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Mechanisms of Elimination Reactions. XVII. The *cis*- and *trans*-1,2-Dichloroacenaphthenes; *trans*-1,2-Dibromoacenaphthene[1,2]

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Both isomers of 1,2-dichloroacenaphthene have been prepared, one for the first time. Treatment of acenaphthylene with chlorine gives *cis*-1,2-dichloroacenaphthene, and chlorination of acenaphthylene with iodobenzene dichloride gives the *trans* isomer. The structures of the isomers have been proved by degradation and by partial resolution of the *dl-trans* isomer by asymmetric elimination with brucine. Treatment of acenaphthylene with bromine or bromination of acenaphthene with N-bromosuccinimide gives resolvable *trans*-1,2-dibromoacenaphthene. The latter substitutive bromination followed by debromination with sodium iodide or with zinc constitutes a useful synthesis for acenaphthylene. Dehydrochlorination with sodium hydroxide proceeds about 750 times faster with the *cis*-dichloride than with the *trans* isomer. As *trans* elimination is significantly faster than *cis* elimination and as it proceeds at a relatively rapid rate, it appears that the geometric requirement of *trans* coplanarity in the transition state for concerted elimination is satisfied with the *cis*-dichloride, and that there is considerable freedom to partial rotation around the C_1–C_2 bond in acenaphthenes.

Previous work on alkaline dehydrochlorination from *cis*- and *trans*-dichlorides has demonstrated that the normal superiority of *trans* elimination in cyclic systems[3–6] disappears in systems containing bicyclo[2,2,2]octane[7] and bicyclo[2,2,1]heptane[8,9] rings. The disappearance of the *trans* superiority has been ascribed[7] to the rigidity of the bridged bicyclic system, such that the hydrogen and chlorine atoms are held firmly in the eclipsed positions available in boat-form cyclohexane rings. Thus the planar transition state[10] for facile *trans*-concerted (*anti*) elimination is not readily available. It seemed of interest to study the dehydrochlorination of the isomeric 1,2-dichloroacenaphthenes to continue the investigation of elimination in cyclic systems.

Preparation and Proof of Structure of Materials.—Campbell[11] has reported the preparation of 1,2-dichloroacenaphthene by the addition of chlorine to acenaphthylene in carbon tetrachloride, but the isomeric substance has not been reported. We have repeated the work of Campbell, and we have obtained the same isomer, m.p. 116°, which he reported. The yield was low (about 20%) and was not improved substantially by the use of other solvents, including benzene, petroleum ether, b.p. 35–60°, and ethyl ether, nor by using temperatures as low as −40°. The reaction proceeded with similar results in the dark or with irradiation with ultraviolet light. A preferred method of synthesis is described in the Experimental section.

On the other hand, when acenaphthylene was treated with iodobenzene dichloride in dry chloroform (preferably containing some 1,3,5-trinitrobenzene), a second isomeric 1,2-dichloroacenaphthene, m.p. 68°, was obtained.

Both isomers gave 1,2-naphthalic anhydride upon oxidation, both gave acenaphthylene upon treatment with zinc dust in ethanol and both gave 1-chloroacenaphthylene upon treatment with ethanolic alkali. These reactions constitute proof that these substances are isomeric 1,2-dichloroacenaphthenes.

The materials have been submitted to dipole moment studies[12] and the higher melting isomer has been found to have the higher electric moment and has thus been assigned the *cis* structure. This was an unexpected result, as it might have been anticipated that chlorination with chlorine would be *trans* and addition *via* iodobenzene dichloride would be *cis*.[13,14] In view of this, a resolution experiment was conducted in order to confirm the structural assignments. The *trans* isomer is the racemic modification, while the *cis* isomer is the inactive *meso* form. Each isomer was treated with enough brucine to convert one-half to 1-chloroacenaphthylene; the remaining dichloride was then tested for optical activity. This test makes use of the difference in reactivity of enantiomorphs in reacting with an optically active substance and has been used previously in a structure proof involving an elimination reaction.[15] The higher melting (*cis-meso*) isomer developed no significant rotation upon treatment with brucine while the lower melting (*dl-trans*) isomer developed a significant rotation. This evidence then is conclusive for the structure of each of the isomers.

Only one isomer of 1,2-dibromoacenaphthene is known; it may be prepared by the addition of bromine to acenaphthylene[16] or by the action of N-bromosuccinimide on acenaphthene. That it is the *dl-trans* isomer has been shown by dipole moment studies,[12] and it has now been partially resolved by the brucine treatment described above for the analogous dichloride. Thus bromination proceeds in the normal *trans* fashion with acenaphthylene as with other olefins.

