The reaction products of cyclohexene with N-bromoacetamide and N-bromomonochloroacetamide were obtained by isolation techniques similar to those described above.

Reactions with Benzyl Alcohol.—In separate experiments, 0.1 mole of the N-bromo compounds was added to 1.0 mole of redistilled benzyl alcohol at room temperature. After a short induction period, the reaction became exothermic enough to raise the temperature to the boiling point of the alcohol. During the reflux period the color changed from yellow to orange to deep red, and finally back to yellow. At this point the hot solution was tested with potassium iodide solution and no liberation of iodine was observed. The reactions were therefore considered complete. The solution was strongly acid to litmus paper due to the formation of hydrogen bromide.

The entire mixture was shaken with sodium bicarbonate solution until the evolution of CO_2 ceased. The organic layer was extracted with ether and the ether extract in turn extracted three times with 100-ml. portions of sodium bisulfite solution (30 g. per 100 ml. of water). Benzaldehyde was obtained by combining the bisulfite extracts, treating them with sodium bicarbonate until the evolution of CO_2 ceased, and steam distilling the resulting mixture. The distillate was extracted thoroughly with ether. The ether extract was dried over sodium sulfate and distilled to remove the ether. Crude benzaldehyde was obtained in 64–70% yields, b.p. 172° at 628 mm., $n^{20}D$ 1.5445. The 2,4-dinitrophenylhydrazone of this material had a melting point of 237–238°; lit. value 237°.

Acknowledgment.—Thanks are due to the Office of Naval Research, United States Navy, for partial support of this work; to the Arapahoe Chemicals, Inc., for the generous supply of N-bromoacetamide used in this work; and to the Minnesota Mining and Manufacturing Company for the supply of trifluoroacetic acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. V. Preparation and Elimination Reactions of *cis-* and *trans-*11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene[1,2,3]

BY STANLEY J. CRISTOL AND NORMAN L. HAUSE

Previous work has indicated the stereochemical preference for *trans* elimination of the elements of hydrogen halides in second-order alkaline dehydrohalogenation reactions of alkyl halides. In a continuation of a study of *cis* and *trans* elimination, work with the *cis–trans* isomers of 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene was undertaken. The isomeric compounds were prepared by diene syntheses involving anthracene with *cis-* and *trans-*dichloroethylenes. Each of the isomers gave 9,10-dihydro-9,10-ethenoanthracene when treated with sodium in isopropyl alcohol or with zinc in ethyl alcohol. The structure of the olefin was confirmed by hydrogenation to the known 9,10-dihydro-9,10-ethanoanthracene. These results show that the *trans-*configuration of halogen substituents is not required for the elimination of halogen from α,β-dihalides with metals. Each isomer was shown to give 11-chloro-9,10-dihydro-9,10-ethenoanthracene on treatment with ethanolic alkali.

A kinetic study has been made of the dehydrochlorination of each of the *cis–trans-*dichlorides with sodium hydroxide in a water–ethanol–dioxane solution at four different temperatures (30° range) for each isomer. The *trans-*dichloride (*cis-*hydrogen and chlorine atoms) unexpectedly reacted seven to nine times faster than the *cis-*dichloride (*trans-*hydrogen and chlorine atoms). To the best of our knowledge, there are no analogous results reported in the literature. This preference in rate for *cis* elimination was found to be entirely due to a favorable entropy of activation (and to the relatively high temperature required for reaction), as *trans* elimination was favored by four kilocalories per mole in activation energy. These results are discussed in terms of a planar transition state for the one-stage elimination process.

In previous papers[1b,1c] the stereochemical preference in E2 (second-order) elimination[4] of the elements of hydrogen halides from alkyl halides has been considered at length, and numerous examples have been cited where *trans* elements of hydrogen and halide are removed more readily than the corresponding *cis* elements. The superiority of *trans* elimination has been attributed[1b] to a difference in mechanism between it and the *cis* process. It was assumed that the *trans* process involved a one-stage concerted mechanism wherein the base attacks the hydrogen on the β-carbon atom, displacing the electron pair of the carbon–hydrogen bond which may simultaneously attack the α-carbon atom by a direct inversion process, forming the carbon–carbon double bond and displacing halide ion.

