79
Pentane	−78	5	80
		10	81
		20	82

In all experiments complete conversion to product was obtained. The variation in *cis*-addition with reaction time is less than the experimental error, indicating that secondary isomerization of the product was not important under the conditions of the reaction. As an additional test we treated a sample of the bromide containing 80% of *cis* isomer with a 2 molar solution of deuterium bromide in methylene chloride at −78°.

(4) C. Courtot and A. Dondelinger, *Compt. rend.*, **179**, 1168 (1924).
(5) R. Weissgerber, *Ber.*, **44**, 1436 (1911).
(6) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

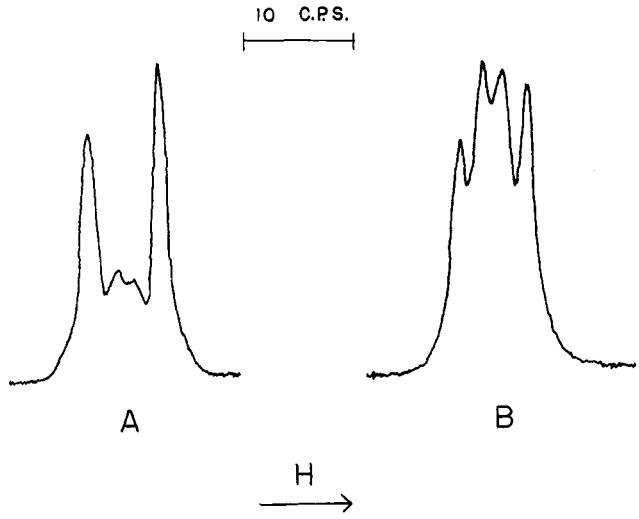


Fig. 1.—C_1–H resonance line of 1-bromo-2-deuterioindane: A, addition product; B, isomerized product.

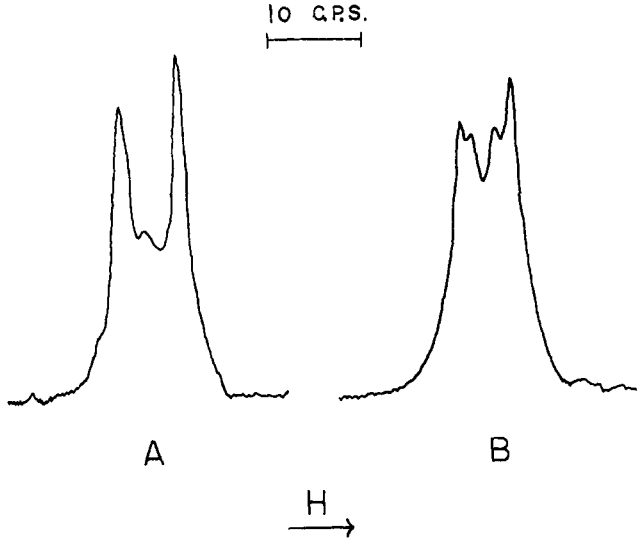


Fig. 2.—C_1–H resonance line of 1-chloro-2-deuterioindane: A, addition product; B, isomerized product.

After 15 min. the sample was worked up. Analysis of the recovered indene deuteriobromide showed it to contain 77% of *cis* isomer. The concentrations of deuterium bromide involved in the experiments reported in Table I were all less than 2 molar. Under these conditions secondary isomerization could not account for the 15–20% of *trans*-addition product formed. The *trans* adduct must therefore have been a primary addition product (*cf.* ref. 1).

Addition of deuterium chloride to indene was also studied. In this case quantitative estimates of the stereochemistry of addition were not possible. The difference in the coupling constant, J_{12}, between the *cis* and *trans* isomers was insufficient to allow resolution of the characteristic doublets. The n.m.r. spectra of the addition products were, however, consistent with predominant *cis*-addition. The product of addition in methylene chloride gave the C_1–H resonance pattern shown in Fig. 2A. Isomerized indene deuteriochloride gave the C_1–H resonance pattern shown in Fig. 2B. Although poorly resolved, four lines are distinguishable in the spectrum of the isomerized sample. Assigning the inner pair of lines to the *trans* isomer, it is seen in Fig. 2A that the product of addition must be predominantly the *cis* isomer.