The steric result obtained in the direct chlorination of acenaphthylene has no obvious explanation. There are a number of cases described in the litera-

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[1] Previous paper in series: S. J. Cristol, J. Q. Weber and M. C. Brindell, THIS JOURNAL, **78**, 598 (1956).

[2] A portion of this work was reported at the 14th National Organic Chemistry Symposium at Lafayette, Indiana, June 13, 1955.

[3] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[4] S. J. Cristol, THIS JOURNAL, **69**, 338 (1947); S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951).

[5] H. C. Stevens and O. Grummitt, *ibid.*, **74**, 4876 (1952).

[6] E. D. Hughes, C. K. Ingold and R. Pasternak, *J. Chem. Soc.*, 3832 (1953).

[7] S. J. Cristol and N. L. Hause, THIS JOURNAL, **74**, 2193 (1952).

[8] J. D. Roberts, F. O. Johnson and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

[9] S. J. Cristol and E. F. Hoegger, unpublished work.

[10] D. H. R. Barton and E. Miller, THIS JOURNAL, **72**, 1066 (1950).

[11] B. Campbell, *J. Chem. Soc.*, **107**, 918 (1915).

[12] M. T. Rogers and S. J. Cristol, THIS JOURNAL, **77**, 764 (1955).

[13] C. J. Berg and E. S. Wallis, *J. Biol. Chem.*, **162**, 683 (1946).

[14] D. H. R. Barton and E. Miller, THIS JOURNAL, **72**, 370 (1950).

[15] S. J. Cristol, *ibid.*, **71**, 1894 (1949).

[16] M. Blumenthal, *Ber.*, **7**, 1092 (1874).

ture,[17] where large percentages of *cis* chlorination with chlorine were observed. However, our yields of dichloride were small, and we do not have sufficient knowledge regarding variables in the reaction to discuss this problem adequately. The same is true for the chlorination with iodobenzene dichloride, which has been suggested as a *cis* chlorinating agent,[14] and which we found, when anhydrous reagents were used and preferably in the presence of a free-radical inhibitor, gave the *trans*-dichloride. It was fortunate for the main purpose of this work that two isomers were indeed obtained, albeit by paths opposite to those originally conceived.

In the course of this work, a preparation of acenaphthylene from acenaphthene has been developed which was found to be convenient. This involves the preparation of 1,2-dibromoacenaphthene by treatment of acenaphthene with 2 moles of N-bromosuccinimide, and the subsequent debromination of this dibromide with sodium iodide or with zinc.[18]

Dehydrochlorination Experiments.—As indicated above, each isomer gave 1-chloroacenaphthylene upon treatment with ethanolic alkali. Reaction-rate constants were determined with sodium hydroxide in ordinary ethanol (92.6 wt.%) using methods for following the extent of reaction and methods for calculation as described earlier.[4] Data, reaction-rate constants and quantities of activation are given in Table I. It will be noted that the reaction is shown to be of the first order with respect to alkali by invariant rate constants with changes in alkali concentration and is shown to be first order in dichloride by the fact that rate constants did not change with time over the range of reaction studied (9 to 73%). E_{act} is the Arrhenius activation energy and $\Delta S^{\ne}$ is the entropy of activation.[19]

It may be seen that *trans* elimination is favored in rate over *cis* elimination by a factor of about 740. This is less than the superiority observed in the benzene hexachlorides (*ca.* 10^4); the lesser value is consistent, however, with the concepts previously proposed where stabilization of the presumed carbanion intermediate involved in *cis* elimination is afforded by resonance with the naphthalene ring system.[20] The fact that *trans* elimination proceeds at a very high rate and with low activation energy suggests that the acenaphthene ring system contains bonds in the 1- and 2-positions which are not rigidly held in eclipsed positions, but rather that there is considerable freedom for rotation around the carbon–carbon axis as to allow for *trans* coplanarity, as opposed to the high degree of rigidity in the bicycloheptane and bicyclooctane systems.[7–9]

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TABLE I

DATA, SECOND-ORDER REACTION-RATE CONSTANTS AND QUANTITIES OF ACTIVATION FOR THE DEHYDROCHLORINATION OF *cis*- AND *trans*-1,2-DICHLOROACENAPHTHENES WITH SODIUM HYDROXIDE IN 92.6 WT. % ETHANOL