It was assumed that, for the concerted process, the α-carbon atom must be in position to undergo inversion in the displacement of halide by the electrons of the carbon–hydrogen bond undergoing rupture, requiring that the hydrogen and halide atoms be in *trans* position to each other. When free rotation is constrained around the carbon–carbon bond so that the hydrogen and halide atoms are *cis* to each other, the above concerted process was not deemed possible, as inversion of the α carbon atom is then not possible in the rate-determining step. It was suggested that under these circumstances the reaction then takes a course different from the one-stage process in which the base removes a proton from the β carbon atom, yielding (in the rate-determining step) a carbanion, which rapidly decomposes to olefin and halide ion.

In order to continue the work on the stereochemical aspects of dehydrohalogenation reactions, the compounds *cis-* and *trans-*11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene seemed to offer an ideal system for such dehydrohalogenation studies. The usual stereochemical selectivity[5] of the diene synthesis makes it useful for the synthesis of these compounds. If the *cis* addition principle is obeyed, then condensation of anthracene with *cis-*1,2-dichloroethylene should yield *cis-*11,12-

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[1] Previous papers in series: (a) S. J. Cristol, THIS JOURNAL, **67**, 1494 (1945); (b) S. J. Cristol, *ibid.*, **69**, 338 (1947); (c) S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951); (d) S. J. Cristol and W. Barasch, *ibid.*, **74**, 1658 (1952).

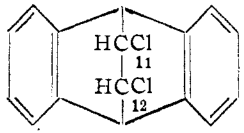
[2] This work was supported by the Office of Naval Research.

[3] Presented at the XIIth Congress of International Congress of Pure and Applied Chemistry, September, 1951, New York, N. Y.

[4] E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

[5] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

dichloro-9,10-dihydro-9,10-ethanoanthracene (I), and condensation of *trans*-1,2-dichloroethylene with anthracene should yield *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene (II). Compound I has the *trans* configuration of hydrogen and halide substituents, and compound II, the *cis* configuration of hydrogen and halide substituents.



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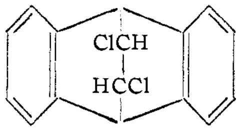