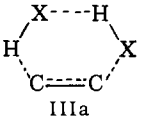
Discussion

In part I[1] we reported that acenaphthylene adds deuterium bromide or chloride predominantly *cis* by a polar mechanism; in the present paper we have reported similar results for indene. We have also found[7] that the polar addition of deuterium bromide to *cis*- or *trans*-1-phenylpropene leads in each case predominantly to *cis* adducts; full details of this work will be published shortly. These results suggest that the behavior of acenaphthylene is by no means a special case and that *cis* addition of hydrogen halides to olefins may indeed be the normal mode of reaction.

Before we discuss possible mechanisms for *cis*-addition, let us first consider some other evidence concerning these addition reactions. The kinetics of polar addition of hydrogen halides to olefins have been studied by Mayo and his collaborators. They have found that the addition of hydrogen chloride to isobutene[8] in heptane and of hydrogen bromide to propene[9] in *n*-pentane follow a rate law which is first order in olefin and close to third order in hydrogen halide. It is generally believed that the role of the extra molecules of hydrogen halide is one of solvation; a similar situation arises in the case of polar additions of halogen to olefins.

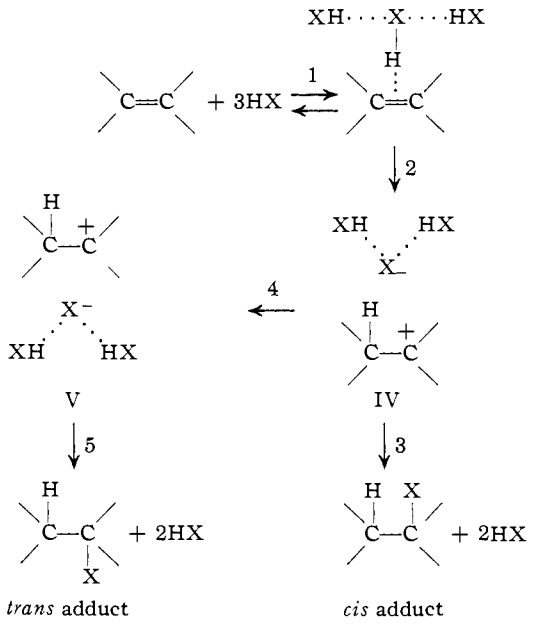
Another important observation is that, in suitable cases, rearrangement may accompany the addition of hydrogen halides to olefins. Whitmore and Johnston[10] have shown that addition of hydrogen chloride to isopropylethylene gives equal amounts of secondary isoamyl chloride and *tert*-amyl chloride. Addition of hydrogen chloride in *tert*-butylethylene gave 60–65% rearranged product while addition of hydrogen iodide gave 10% rearranged product.[11]

The number of reasonable mechanisms that can be written to explain *cis*-addition is limited. One of the more obvious possibilities is a concerted process proceeding *via* a cyclic transition state (IIIa). This process does not account for the formation of *trans* adduct as a primary reaction product. If the *cis* isomer is formed by a concerted process, there must be an additional competing route leading to *trans* adduct. Further, a concerted process does not allow for rearrangement during addition. Rearrangement during addition is most easily accounted for in terms of a classical carbonium ion.



IIIa

We believe that all the available evidence can be accommodated in terms of a reaction mechanism involving a classical carbonium ion, formed in the rate-determining step as an ion pair with a halide ion, as illustrated in the scheme in the following column. Three molecules of hydrogen halide associate with olefin to form a loose complex in the reversible step 1. Step 2 is rate determining and leads to the ion pair IV. In such an ion pair the halide ion will be held to one side or the other of the planar carbonium center; in IV, the halide ion will be attached on the same side of the original C=C bond as the entering proton. Collapse of IV leads exclusively to *cis* adduct (step 3). Alternatively, IV can rearrange to the isomeric ion pair V in which the halide ion is now on the other face of the carbonium ion (step 4); collapse of V leads to *trans* adduct (step 5).



