Electrophilic Addition to Olefins. I. The Stereochemistry of Addition of Deuterium Halides to Acenaphthylene[1]

By Michael J. S. Dewar and Robert C. Fahey[2]

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It has been generally believed that the polar addition of hydrogen halides to olefins takes place stereospecifically *trans*, although the evidence for this has been limited. We have now found that the addition of deuterium bromide or deuterium chloride to acenaphthylene under polar conditions takes place predominantly *cis* (74–90%), the amount of *cis*-addition being greater in non-polar solvents. The *trans* adduct was shown to be a primary product of polar addition, being formed neither by secondary isomerization nor by radical addition. These results rule out a π-complex mechanism and emphasize the need for further study of polar additions to olefins.

Introduction

The stereochemistry of the free radical addition of hydrogen halides to olefins has received extensive study[3] but interest in the corresponding polar additions has been limited. It has been generally thought that these polar additions take place stereospecifically *trans*.[4] Addition to α,β-unsaturated acids usually gives the *trans* adduct.[5] However, little consideration was given in these studies to the possibility that products might be formed by secondary isomerizations and in many cases no material balance was given. There is in any case no certainty that the conclusions reached for α,β-unsaturated acids will apply to olefins in general.

The only systematic studies of addition to simple olefins are those of Hammond and his co-workers. They found that addition of hydrogen bromide to 1,2-dimethylcyclohexene[6] and of hydrogen chloride to 1,2-dimethylcyclopentene,[7] gave predominantly the *trans*-addition product. Hammond suggests that these results may be accommodated either by a π-complex mechanism or by a completely concerted process in which a proton and a bromide ion enter simultaneously from opposite sides of the olefin plane; the latter mechanism seems unlikely since concerted addition would be expected to give *cis* adduct, as in the reaction between olefins and phenyliodo dichloride.

In these cases observation of predominant *trans*-addition does not necessarily rule out a two-step mechanism involving a classical carbonium ion since steric factors may favor *trans*-addition. In both cases the *trans*-addition product is more stable than the *cis*-addition product. It can be argued that steric interactions would be more important in the transition state than in the product and that *trans*-addition might be observed even though a classical carbonium ion intermediate were involved.

We felt that further study was warranted and that an olefin should be chosen such that no ambiguity would arise concerning possible steric effects. For our initial studies we chose to study the addition of deuterium halides to acenaphthylene (I). In this case formation of a free classical carbonium ion (II) would lead to equal amounts of *cis*- and *trans*-addition,


I   II   III
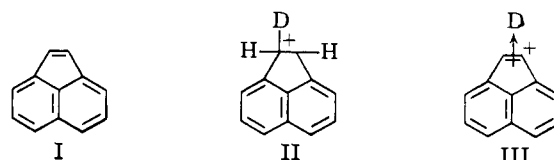
whereas if a π-complex (III) were involved only *trans*-addition would be found. This case provides an extreme test for the π-complex mechanism since a classical ion would be stabilized by resonance and would be lowered in energy relative to the π-complex by relief of strain in the five-membered ring. Demonstration of *trans*-addition in this case would provide strong evidence for the stability of proton π-complexes.

Results

We needed first to establish that the addition of deuterium bromide to acenaphthylene was occurring *via* a polar rather than a free radical mechanism. The fact that the addition was rapid in the absence of light at −78° suggested that free radicals were not involved. Further evidence was obtained by adding hydrogen bromide to acenaphthylene in the presence of styrene. The sole product of addition to styrene was found to be (2-bromoethyl)-benzene, the polar addition product.

The stereochemistry of the addition could be established by isolating the addition product, dehydrobrominating with base, and determining the amount of deuterium in the acenaphthylene recovered. It seems safe to assume that the elimination reaction is stereospecifically *trans* since it has been shown that in dehydrochlorination of *cis*- and *trans*-1,2-dichloroacenaphthene *trans*-elimination is 740 times faster than
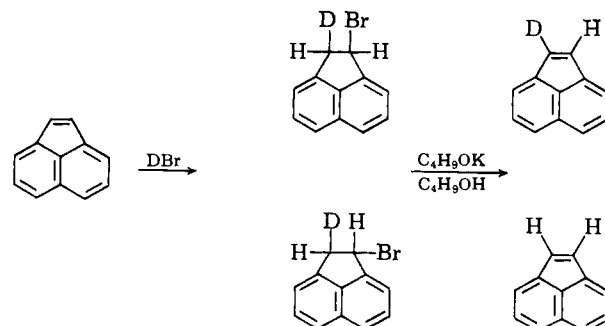
cis-elimination.[8] It follows that formation of 1-deuterioacenaphthylene corresponds to *cis*-addition of deuterium bromide and formation of undeuterated acenaphthylene to *trans*-addition of deuterium bromide. The amount of 1-deuterioacenaphthylene in the product was established by mass spectral analysis.