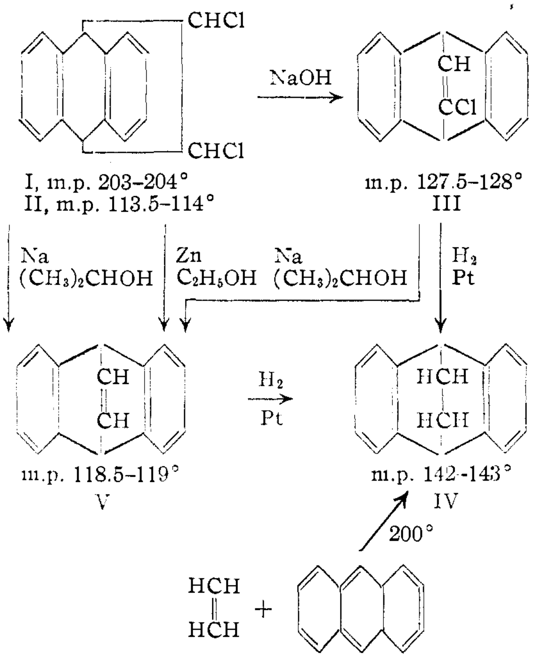
II

Arbuzov and Zoroastrova found[6] that 1,2-dichloroethylene and anthracene could be condensed to give an adduct (m.p. 203–204°) which gave the correct chlorine analysis for $C_{16}H_{12}Cl_2$. Apparently they made no attempt to separate 1,2-dichloroethylene into its *cis* and *trans* isomers prior to condensation. Under conditions similar to those employed by these workers, *cis*- and *trans*-1,2-dichloroethylene were condensed separately with anthracene. It was found that I with a melting point of 203–204° was isolated from the condensation of anthracene with *cis*-1,2-dichloroethylene, and II with a melting point of 113.5–114° was isolated from a similar condensation with *trans*-1,2-dichloroethylene. The yields were excellent in these condensations. The stereospecificity demanded by the Alder rules[5] is fulfilled, for only one isomer was isolated from the adduct obtained by the condensation of each pure geometrical isomer of 1,2-dichloroethylene, and dipole moment data on compounds I and II have confirmed[7] the fact that *cis* addition had occurred.

It was found that both I and II could be dehydrochlorinated with ethanolic sodium hydroxide to give 11-chloro-9,10-dihydro-9,10-ethenoanthracene (III). When III was hydrogenated at room temperature using platinum catalyst, one mole of chloride ion was released per mole of compound, while two moles of hydrogen per mole of compound was required for the hydrogenation. The product obtained in the hydrogenation was found to be identical with 9,10-dihydro-9,10-ethanoanthracene (IV) prepared by the condensation of ethylene with anthracene in the diene synthesis as described by Thomas.[8]

Compounds I, II and III yielded 9,10-dihydro-9,10-ethenoanthracene (V) when treated with sodium in isopropyl alcohol. Compound V was also formed when I and II were treated with zinc in ethyl alcohol. When V was hydrogenated using platinum catalyst, IV was obtained.

Since it was found that I and II could be dehydrochlorinated, kinetic studies were undertaken to determine the rate constants for the bimolecular dehydrochlorination of these compounds and to use these rate constants for determining the entropies and energies of activation for the reaction. The solvent used was a 50–50 volume per cent. mixture of 92.6 weight per cent. ethanol and dioxane. This solvent was used because of the solubilities of the dichloro isomers and of sodium hydroxide.



The reaction rate data for the reaction

$$C_{16}H_{12}Cl_2 + OH^- \longrightarrow C_{16}H_{11}Cl + Cl^- + H_2O$$

were calculated as described previously.[1a] Sodium hydroxide was used as base, and the extent of the reaction was estimated by a Volhard titration for chloride ion. It was necessary to employ conditions which were approximately "pseudo-unimolecular," with a large excess of base. The second-order character of the reaction was shown by the constancy of the reaction rate constants with large changes in base concentration. The reaction rate constants are given in Table I.

TABLE I

DATA AND REACTION RATE CONSTANTS FOR THE REACTION OF THE ISOMERS OF 11,12-DICHLORO-9,10-DIHYDRO-9,10-ETHANOANTHRACENE AND SODIUM HYDROXIDE IN ETHANOLIC DIOXANE

Isomer	Temp., °C.	[Halide], *M*	[NaOH], *M*	10^5k, l./sec./mole	av.	Deviation, %
trans	119.71	0.008553	0.2139	130	134	3.0
		.008565	.4210	138		
	109.56	.008863	.4270	44.0	45.9	4.1
		.008963	.4270	47.8		
	101.88	.008937	.4314	22.3	21.8	2.3
		.009358	.4314	21.3		
	90.68	.008877	.4377	5.59	5.70	1.9
		.008948	.4377	5.81		
cis	128.88	.008588	.4165	35.2	34.3	2.6
		.008595	.4165	33.4		
	119.71	.008845	.4210	14.7	14.5	1.4
		.008834	.2141	14.3		
	109.56	.008928	.4270	6.63	6.42	3.2
		.008915	.4270	6.21		
	101.76	.008749	.4314	3.06	3.01	1.7
		.008670	.4295	2.96		

Using these data, the entropies and energies of

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(6) V. M. Zoroastrova and B. A. Arbuzov, *Doklady Akad. Nauk. S. S. S. R.*, **60**, 59 (1948).