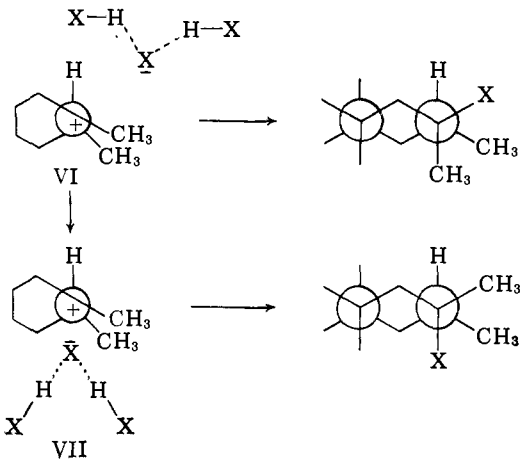
The predominant *cis*-addition observed with acenaphthylene, indene and 1-phenylpropene is explained if the collapse of the ion pair IV to *cis* adduct is fast compared with its rearrangement to V; this certainly seems a very reasonable possibility. The ion pair mechanism of course immediately explains the rearrangements observed by Whitmore, *et al.*,[11] in the addition of hydrogen halides to *t*-butylethylene; the fact that hydrogen iodide gave less rearrangement than did hydrogen chloride is also easily understood since the lifetime of the intermediate carbonium ion would be greater in an ion pair with chloride than in one containing the more nucleophilic iodide ion.

According to this mechanism, *cis*-addition should predominate in cases where electrophilic addition to an olefin takes place through a classical carbonium ion intermediate, and this should be generally true for addition of hydrogen halides. The cases of *trans*-addition of hydrogen halides reported in the literature must then be ascribed to steric effects. Any steric effect that hinders collapse of the primary ion pair IV will increase the proportion of *trans* adduct; if the *trans* adduct is the more stable isomer, steric effects of this kind can then lead to its being formed almost exclusively.

Hammond and his collaborators have reported that hydrogen halides add *trans* to 1,2-dimethylcyclohexene[12] and to 1,2-dimethylcyclopentene.[13] Consider first the case of 1,2-dimethylcyclohexene. Here the rate-determining protonation of the double bond will lead to an ion-pair of the form VI in a Newman projection. Collapse of VI to give *cis* adduct, corresponding to step 3 in the above scheme, must pass through a state in which the two methyl groups are eclipsed. On the other hand, collapse of the other ion pair VII does not involve this unfavorable eclipsing of methyl groups. It is therefore entirely reasonable to expect *trans*-addition *via* steps 4 and 5 to dominate over *cis*-addition *via* step 3. This argument assumes that the intermediates VI and VII are sufficiently short-lived that ring inversion does not occur prior to collapse to product. The activation energy for ring inversion is reported[14] to be of the order of 11 kcal. for cyclohexane so that this assumption seems well founded. A similar argument can be applied to addition to 1,2-dimethylcyclopentene;

(7) M. J. S. Dewar and R. C. Fahey, unpublished results.
(8) F. R. Mayo and J. J. Katz, *J. Am. Chem. Soc.*, **69**, 1339 (1947).
(9) F. R. Mayo and M. G. Savoy, *ibid.*, **69**, 1348 (1947).
(10) F. C. Whitmore and F. Johnston, *ibid.*, **55**, 5020 (1933).
(11) G. G. Ecke, N. C. Cook and F. C. Whitmore, *ibid.*, **72**, 1511 (1950).
(12) G. S. Hammond and T. D. Nevitt, *ibid.*, **76**, 4121 (1954).
(13) G. S. Hammond and C. H. Collins, *ibid.*, **82**, 4323 (1960).
(14) R. K. Harris and N. Sheppard, *Proc. Chem. Soc.*, 418 (1961).

the ring in cyclopentane is of course known to be nonplanar.