Temp., °C.	(Halide) *M*	(NaOH) *M*	Reaction-rate constant $10^3 k$ l./sec./mole	E_{act} kcal./mole	$\Delta S^{\ne}_{30}$ cal./deg./mole
		cis Isomer			
3.20	0.001	0.003	17.5		
	.001	.003	17.3		
	.0012	.0067	18.4		
		Ave.	17.7		
10.45	.0011	.0033	54.2		
	.0011	.0033	52.3		
		Ave.	53.2		
22.10	.0012	.0033	202		
	.0010	.0033	194		
		Ave.	198		
30.00 (extrap.)			533	20.8	6.9
		trans Isomer			
30.46	.0012	.042	0.782		
	.0010	.042	.763		
	.0011	.084	.750		
		Ave.	.765		
36.40	.0011	.042	1.69		
	.0010	.042	1.69		
		Ave.	1.69		
43.10	.0011	.042	4.00		
	.0011	.042	3.78		
		Ave.	3.89		
30.00 (extrap.)			0.721	24.8	6.9

Experimental

Preparation of 1,2-Dibromoacenaphthene.—A mixture of 75 g. (0.5 mole) of acenaphthene, 180 g. (1 mole) of N-bromosuccinimide, 4 g. (0.016 mole) of benzoyl peroxide and 180 g. of anhydrous potassium carbonate in 600 ml. of carbon tetrachloride was heated at reflux for two hours. The system was protected from moisture by a calcium chloride tube. The orange-colored mixture was filtered, the residue was washed with 50 ml. of hot carbon tetrachloride, and 400 ml. of hot ethanol was added to the filtrate. The solution was cooled and filtered giving 76 g. (48%) of tan crystals, m.p. 120–122°. Further recrystallization from petroleum ether, b.p. 60–70°, gave a white product, m.p. 124°, but much of the dibromide was decomposed in the process. The crude material obtained above may be used directly to prepare acenaphthylene.

Slow addition of a solution of bromine in petroleum ether to an equimolar amount of acenaphthylene in petroleum ether yielded 50% of 1,2-dibromoacenaphthene, m.p. 124°.[11] Both solutions were kept cold during the addition which took place over a period of 20 minutes. A mixed melting point of the product with a sample of 1,2-dibromoacenaphthene obtained from the reaction of acenaphthene and N-bromosuccinimide gave no depression.

Preparation of Acenaphthylene.—One-hundred-twenty grams (0.8 mole) of sodium iodide, 180 g. (0.7 mole) of sodium thiosulfate pentahydrate and 700 ml. of acetone were brought to reflux with stirring; 64 g. (0.205 mole) of *trans*-1,2-dibromoacenaphthene, m.p. 120–122°, was added over a four-hour period. The mixture was stirred vigorously during this time and for one additional hour. If the dibromide is added all at once, the mixture is more difficult to work up. Free iodine polymerizes either starting material or product, necessitating the use of sodium thiosulfate. The mixture was filtered, the residue was washed white with

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[17] See, for example: T. Zincke, *Ber.*, **10**, 999 (1877); S. Winstein and D. Seymour, THIS JOURNAL, **68**, 119 (1946); G. Calingaert, M. E. Griffing, E. R. Kerr, A. J. Kolka and H. D. Orloff, *ibid.*, **73**, 5224 (1951).

[18] A. A. Anderson, Jr., and R. G. Anderson, *ibid.*, **77**, 6610 (1955), recently have described the zinc debromination.

[19] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

[20] S. J. Cristol and W. P. Norris, THIS JOURNAL, **76**, 3005 (1954).

acetone, and the acetone was partially distilled from the filtrate to reduce it to a volume of approximately 300 ml.; the resulting yellow oily mixture was poured into 500 ml. of cold water, which was then extracted with petroleum ether. This extract was reduced to 100 ml. by removal of solvent by distillation, and the resulting solution was treated on a column of 100 g. of alumina using petroleum ether as eluent. After the solvent was removed by distillation, the yellow solid was recrystallized from aqueous ethanol. The yield was 22 g., or 71%, m.p. 92–93°. Treatment with zinc dust also gave acenaphthylene.[18]

Preparation of *trans*-1,2-Dichloroacenaphthene.—To 3 g. (0.02 mole) of acenaphthylene and 0.15 g. (0.0007 mole) of 1,3,5-trinitrobenzene in 120 ml. of refluxing dry chloroform was added 7 g. (0.026 mole) of iodobenzene dichloride over a 4-hour period. After two hours a darkening of color was noted and 0.15 g. additional trinitrobenzene was added. The solution was heated at reflux for 1.5 hours after the addition of the iodobenzene dichloride was complete. The chloroform was removed by distillation, the oily residue was extracted with petroleum ether, b.p. 35–60°, the solvent was evaporated, and the residual solid was recrystallized from aqueous ethanol. After two such recrystallizations, 1.2 g. (28%), m.p. 66.5–68°, was obtained. One more recrystallization gave 0.9 g., m.p. 67–68°.