(7) M. T. Rogers and S. J. Cristol, unpublished work.

(8) C. L. Thomas (to Universal Oil Products Company), U. S. Patent 2,406,245 (1946).

activation were calculated by the method described previously.[1c] The experimental uncertainties in E_{act} are estimated at less than 0.8 kcal./mole, with corresponding uncertainties of $\Delta S^{\ddagger}$ at less than 2.4 e.u./mole. The values are given in Table II.

TABLE II

ACTIVATION ENERGIES AND ENTROPIES FOR THE ISOMERS OF 11,12-DICHLORO-9,10-DIHYDRO-9,10-ETHANOANTHRACENE

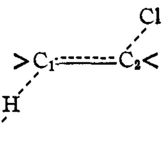
Isomer	$10^5 k_{110°}$, l./sec./mole	Eact, kcal./mole	$\Delta S^{\ddagger}_{110°}$, cal./deg./mole	$PZ_{110°}$, l./sec./mole
cis-(*trans*-hydrogen and chlorine)	6.38	26.5	−11.2	8×10^{10}
trans-(*cis*-hydrogen and chlorine)	49.9	30.6	3.2	1.5×10^{14}

The results are extremely interesting, as this is the first case known to us where *cis*-E2 elimination appears to be favored in rate over *trans* elimination; the *trans* compound with hydrogen atoms *cis* to chlorine atoms reacts approximately eight times as rapidly as the *cis* compound (where *trans* elimination is permitted). Although *trans* elimination is less favored in rate due to an unfavorable entropy term, the energy of activation is 4 kcal./mole lower than that for *cis* elimination. The entropy term in the rate expression favors the *cis* elimination case by a factor of about 2000. We have noted previously[1c] a favorable activation entropy term in *cis* elimination over *trans* in isomeric systems, and in that case as well, the higher entropy value was associated with the higher activation energy. Higher activation entropy terms for *cis* elimination are not general, however (Cristol and Begoon, unpublished work).

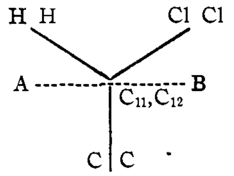
These compounds are quite unreactive toward alkaline dehydrochlorination as compared with the isomers of benzene hexachloride.[1c] A comparison of activation energies with this series of compounds seems significant. Of the benzene hexachloride isomers, the β-isomer, in which all pairs of vicinal hydrogen and chlorine atoms are *cis*, is equivalent to the *trans*-dichloride of Table II. The activation energies for these two compounds were 31.0 and 30.6 kcal./mole, respectively. The α-, γ- and ϵ-isomers, which allow *trans* elimination, had activation energies of 18.5, 20.6 and 21.4 kcal./mole, respectively, in contrast to the equivalent *cis*-dichloride of Table II, with $E_{act} = 26.5$ kcal./mole.

Although it is not possible to make exact comparisons due to differences in the solvents used in the two series of compounds, it appears that in the present case, the reversal in reactivities in *cis* and *trans* elimination seems to be due principally to the increase in activation energy in the *trans* elimination case. It should be noted that calculations, assuming constancy of E_{act} and $\Delta S^{\ddagger}$, indicate that *trans* elimination would be favored at temperatures below about 0°.

In order to correlate structure with reactivity of isomeric cholesterol dibromides and dichlorides in elimination reactions, Barton and Miller[9] suggested that a planar four-centered transition state is necessary for facile *trans* elimination.



In the case of bimolecular dehydrohalogenation as depicted by the preceding diagram, HC_1C_2Cl must lie in the same plane for a minimization of activation energy. In systems which we have studied previously,[1b,1c] this necessity for a planar four-centered transition state can be fulfilled by rotation around the C_1–C_2 bond, and bimolecular dehydrochlorination of *trans* substituents was favored in rate by a factor of 7000 to 24000 over the dehydrochlorination of similar *cis* substituents. In I, which carries *trans* substituents of hydrogen and halogen, the four centers of reaction (H, C_{11}, C_{12} and Cl) do not lie in the same plane.