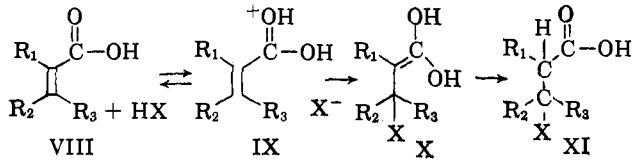
VI VII

According to this argument the predominant *trans*-addition to 1,2-dimethylcyclohexene or 1,2-dimethylcyclopentene is a steric effect; this should be less in cases where the double bond carries no alkyl substituents and here *cis*-addition might be observed. Indeed Smirnov-Zamkov and Piskovitina[15] have reported that addition of deuterium bromide to cyclohexene gives large amounts of the *cis* adduct. A similar situation might be expected to arise in the case of 1,3-cyclohexadiene. Hammond and Warkentin[16] studied the addition of deuterium bromide to this diene and obtained a mixture of adducts in the proportions: 1,2-*trans*, 12.5%; 1,2-*cis*, 33.5%, 1,4-*cis* and 1,4-*trans*, 54%. Since they believed that the primary 1,2-addition would be almost exclusively *trans*, they were forced to ascribe the large yield of *cis*-1,2-adduct to a secondary rearrangment of 1,4-adduct. However it seems more likely in view of our results and those of Smirnov-Zamkov and Piskovitina that the *cis*-1,2-adduct was in fact formed in the primary addition step.

The acid-catalyzed hydration of 1,2-dimethylcyclohexene gives almost equal amounts of *cis* and *trans* adducts,[17] unlike the additions of hydrogen bromide which took place exclusively *trans*. Collins and Hammond[17] attributed this to a difference in mechanism, the hydration alone involving intermediate carbonium ions. If we are right *both* reactions take place by a carbonium ion mechanism. However in an aqueous solution the carbonium ion will be present as a free solvated ion rather than an ion pair, and its lifetime should be much longer; now there is time for the ring to invert, leading to loss of stereospecificity.

Hydrogen halides, in particular hydrogen iodide, have been reported to add *trans* to derivatives of α-substituted acrylic acids.[18] The mechanism of these reactions has not been studied in detail and there are good grounds for believing that it may be different from that of electrophilic addition to simple olefins. Protonation of an acrylic acid derivative (VIII) would be expected to occur most easily on the carbonyl oxygen. The resulting ion IX could then add halide ion in the rate-determining step.

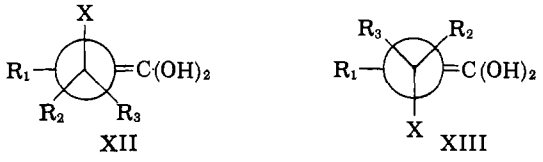
The rate-determining step would then be an acid-catalyzed nucleophilic addition analogous to the Michael reaction, and it would have no bearing on the



VIII IX X XI

entirely different electrophilic additions undergone by simple olefins.

If the reaction follows the path indicated above, the geometry of addition will depend only on the final step, in which the enolic form X of the final adduct ketonizes to XI. This reaction will take place, under acid conditions, by protonation of X followed by deprotonation. Examination of models shows that approach of a proton to X to give *cis* adduct must be sterically hindered, particularly in the case of hydrogen iodide; this is also evident from the Newman projection (XII).



XII XIII

In order to get *cis* adduct, it is necessary to rotate the molecule into the configuration indicated in XIII; examination of models shows that this rotation will be hindered if X is a bulky halogen atom and R_1 an alkyl group.

If these ideas are correct, the stereospecificity of the *trans*-addition should decrease with decreasing size of the halogen atom and it should also be less for addition to acids without an α-substituent (R_1 = H in VIII–XIII).