Anal. Calcd. for $C_{12}H_8Cl_2$: C, 64.60; H, 3.62; Cl, 31.78. Found: C, 64.69; H, 3.75; Cl, 31.65.

The *trans* isomer crystallized in needles. When the chloroform used in the preparation was not dry, a mixture of *cis* and *trans* isomers was formed and the yield was reduced. The yield was less than 10% in the absence of trinitrobenzene.

Preparation of *cis*-1,2-Dichloroacenaphthene.—This compound has been prepared previously by Campbell[11] by chlorination of acenaphthylene in carbon tetrachloride. We tried a number of solvents and conditions, but the following preparation gave a product which was easiest to work up. A large, tared, foil-wrapped test-tube, containing 1.00 g. (0.66 mmole) of acenaphthylene in 15 ml. of benzene and equipped with a sintered glass delivery tube and an outlet tube with an attached calcium chloride tube, was submerged in an ice–water-bath. Chlorine (0.75 g.) (1 mmole) was passed into the solution over a 20-minute period. The benzene was removed (fumes of hydrogen chloride were often noticed at this stage) and the sticky solid was washed with cold petroleum ether to give 0.40 g. (27%) of crude product, m.p. 112–114°. Recrystallization from ether–petroleum ether gave 0.27 g. (18%), m.p. 116°.

Oxidation of Dihalides to Naphthalic Anhydride.—Sodium dichromate, 1.2 g. (4 mmoles), was added in small portions over a period of 15 minutes to 0.22 g. (1 mmole) of 1,2-dichloroacenaphthene, m.p. 67–68°, in 3 ml. of boiling glacial acetic acid. The mixture was heated at reflux for 45 minutes, 7 ml. of warm water was added, and the precipitate was filtered (0.12 g.). This was dissolved in approximately 1% sodium hydroxide and reprecipitated with dilute hydrochloric acid to give 0.1 g., m.p. 271–273°. Mixing the compound with an authentic sample of naphthalic anhydride did not depress the melting point. The dichloride with a melting point of 116° and the dibromide with a melting point of 122° were treated in the above manner, and each gave similar results. The yields of naphthalic anhydride isolated were: *trans*-dichloride, 48%; *cis*-dichloride, 44%; *trans*-dibromide, 71%.

Dehalogenation of Dihalides to Acenaphthylene.—Twenty-two hundredths grams (1 mmole) of *cis*-1,2-dichloroacenaphthene, dissolved in 10 ml. of warm ethanol, was added slowly to 0.065 g. (1 mmole) of zinc dust in 5 ml. of boiling ethanol in a small flask. The mixture was stirred over a period of 30 minutes. At this time all the zinc appeared to have reacted. Excess zinc (0.03 g.) was added, and the mixture was boiled five minutes longer; it was then poured into 15 ml. of cold water and extracted with two 15-ml. portions of petroleum ether. The solution was then dried over anhydrous sodium sulfate. After removal of the solvent, 0.12 g. of acenaphthylene was obtained, m.p. 90–91°. A mixed melting point with acenaphthylene, as prepared previously, showed no depression. The *trans*-dichloride and the *trans*-dibromide were treated in the same way. The yields of acenaphthylene isolated were: *cis*-dichloride, 70%; *trans*-dichloride, 53%; *trans*-dibromide, 60%.

Dehydrochlorination of 1,2-Dichloroacenaphthenes to 1-Chloroacenaphthylene.—A solution of 0.4 g. (1.81 mmoles) of *trans*-1,2-dichloroacenaphthene and 0.16 g. (5 mmoles) of sodium hydroxide in 5 ml. of ethanol was heated at reflux for two hours. The yellow solution was poured into 15 ml. of ice and water, the mixture was extracted with ethyl ether, and the ethereal solution was dried over anhydrous sodium sulfate. After removal of the solvent, the remaining 0.3 g. of yellow-orange oil was dissolved in 5 ml. of petroleum ether and placed on a 1 cm. × 30 cm. column containing 10 g. of alumina. After elution with 200 ml. of petroleum ether and evaporation of the solvent, about 0.2 g. of 1-chloroacenaphthylene, m.p. 19–20°,[21] was obtained.