An independent and more direct estimate of the stereochemistry of the addition could be obtained

(1) This work, which has been supported by a grant from the National Science Foundation, was presented in part at the 144th National Meeting of the American Chemical Society at Los Angeles, Calif., April, 1963, and a preliminary account has appeared (M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **84**, 2012 (1962)).

(2) National Science Foundation Predoctoral Fellow.

(3) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962).

(4) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 405; E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 519; M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 242.

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

(6) G. S. Hammond and T. D. Nevitt, *ibid.*, **76**, 4121 (1954).

(7) G. S. Hammond and C. H. Collins, *ibid.*, **82**, 4323 (1960).

(8) S. J. Cristol, F. R. Stermitz and P. S. Ramey, *ibid.*, **78**, 4939 (1956).
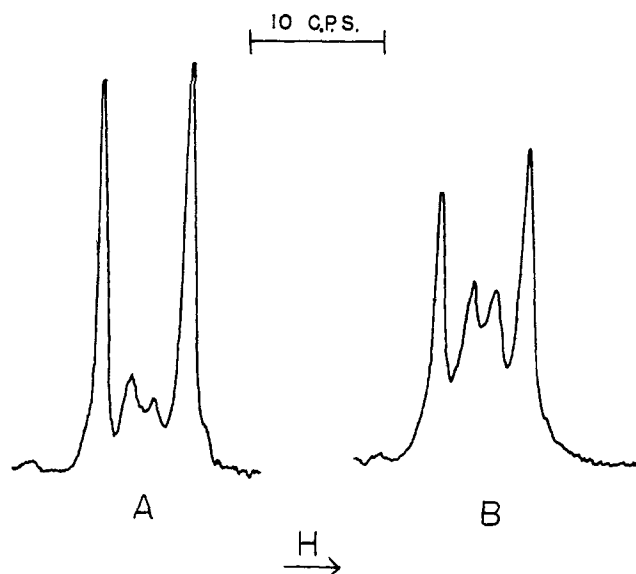
Fig. 1.—C_1-H resonance of 1-bromo-2-deuterioacenaphthene: A, addition product; B, partially isomerized.

from the n.m.r. spectrum of the addition product. It is known that the magnitude of vicinal coupling constants depends upon the dihedral angle involved.[9] Thus the C_1–H proton resonance signal in the deuteriobromide is expected to be a doublet (neglecting coupling to deuterium) with a splitting of about 2 c.p.s. in the *trans* isomer and a splitting of about 7 c.p.s. in the *cis* isomer. Actually the spectrum is complicated by a long-range coupling with the aromatic protons, but we were able to overcome this difficulty by employing spin decoupling techniques. A partial analysis of the spectrum of the hydrobromide of acenaphthylene showed that $J_{12}(cis) = 6.8$ and $J_{12}(trans) = 2.7$. Details of this analysis and further discussion of the n.m.r. spectra of these and other acenaphthene derivatives will be reported elsewhere.

The difference in the coupling was sufficient to allow resolution of the signals. Evaluation of the signal intensities gave an estimate of the amounts of each isomer present. A trace of the C_1-H proton signal for the product of a typical addition reaction is shown in Fig. 1A. A similar trace for a sample which had been partially isomerized is shown in Fig. 1B.

The two methods of analysis are compared in Table I for a series of reactions carried out in methylene chloride. In expt. 6 the product was isomerized by treatment with lithium bromide in acetone so that a check could be made at a different composition of isomers. Agreement between the two methods is good. The striking and unexpected feature is that predominant *cis*-addition occurred; in view of this we needed to find out whether the *trans* product was being formed in the addition step or arose from subsequent isomerization of the *cis* product. We also decided to study the influence of the reaction conditions on the stereochemistry of the addition.

Results for additions in pentane, methylene chloride and deuterioacetic acid are given in Table II. The n.m.r. method of analysis was used to establish the stereochemistry of addition. In pentane at $-78°$ (expt. 7) neither reactant nor product was completely soluble and the reaction mixture was heterogeneous. A homogeneous reaction was obtained at 0° in pentane containing 10% methylene chloride (expt. 8 and 9).

(9) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

TABLE I
COMPARISON OF METHODS OF ANALYSIS[a]

| | *cis*-Addition, % | |
Expt.	By elimination	By n.m.r.
1	79	80
2	83	82
3	83	..
4	..	83
5	..	81
6	53[b]	54[b]

[a] Samples obtained from the addition of deuterium bromide to acenaphthylene in methylene chloride. [b] After isomerization in a solution of lithium bromide in acetone.

In all cases the changes in observed *cis*-addition with increasing reaction time were small, suggesting that isomerization of the product was unimportant under the conditions of the reaction.