Looking down an axis through the C_{11} and C_{12}-carbons, it can be seen that the hydrogens and chlorines are each out of the hypothetical plane AB by about thirty-five degrees, and free rotation is forbidden due to the stereochemistry of the polycyclic ring system. Compound I fulfills the steric requirement of *trans* substituents but not the requirement of the reaction centers lying in the same plane.

Our results are thus in agreement with the idea that a planar transition state, allowing for maximum bond overlap in the transition state, is necessary for facile *trans* elimination. We are planning further studies with other *cis–trans* isomers with similar restricted systems.

The results of the eliminations with metals are interesting. In the case of zinc eliminations, product specificity has been noted[10] when diastereomeric α,β-dihalides are treated with zinc in ethyl alcohol. In order to explain the product specificity in zinc eliminations, it is necessary to assume that elimination of *trans* halogen substituents is preferred over elimination of similar *cis* substituents. Consequently, a mechanism similar to that proposed[11] for the reaction of iodide ion with α,β-dihalides has been suggested,[10b] in which the surface of the zinc metal donates two electrons to the halogen, thereby releasing to the β-carbon atom electrons which simultaneously attack the α-carbon, bringing about inversion of the α-carbon atom and release of the halide ion.

As both the *cis*- and *trans*-dichlorides give olefin when treated with metals in alcohols, a *trans*-concerted process for elimination in systems of this type is apparently not mandatory.

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

(10) (a) W. G. Young, Z. Jasaitis and L. Levanas, *ibid.*, **59**, 403 (1937); (b) W. G. Young, S. J. Cristol and T. Skei, *ibid.*, **65**, 2099 (1943).

(11) S. Winstein, D. Pressman and W. G. Young, *ibid.*, **61**, 1645 (1939).

Experimental

1,2-Dichloroethylene.—A mixture of the 1,2-dichloroethylenes was fractionally distilled in a helix-packed column to give *trans*-1,2-dichloroethylene, b.p. 41–41.5° (628 mm.), and *cis*-1,2-dichloroethylene, b.p. 53.8–54.2° (628 mm.).

***trans*-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene.**—Five grams (0.028 mole) of anthracene and 25 g. (0.26 mole) of *trans*-1,2-dichloroethylene reacted for 24 hours at 198–202° in a sealed glass tube (19 × 25 × 600 mm.). After cooling, the sealed tube was opened; the reaction mixture was dissolved in 400 ml. of ligroin (b.p. 60–70°) and passed through a (25 × 450 mm.) column packed with activated alumina (80–200 mesh). The column was washed with ligroin and subsequently with carbon tetrachloride until solid material was no longer detectable when the eluting solvent was evaporated. The solvent was evaporated and 6.4 g. (0.023 mole, 82%) of product was obtained, m.p. 105–110°. After several recrystallizations from ethanol, a product m.p. 113.5–114° was obtained.

Anal. Calcd. for $C_{16}H_{12}Cl_2$: C, 69.83; H, 4.40. Found: C, 69.75; H, 4.53.

***cis*-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene.**—Five grams (0.028 mole) of anthracene and 25 g. (0.26 mole) of *cis*-1,2-dichloroethylene reacted for 24 hours at 200–210° in a sealed glass tube (19 × 25 × 600 mm.). The sealed tube was opened and the reaction mixture was dissolved in carbon tetrachloride and passed through a (25 × 450 mm.) column packed with activated alumina (80–200 mesh). The column was washed with chloroform until the dark area on the alumina had moved to within about a centimeter distance from the bottom of the column. The solvent was evaporated and was found to contain 5.8 g. (0.021 mole, 75%) of eluted product, m.p. 175–197°. After several recrystallizations from carbon tetrachloride, a product melting at 203–204° was obtained.