Similar results were obtained with the *cis* isomer, except that a shorter reflux time was used. Each of the samples of 1-chloroacenaphthylene was converted to the picrate and 1,3,5-trinitrobenzene molecular compounds by treatment of equimolar amounts of chloride in ethanol with the appropriate reagent in ethanol. Appropriate mixed melting points were not depressed. The derivatives decomposed upon standing, as did the chloroölefin; picrate, m.p. 148°.

Anal. Calcd. for $C_{18}H_{10}O_7N_3Cl$: C, 52.00; H, 2.42; N, 10.10. Found: C, 51.95; H, 2.41; N, 10.09.

Trinitrobenzene addition compound, m.p. 163°.

Anal. Calcd. for $C_{18}H_{10}O_6N_3Cl$: C, 54.08; H, 2.52. Found: C, 54.07; H, 2.49.

Resolution Experiments.—A solution of 0.58 g. (2.6 mmoles) of *trans*-1,2-dichloroacenaphthene, m.p. 68°, and 0.51 g. (1.3 mmoles) of brucine in 10 ml. of dioxane was heated in an oil-bath at 62° for two weeks. A large amount of solid precipitated, which was shown to be brucine hydrochloride by analysis for chloride ion (*Anal.* Calcd. for $C_{23}H_{27}O_4N_2Cl$: Cl, 8.47. Found: Cl, 8.34). The salt was removed by filtration and the filtrate was washed several times with cold water. Estimation based on total chloride formed indicated that 83% of the brucine had reacted at the end of the reaction period. The resulting oily solid was dissolved in ether and was washed three times with dilute hydrochloric acid to remove residual brucine and was then washed with cold water. The solution was dried over anhydrous sodium sulfate. Distillation of the ether gave 0.41 g. of oily solid, $[\alpha]^{25}\mathrm{D}$ −4.4° (*l* 2, *c* 0.041 g./ml., ethyl ether). Washing with petroleum ether and recrystallization from aqueous ethanol gave 50 mg., m.p. 65–80°, $[\alpha]^{25}\mathrm{D}$ −27° (*l* 2, *c* 0.004 g./ml., ethyl ether). This white solid gave a negative test for brucine with concentrated nitric acid.[22]

Anal. Calcd. for $C_{12}H_8Cl_2$: C, 64.60; H, 3.62; N, 0.0. Found: C, 64.74; H, 3.82; N, 0.00.

This dichloride, m.p. 68°, has therefore been assigned the *dl-trans* structure. The melting point of the partially resolved material suggests that the *dl*-substance may be a racemic mixture.

A solution of 1 g. (3.2 mmoles) of *trans*-1,2-dibromoacenaphthene, m.p. 122°, and 0.74 g. (1.6 mmoles) of brucine in 10 ml. of dioxane was allowed to stand at room temperature for 2 days. The solid was removed by filtration, and the filtrate was washed several times with cold water. The resulting yellow oily solid was dissolved in ether, and the solution was extracted several times with dilute hydrochloric acid and then washed with water. The ethereal solution was dried over anhydrous sodium sulfate, and the ether was removed by distillation. The sticky yellow solid which remained was washed with petroleum ether. The residue (0.18 g.) was a white solid, m.p. 110–115°, $[\alpha]^{25}\mathrm{D}$ −24.4° (*l* 2, *c* 0.023 g./ml., ethyl ether). Recrystallization from petroleum ether, b.p. 60–70°, gave 47 mg., m.p. 120–122°, $[\alpha]^{25}\mathrm{D}$ −40° (*l* 2, *c* 0.0047 g./ml., ethyl ether). This solid gave a negative test for brucine[22] and a negative qualitative test for nitrogen. This dibromide, m.p. 122°, may, therefore, be assigned the *dl-trans* structure.

When *cis*-1,2-dichloroacenaphthene, m.p. 116°, was treated by the procedure described in the previous section, the resulting oily solid isolated had $[\alpha]^{25}\mathrm{D} \leqslant +0.1°$ (*l* 2, *c* 0.065 g./ml., ethyl ether). After a petroleum ether wash, the white solid was slightly impure *cis*-dichloride, m.p. 110–114°. The petroleum ether extracts were shown to contain 1-chloroacenaphthylene by the preparation of appropriate derivatives of the chloroölefin. As this isomer was not resolvable, it may be assigned the *cis-meso* structure.

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(21) Campbell[11] reports this as an oil.

(22) R. Kersting, *Ann.*, **125**, 254 (1863).