TABLE II
STEREOCHEMISTRY OF ADDITION OF DEUTERIUM BROMIDE TO ACENAPHTHYLENE

Expt.	Temp., °C.	Solvent	Time, min.	Reaction, %	% cis-addition
7	−78	Pentane[a]	30	75	87
8	0	Pentane[b] CH₂Cl₂	5	55	89
9	0	Pentane[b] CH₂Cl₂	15	65	85
10	−78	CH₂Cl₂	10	50	83
11	−78	CH₂Cl₂	20	60	84
12	−78	CH₂Cl₂	30	75	85
13	0	CH₂Cl₂	5	80	84
14	0	CH₂Cl₂	15	100	82
15	25	DOAc	0.5	22	74
16	25	DOAc	1.0	28	74
17	25	DOAc	2.0	39	73
18	25	DOAc	10.0	45	74

[a] Heterogeneous reaction. [b] Pentane containing 10% methylene chloride.

More direct tests for isomerization were made by treating samples of the pure deuteriobromide with deuterium bromide dissolved in methylene chloride. Samples were analyzed at intervals. The results are shown in Table III. At $-78°$ isomerization was significant only at high deuterium bromide concentrations $(>>1.0\ M)$.

TABLE III
ISOMERIZATION STUDIES

Expt.	Temp., °C.	DBr concn., M	% cis (time, min.)
19	−78	0.14	84 (0), 84 (480), 85 (1480)
20	−78	1.0	82 (0), 83 (15)
21	−78	7.3	86 (0), 62 (28)
22	0	0.14	84 (0), 71 (140), 55 (435)

The concentrations involved in the experiments reported in Table II were all below $1.0\ M$. At 0°, isomerization was detectable, suggesting that the decrease in observed *cis*-addition with time found in experiments 8, 9, 13 and 14 was significant and a correction of 1–2% should be applied.

Another possible source of the *trans* adduct would be a competing *trans* free radical addition undetected in the experiment with styrene. If this were the case, irradiation during the reaction period should increase the amount of observed *trans*-addition. However strong irradiation of the reaction mixture with ultraviolet light was found to have no effect on the course of addition.

It seems evident that both *cis* and *trans* adducts were being formed in the polar addition of hydrogen

bromide to acenaphthylene. Less polar solvents favor *cis*-addition. The results may be summarized as:

Solvent	Temp., °C.	*cis*-Addition, %
Pentane–CH₂Cl₂	0	90
CH₂Cl₂	−78	84
CH₂Cl₂	0	85
DOAc	25	74

These results are probably reliable to ±3%.

We were interested to see if the stereochemistry of the addition would vary with the concentration of deuterium bromide. Reactions were therefore carried out in such a way as to keep the deuterium bromide concentration between known limits. The results of these experiments are given in Table IV.

TABLE IV

EFFECT OF DEUTERIUM BROMIDE CONCENTRATION ON THE STEREOCHEMISTRY OF ADDITION

Expt.	Temp., °C.	Init. DBr concn., M	Final DBr concn., M	Time, min.	% Rx.	% cis- addition
23	−78	0.23	0.21	165	<10	..
24	−78	2.0	0.4	10	90	81
25	−78	11	7	10	100	54
26	0	0.26	0.07	15	100	82

At −78° with deuterium bromide concentrations below 0.2 *M*, the reaction was too slow for study. At high deuterium bromide concentrations (expt. 25), isomerization of the product made definitive study impossible. The only useful comparison is between expt. 24 and 26. Here a tenfold difference in deuterium bromide concentration produced no significant change in the stereochemistry of addition. The importance of this observation is somewhat obscured by the fact that the reactions were run at different temperatures.

One additional point may be made in connection with the additions of deuterium bromide. Significant amounts of deuterium were not being incorporated into the acenaphthylene prior to formation of the product. Were this to be the case, acenaphthylene containing two atoms of deuterium would have been found in the product of dehydrobromination. The mass spectral analysis of these products showed only traces (∼1%) of dideuterioacenaphthylene.

The addition of deuterium chloride to acenaphthylene could also be studied by the n.m.r. method. The reaction was slower and isomerization under the reaction conditions was significant. An estimate of the amount of *cis*-addition occurring was made by extrapolating the observed values to zero reaction time. Results for addition in methylene chloride and deuterioacetic acid are shown in Table V and are probably reliable to ±5%. The slowness of the reaction and the problem of product isomerization discouraged more detailed studies. Here again *cis*-addition predominated and occurred to roughly the same extent as in the addition of deuterium bromide.