Anal. Calcd. for $C_{16}H_{12}Cl_2$: C, 69.83; H, 4.40. Found: C, 69.65; H, 4.43.

Maleic Anhydride Method of Purification.—When larger batches of the 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracenes were prepared, it was found that they were contaminated with unreacted anthracene. In these cases, the excess 1,2-dichloroethylene was evaporated from the adduct. The adduct (12–15 g.) and 10 g. of maleic anhydride were added to 150 ml. of xylene, and the reaction mixture was refluxed for 1 hour. The solution in xylene was then transferred to an apparatus set for steam distillation. Twenty grams of sodium bicarbonate was added and the xylene was removed by steam distillation. The steam distillation was continued for half an hour after the last xylene had distilled over. The mixture of sodium bicarbonate solution and adduct remaining in the distilling flask was extracted with benzene, and the benzene extract was washed with water. The benzene was evaporated, and the semi-pure adduct which remained was dissolved in the appropriate solvent and purified by use of an activated alumina column, as described previously.

11-Chloro-9,10-dihydro-9,10-ethenoanthracene.—In 10 ml. of approximately normal ethanolic sodium hydroxide was dissolved in 710 mg. (0.0027 mole) of *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene. The solution was sealed in a test-tube (18 × 150 mm.) which was placed in an oil-bath at 122–128°. After three days the sealed tube was removed, broken, and washed with water. To the solution and washings from the test-tube was added enough water to make the total volume 100 ml. A flocculent precipitate which formed on the addition of the water was removed by filtration. A rough Volhard titration on a sample of the filtrate showed that approximately 90% of the theoretical amount of chloride ion had formed, assuming the formation of one mole of chloride ion per mole of compound. The precipitate contained 550 mg. (0.0023 mole, 85%) of product, m.p. 127.5–128°. After two recrystallizations from ethanol, the melting point remained at 127.5–128°.

Anal. Calcd. for $C_{16}H_{11}Cl$: C, 80.50; H, 4.64. Found: C, 80.41; H, 4.81.

cis-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene gave the same monochloroölefin in 83% yield when treated with base in a similar manner. A mixed melting point of the products obtained from both isomers showed no depression.

9,10-Dihydro-9,10-ethenoanthracene.—Into a solution of 133 mg. (0.0005 mole) of *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene in 20 ml. of refluxing isopropyl alcohol small pieces of sodium metal were dropped through the reflux condenser at time intervals determined by the intensity of the reaction. The total sodium added was 120 mg. (0.005 g. atom). The heating of the reaction mixture was continued until all the sodium was destroyed. The reaction was stopped, and sufficient water was added to make the total volume of solution 100 ml. The flocculent precipitate which formed upon addition of water was allowed to settle, and a 10-ml. sample of the supernatant liquid was pipetted and analyzed for chloride ion content by a Volhard titration. It showed that 97% of the chlorine in the molecule had been removed. The precipitate was filtered off to give 64 mg. (0.0003 mole, 60%) of material, m.p. 109–115°. After several recrystallizations from aqueous ethanol, the melting point was 118.5–119°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 93.92; H, 6.12.

cis-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene gave the same product in 52% yield when similarly treated in isopropyl alcohol with sodium. A mixed melting point of the products obtained from both isomers showed no depression.

11-Chloro-9,10-dihydro-9,10-ethenoanthracene, when treated similarly in isopropyl alcohol with sodium, gave a 50% yield of the same product, as determined by a mixed melting point.

In 20 ml. of ethanol was dissolved 102 mg. (0.0004 mole) of *cis*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene. To this solution was added 3.8 g. of 80-mesh zinc. The reaction was refluxed for 12 days, and the extent of the reaction was followed by taking samples at given intervals and analyzing for chloride ion content, using the Volhard procedure. After the reaction had gone to completion, the zinc was filtered from the reaction solution. Water was added, and the precipitate which was formed on the addition of water was filtered, yielding 20 mg. (0.0001 mole) of product. This represents a 43% yield when correction is made for four 2-ml. samples which were removed for the Volhard titrations. After several recrystallizations from aqueous ethanol, the product melted at 118.5–119°. A mixed melting point with the product obtained by the sodium elimination showed no depression.