The π-Complex and Classical Mechanisms for Electrophilic Addition.—Our original purpose in studying addition of hydrogen halides to olefins was to obtain more definite evidence for the participation of π-complex intermediates. This objective has not been achieved; indeed, our work makes it seem almost certain that the intermediates in these reactions are *not* π-complexes, but classical carbonium ions. Collapse of the intermediate ion pairs may tend to give predominant *cis*-addition, as we have observed in the reactions of acenaphthylene, indene and 1-phenylpropene. In other cases steric effects may lead to predominant formation of *trans* adduct.

These results suggest that the mechanism of electrophilic addition to olefins needs re-examination, for it can no longer be assumed that the intermediates will necessarily be π-complexes, nor can stereospecific *trans*-addition be taken as evidence for this.

The following simple argument throws light on the possible effect of changing the electrophilic reagent on the choice between π-complex and carbonium ion intermediates. Consider the heats of formation of the carbonium ion XIV, and of the isomeric π-complex XV, formed by combination of an olefin with the electrophilic ion X^+.

XIV XV

The total energies of XIV and XV can be written

$$E(\text{XIV}) = A + E_{C-C} + E_{C-X} \quad (1)$$

$$E(\text{XV}) = A + E_{C=C} + E_{\pi} \quad (2)$$

where A is the sum of bond energies of the other bonds (which are the same in XIV and XV), E_π is the

(15) J. V. Smirnov-Zamkov and G. A. Piskovitina, *Ukr. Khim. Zh.*, **28**, no. 4 (1962), and personal communication from Professor Smirnov-Zamkov.

(16) G. S. Hammond and J. Warkentin, *J. Am. Chem. Soc.*, **83**, 2554 (1961).

(17) G. H. Collins and G. S. Hammond, *J. Org. Chem.*, **25**, 911 (1960).

(18) See W. R. Vaughan, R. L. Craven, R. Q. Little and A. C. Schoenthaler, *J. Am. Chem. Soc.*, **77**, 1594 (1955).

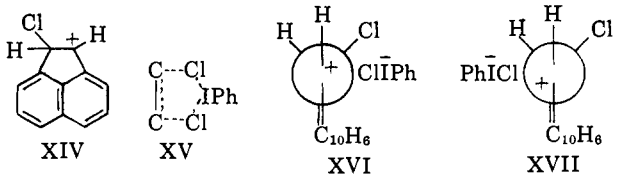
bond energy of the dative μ-bond[19] formed by the olefin with X^+, and E_{C-C}, E_{C-X} and $E_{C=C}$ are bond energies of the C—C, C—X and C=C bonds, respectively. Using Pauling's bond energies, we find that XV has the higher total bond energy unless

$$E_{C-X} > 64 + E_\pi \qquad (3)$$

Now of course there are other factors favoring the classical structure XIV; for example, the solvation energy of XIV will be greater than that of XV since the positive charge in XIV is more concentrated. Also the atom X is more or less neutral in XIV but positively charged in XV; if X is more electronegative than carbon, as is usually the case, the isomerization of XIV to XV will be hindered by the concomitant transfer of charge from carbon to X. Nevertheless this argument suggests that there should be a tendency for the π-complex structure to be favored more strongly, the smaller the bond energy of the CX bond. In an electrophilic addition of XY (in the form X^+ Y^-), the π-complex mechanism should be favored in cases where it is weak. Since the CH bond is a very strong one, it is not surprising to find that hydrogen halides add by a carbonium ion mechanism.

These conclusions are interesting in view of conflicting evidence in the literature concerning the stereochemistry of chlorine addition. Since bond energy increases in the series Cl < CBr < CCl, the tendency for electrophilic addition of halogen to proceed by the π-complex mechanism should fall along the same series. Electrophilic additions involving a primary attack by Br^+ or I^+, as in the additions of Br_2 or ICl, invariably give *trans* adducts, but cases are known where chlorine adds *cis*. A good example is provided by acenaphthylene, which adds bromine *trans* but chlorine *cis*.[20] As we have seen, both steric and electronic effects favor a classical carbonium ion mechanism for addition to acenaphthylene; apparently these factors are not enough to prevent bromine from adding *via* a π-complex, but chlorine adds *via* an intermediate carbonium ion (XIV).