TABLE V

ADDITION OF DEUTERIUM CHLORIDE TO ACENAPHTHYLENE

Solvent	Time, min.	Reaction, %	% cis- addition
H₂Cl₂	(0)	(0)	(85)
	60	45	76
	140	55	72
	210	80	62
DOAc	(0)	(0)	(85)
	25	45	75
	60	90	58
	100	100	57

Discussion

These experiments have shown that the polar addition of deuterium bromide or deuterium chloride to acenaphthylene takes place predominantly, but not exclusively, *cis*. The formation of small amounts of *trans*-adduct can be ascribed neither to a concomitant radical addition nor to secondary isomerization. The stereochemistry of the reaction in methylene chloride was unaffected by changes in temperature and seemed also to be independent of the concentration of deuterium bromide. The amount of *cis*-addition decreased, however, with increasing polarity of the solvent.

It is obvious that a π-complex is not involved in the product-determining step of the reaction. A concerted process involving a cyclic transition state would account for a stereospecific *cis*-addition but not for the simultaneous formation of small amounts of *trans* isomer. We believe that the results can be adequately explained in terms of a mechanism involving a classical carbonium ion, formed in the rate-determining step as an ion pair with the halide ion. A detailed discussion is given in the following paper.

Experimental

Materials.—Acenaphthylene, purity 98–100%, was purchased from Rutgerswerke Aktiengesellschaft, Castrop-Rauxel 2, Germany. Phosphorus tribromide, methylene chloride and pentane were purchased from M.C.B., reagent grade acetyl chloride from B. and A., and deuterium oxide, 99.5%, from Abbott Laboratories. Solvents were dried before use.

Preparation and Purity of Deuterium Halides.—Deuterium bromide and deuterium chloride were prepared by addition of deuterium oxide to phosphorus tribromide and acetyl chloride, respectively. The reaction was carried out in a three-neck reaction flask and gases collected in a trap as formed. The deuterium halide was partially distilled twice, trap to trap, before use. Traps were cooled in Dry Ice–acetone for deuterium bromide and in frozen pentane for deuterium chloride.

Contamination by hydrogen halide was established by preparing a concentrated solution of the deuterium halide in deuterium oxide. An accurate determination of the amount of acid present was made by titrating with standard base. Contamination by hydrogen halide was determined from the proton resonance spectrum of the solution in deuterium oxide. Only one weak resonance line was found in the proton region and the integrated intensity was measured. Standards containing known amounts of hydrogen contamination were measured under identical conditions for calibration and corrections were made for 0.5% of water present in the deuterium oxide. The deuterium bromide was found to contain 0.5 ± 0.2% of hydrogen bromide and the deuterium chloride to contain 2.5 ± 1.5% of hydrogen chloride.

Deuterioacetic Acid.—Reagent grade acetic anhydride and a stoichiometric amount of deuterium oxide were stirred overnight and then refluxed for 2 hr.; n.m.r. analysis of the deuterioacetic acid obtained showed less than 1% contamination by hydroxyl hydrogen and less than 1% unreacted acetic anhydride.

Addition of Deuterium Bromide to Acenaphthylene.—The following procedure is typical for additions carried out in methylene chloride and pentane solutions. A 3-neck reaction flask fitted with gas inlet tube, drying tube, and syringe cap was attached by a ground joint to a stopcock leading to the last trap in the line used to collect deuterium bromide. The system, from stopcock on, was flame-dried under a flow of dry nitrogen. The reaction flask was immersed in the cooling bath and light was excluded. A solution of acenaphthylene (6.6 mmoles) in methylene chloride (10 ml.) was added through the syringe cap and the solution allowed to equilibrate to the bath temperature. The stopcock was opened to the calibrated trap containing deuterium bromide and 6.6 to 8.5 mmoles of the deuterium bromide allowed to distil into the reaction mixture over a period of 3 min. The reaction mixture was allowed to stand 7 min. (total reaction time of 10 min.). The reaction flask was then transferred to a rotary evaporator and the solvent removed under vacuum, leaving a cream-colored solid. A saturated solution of the solid in deuteriochloroform was prepared immediately and stored in Dry Ice pending n.m.r. analysis.

Reactions on a larger scale were run in a similar fashion. The product obtained was recrystallized twice from pentane to give white needles, m.p. 69–70° (lit. for 1-bromoacenaphthene[10,11]

(10) M. Julia and M. Baillarge, *Bull. soc. chim. France*, **19**, 1065 (1952).
(11) W. E. Bachmann and J. C. Sheehan, *J. Am. Chem. Soc.*, **63**, 204 (1941).

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 deuterioacetic 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%.

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

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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

(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.

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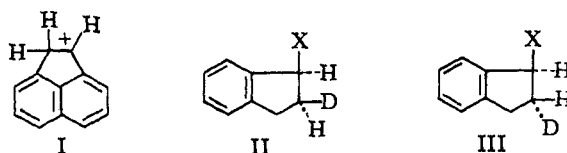
One advantage of acenaphthylene was the absence of complications due to possible conformational effects. Owing to the rigid planarity of the five-membered ring, the classical ion I has a plan of symmetry and the two sides of the carbonium carbon are therefore equally open to attack by anions. The same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