The *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene, when treated in the same manner with zinc in ethanol, gave a product in 42% yield which showed no depression in melting point when mixed with the product obtained from the *cis* isomer.

9,10-Dihydro-9,10-ethanoanthracene.—Sixty-eight milligrams of 9,10-dihydro-9,10-ethenoanthracene was dissolved in 10 ml. of ethanol. About 10 mg. of platinum oxide was added to the solution, and the hydrogenation was conducted at room temperature in a semi-micro hydrogenation apparatus. Upon completion of the hydrogenation, the catalyst was filtered off, and the alcohol was evaporated. After two recrystallizations from ethanol, a product melting at 142–143° was obtained. A mixed melting point of this compound with that[12] obtained by the method of Thomas[8] showed it to be 9,10-dihydro-9,10-ethanoanthracene.

When 11-chloro-9,10-dihydro-9,10-ethenoanthracene was hydrogenated under the same conditions, one mole of chloride ion was formed per mole of compound, as determined by a Volhard titration, and a mixed melting point of the product with 9,10-dihydro-9,10-ethanoanthracene showed no depression.

Determination of Rates of Dehydrohalogenation.—The procedure used may be illustrated by the description of a typical kinetic run. In 50 ml. of 0.9514 *N* ethanolic sodium hydroxide in a 100-ml. volumetric flask at room temperature was dissolved 0.2663 g. (0.0009678 mole) of *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene. The total volume of the solution was then made up to 100 ml.[13] by the addition of a sufficient quantity of dioxane.[14] Ten-ml. ali-

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[12] Thomas reports[8] a melting point of 142–153° for this compound. However, it would appear that this was a typographical error, for the compound obtained melted at 142–143°. This has been confirmed by correspondence with Mr. J. R. Hoatson of the Universal Oil Products Co.

[13] The temperature of the room was held at about 22.5° in order to minimize volumetric errors.

[14] Purified. See L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 368.

quots of this solution were carefully sealed in test-tubes (18 × 150 cm.) which were weighted and placed in an oil-bath at 119.71 ± 0.08°. As the reaction progressed, samples were removed and placed in an ice-bath. After careful washing, the sample tubes were then opened in erlenmeyer flasks and titrated for chloride ion content by the Volhard method. The rate constants were determined in the manner described previously. A correction was applied to the rate constants for volume expansion, as the reaction temperature was much higher than that at which the solutions were made up for the kinetic run.

Because of the peculiar solvent and high temperatures used, coefficient of expansion data were not available; so a special method was developed for measuring volume expansion. Twenty-five milliliters of a 50% (by vol.) solution of dioxane in 92.6% (by wt.) ethanol were sealed in a Kimble glass buret. The height of the liquid in the buret at 22.5° was determined by reading the buret markings. The buret was then completely immersed in the oil-bath at the temperature used for the kinetic run and, after equilibrating, the new height of the liquid in the buret was observed. The difference in level between that at 22.5° and that at the temperature of the kinetic run represents the volume expansion for 25 ml. of the solution. Of course, this increase in volume had to be corrected for the expansion of Kimble glass.

The correction factor, C, by which the rate constant is multiplied is given by the equation

$$C = (V + \Delta V + A)/V$$

where V is 25 ml., ΔV is the observed volume expansion and A is a correction factor for the expansion of Kimble glass. The factor A may be determined from the equation

$$A = nl\pi d^2/4[(l + \alpha\Delta T)^3 - l]$$

where n is the distance in centimeters between milliliter buret markings, l is the buret reading at the temperature of the kinetic run, d is the inside diameter of the buret at 22.5°, α[15] is the linear coefficient of expansion of Kimble glass, and ΔT is the difference between the temperature of the kinetic run and 22.5°. Correction factors are given in Table III.