It should be noted that this *cis*-addition of chlorine is definitely not a concerted process, for iodobenzene dichloride reacts with acenaphthylene to give *trans*-1,2-dichloroacenaphthene.[20] Now iodobenzene dichloride normally reacts with olefins to give *cis*-dichlorides by a concerted process involving a cyclic transition state[21]; cases are known where olefins react with chlorine to give *trans*-dichlorides but with iodobenzene dichloride to give *cis*-dichlorides. Since acenaphthylene evidently does not react with iodobenzene dichloride by a concerted mechanism it seems out of the question that chlorine should do so. The apparently abnormal behavior of iodobenzene dichloride can be attributed to the strong tendency of acenaphthylene to undergo electrophilic addition; steric hindrance in the initially formed ion pair between chlorine and the bulky ion $(PhICl)^-$ (XVI) will lead to its rapid conversion to the less hindered ion pair XVII; collapse of this gives *trans*-1,2-dichloroacenaphthene.



XIV XV XVI XVII

The fact that chlorine adds at least predominantly *trans* to simple olefins such as 2-butene[22] certainly seems to suggest that a π-complex mechanism operates in such cases; but the whole problem clearly needs to be re-examined. Our preliminary studies suggest that addition of chlorine to indene takes place *cis*, and stilbene has also been reported[23] to give extensive *cis*-addition. It seems not unlikely that the carbonium ion mechanism may be favored whenever the intermediate ion is resonance stabilized.

Neighboring group effects provide further support for these arguments.[24] Neighboring group participation in solvolytic reactions should be greater, the greater the stability of the π-complex intermediate relative to that of an isomeric carbonium ion. On this basis we would expect neighboring group participation in 2-haloalkyl derivatives to increase in the order Cl < Br < I; this is certainly observed.[24] At the same time the fact that chlorine can act as a neighboring group shows that, in some cases at least, the π-complex form of the ion must be the most stable; electrophilic addition proceeding *via* the same intermediate should then follow a π-complex mechanism and take place stereospecifically *trans*.

Experimental

Indene, 95–98% pure, was purchased from Rutgerswerke Aktiengesellshaft and purified by fractionation through a 8 mm. by 24 in. Podbielniak heli-grid column at 40 mm. A constant boiling center fraction was collected and stored at 0° until used. All other materials were as previously described.[1]

Addition of deuterium bromide was carried out according to the procedure described for acenaphthylene.[1] In a typical reaction indene (10 mmoles) in pentane (10 ml.) was placed in the reaction flask and cooled in a Dry Ice–acetone bath. Light was excluded and deuterium bromide (14 mmoles) distilled into the reaction mixture. After 10 min. the solvent and excess deuterium bromide were removed under vacuum. The deuteriobromide, a colorless liquid, was stored in Dry Ice until analyzed by n.m.r. The absence in the n.m.r. spectrum of peaks characteristic of indene showed that the reaction had gone to completion. Reactions in methylene chloride were run in a similar fashion.

As a test for isomerization under the reaction conditions, a sample of indene deuteriobromide (0.5 g.) analyzing as 80% *cis*-isomer was dissolved in a solution of deuterium bromide (2 *M*) in methylene chloride. After 15 min. the reaction mixture was worked up and the n.m.r. analysis repeated. The sample was found to contain 77% of *cis* isomer.

Additions of deuterium chloride to indene in methylene chloride and in deuterioacetic acid were carried out exactly as described for acenaphthylene.[1] Samples worked up at various reaction intervals were examined by n.m.r. The C_1–H resonance shown in Fig. 2a was obtained from a reaction in methylene chloride after 1 hr. when the reaction was 50% complete. A similar trace was found for addition in deuterioacetic acid after 20 min. (40% reaction). At longer reaction times the n.m.r. pattern approached that shown in Fig. 2b for an isomerized sample.

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