TABLE III

CORRECTION FACTORS

V = 25 ml. at 22.5°

T, °C.	ΔV, ml.	A, ml.	C
90.68	2.10	0.05	1.086
101.88	2.50	.06	1.102
109.56	2.80	.06	1.114
119.71	3.17	.07	1.130
128.88	3.47	.08	1.142

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(15) α = 0.0000092 cm./cm./°C.

BOULDER, COLORADO

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

Synthesis of Sedoheptulose (D-Altroheptulose)[1]

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Sedoheptulose, as its 2,7-anhydropyranose form, has been synthesized from D-altronic acid. This further verifies its structure as D-altroheptulose.

Sedoheptulose, originally designated sedoheptose, was isolated from the common garden plant *Sedum spectabile* by LaForge and Hudson[2] as its characteristic anhydro form designated sedoheptulosan. The structure of the basic sugar unit was established as D-altroheptulose by Ettel[3] and sedoheptulosan was later demonstrated[4] to be 2,7-anhydro-D-altroheptulopyranose. Recently it has been shown that phosphorylated sedoheptulose is an apparent intermediate in plant photosynthesis.[5] We report herein a synthesis of this ketoheptose from D-altronic acid by a procedure which verifies its structure as D-altroheptulose. All intermediates were unfortunately not crystallizable but the inherent and unusual ease of crystallization of the final product, the anhydro sugar, allowed the synthesis to be completed successfully.

Experimental

Sedoheptulosan from Cadmium D-Altronate.—Following the general procedure of Ladenburg and co-workers[6] for the preparation of fully acetylated aldonic acids, 60 g. of the crystalline cadmium salt of D-altronic acid[7] was added under mechanical stirring to 350 ml. of acetic anhydride. This reaction mixture was cooled to 10° and dry hydrogen chloride gas was passed slowly through the agitated slurry. After 15–20 min. the temperature of the solution rose rapidly and then slowly subsided. When a constant temperature was reached, a water-bath was substituted for the ice-bath, the stirring of the solution and the passage of hydrogen chloride being continued. Concluding 1 hr. at 50°, this acetylation mixture was allowed to stand for 12 hr. at room temperature. The solution was concentrated under reduced pressure at 50–60° until a thick slurry resulted. The cooled residue was treated with 500 ml. of ice and water to hydrolyze the acetic anhydride and to dissolve the cadmium salts. This solution was thrice extracted with chloroform and the combined extracts were washed once with water, dried over Na_2SO_4, decolorized with charcoal and concentrated under reduced pressure to a sirupy D-altronic acid pentaacetate which resisted crystallization.

An amount of 25 g. of the above product was dissolved in 200 ml. of toluene, 25 g. of purified[8] thionyl chloride added, and the solution brought to reflux. After 2 hr. of gentle reflux, the excess thionyl chloride and toluene were removed under reduced pressure to yield a sirupy D-altronyl chloride pentaacetate which resisted crystallization.

An amount of 20 g. of the above sirupy product dissolved in 100 ml. of abs. ether was added slowly to 200 ml. of abs. ether containing 6.0 g. of diazomethane. The solution stood at room temperature for several hours and was then kept at ice-box temperature for 24 hr. Solvent removal yielded a sirupy 1-diazo-1-desoxy-*keto*-D-altroheptulose pentaacetate which resisted crystallization. One gram of this preparation was dissolved in 10 ml. of benzene and chromatographed on a 230 × 35 mm. (i.d.)[9] column of Magnesol[10]–Celite[10] (5:1 by wt.) by development with 600 ml. of benzene–ethanol (100:1 by vol.). An alkaline permanganate streak[10] indicated one main zone near the bottom of the

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(1) Paper No. 14 in the series entitled "The Action of Diazomethane upon Acyclic Sugar Derivatives"; previous communication, M. L. Wolfrom and H. B. Wood, THIS JOURNAL, **73**, 730 (1951).

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