the reaction was run for nine half-lives under pseudo first-order conditions (large excess of base), only 70–75% of the theoretical amount of chloride was produced. This amount did not appear to depend upon the concentration of alkali, so no base-insensitive transformation to a material which does not liberate chloride ion rapidly was involved. We suspect that our *trans* material was contaminated with the *cis-endo* isomer which, of course, is about 1/85 as reactive as the *trans* isomer. To correct for this, we attempted plots of our data feeding into our calculations various factors depending upon the percentage of *trans*-dichloride in the starting material. The data on all of the runs gave excellent straight lines when the value 71% was used to correct the initial concentration of dichloride and, of course, the extent of reaction as well. The rate constants in Table I are thus corrected.

As the solutions were made up at 20° and the reactions were run at 101 and 116°, the rate constants were further corrected for solvent expansion. The observed rate constants were multiplied by 1.09 and 1.11 at 101 and 116°, respectively.[17]

The rates at 12° were carried out in a thermostated water-bath in a room also held at 12°. Appropriate solutions of the chlorosulfone and base in 1-pentanol were equilibrated in the bath, were rapidly mixed in a volumetric flask, which was then filled to the mark with temperature-equilibrated 1-pentanol. The flask was shaken to mix the solution thoroughly and was then immersed in the bath. Samples were withdrawn every few minutes with a pipet having a tip which had been blown out to give rapid delivery, and these were run into an erlenmeyer flask containing 10 ml. of 2 *N* nitric acid. The runs at 0° were conducted in a water-ice bath in a room held at 5°. The pipets used for withdrawing samples were insulated by wrapping them with asbestos string and were stored in a long test-tube at 0°. In other respects the procedure followed was similar to that at the higher temperature.

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[17] A. Zander, *Ann.*, **224**, 56 (1884).

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

Mechanisms of Elimination Reactions. XIX. Elimination and Solvolytic Reactivities in Some Bicyclo[2,2,1]heptane and Bicyclo[2,2,2]octane Derivatives[1,2]

BY STANLEY J. CRISTOL AND ROBERT P. ARGANBRIGHT

RECEIVED JANUARY 18, 1957

A striking lack of stereospecificity in elimination reactions involving bonds held in the rigid eclipsed positions available in boat-form cyclohexane molecules has been noted in the reaction of sodium hydroxide with the *cis* and *trans* isomers of 11-*p*-toluenesulfonyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. Both compounds reacted rapidly with alkali at 0 and 12°, the *cis* compound (*trans* elimination) reacting about three times as fast as the *trans* isomer. These results compared with those reported earlier for 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene are well accommodated by the assumption that a carbanion is formed in the first step of the elimination reaction. Solvolysis rate constants for several β-chlorothioethers in bicycloheptane and bicycloöctane ring systems were determined in 85% ethanol at 116°. The extremely low reactivities and the minor difference in reactivity between *cis* and *trans* isomers demonstrate the lack of significant neighboring-group acceleration of solvolysis with groups held at rigid eclipsed bond angles.

Previous work[3] has shown that the normal preference for *trans* elimination disappears when groups are held rigidly in fixed positions such that *trans* coplanarity cannot be attained readily in the transition state for elimination. Evidence has been adduced to suggest that in these circumstances an alternative mechanism involving a carbanion is operative. It is the purpose of the present paper to supply further data in support of this postulate.

We have studied the rates of elimination of hydrogen chloride with sodium hydroxide from *cis*-(I) and *trans*-11-*p*-toluenesulfonyl-12-chloro-9,10-dihydro-9,10-ethanoanthracenes (II) to compare the rate constants and quantities of activation with those of the corresponding 11,12-dichlorides previously studied.[4] The rates were measured in a solvent consisting of 50% by volume of ordinary ethanol and 50% of dioxane. The rate data are given in Table I.

It will be noted that these compounds show extremely high reactivity toward elimination; the reactions proceed at quite rapid rates at 0 and 12°. These results may be contrasted with the results on the corresponding dichlorides,[4] which react at comparable rates at temperatures about 150° higher. If the data obtained on the dichlorides are extrapolated to 12°, the comparison of these values with the values given in Table I for the chlorosulfones indicate that substitution of a chlorine atom by a *p*-toluenesulfonyl group increases the rate of elimination by about 10 powers of 10. In addition, it should be noted that these compounds show little stereospecificity in the elimination reaction, *trans* elimination being favored over *cis* by a factor of only 3. It is of interest to note that in the two dichloride systems previously studied, that is, the dichlorodihydroethanoanthracenes[4] and the 2,3-dichloronorbornanes,[1] *cis* elimination was favored slightly over *trans*. In the present system, however, *trans* elimination is slightly favored over *cis*.

The striking lack of stereospecificity in this system, as well as in the systems previously studied, seems to us to be best explained on the basis that carbanion intermediates are involved and that a multiple-stage mechanism for elimination is utilized in these systems where bonds are rigidly held in eclipsed positions and a *trans* coplanar transition state is geometrically improbable. The tremendous increase in reactivity observed when an arenesulfonyl group replaces a chlorine atom in these systems may also be rationalized by the assumption that a carbanion mechanism is involved. We feel that the results given here lend additional support to the arguments given earlier.[1]

In addition it should be noted that a comparison

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[1] Previous paper in series: S. J. Cristol and E. F. Hoegger, THIS JOURNAL, **79**, 3438 (1957).

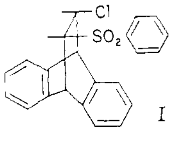
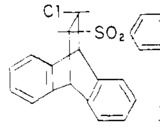
[2] This work was reported at the 130th meeting of the American Chemical Society in Atlantic City, New Jersey, September, 1956.

[3] References to previous work in this field are given in reference 1.

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

TABLE I

DATA AND SPECIFIC RATE CONSTANTS FOR THE REACTION OF β-CHLOROSULFONES AND SODIUM HYDROXIDE IN ETHANOLIC DIOXANE

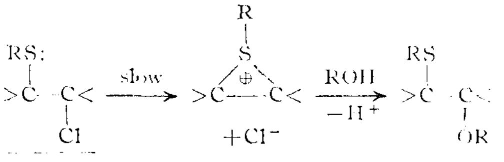
Compound	Temp., °C.	Halide, *M*	NaOH, *M*	*k*, l./mole/sec.	Av.	Dev., %	E_{act}, kcal./mole
 I	12.1	0.00192	0.00253	8.85	9.65	8.3	
		.00189	.00209	10.46			
	0.0	.00194	.00211	2.84			16.3
		.00189	.00211	2.61	2.65	7.0	
		.00199	.00211	2.51			
 II	12.1	.00524	.00421	2.83			
		.00612	.00419	3.01	3.10	7.8	
		.00225	.00253	3.47			
	0.0	.00389	.00422	0.926	0.920	0.6	15.6
		.00376	.00422	0.914			

of the rate data obtained on the dichlorides[1,4] with those data reported for *cis*- and *trans*-1,2-dichlorocyclohexane[5] is also consistent with the assumption that a carbanion intermediate is involved in systems which do not have favorable geometry for the concerted process.

Barton and Cookson[6] have recently discussed the effect of conformation upon neighboring-group participation in solvolytic reactions[7] and have pointed out the necessity for axial–axial relationships in providing neighboring-group assistance in chair-form cyclohexane derivatives. We were interested in a study of solvolysis rates for β-chlorosulfides which have the fixed eclipsed structures of boat-form cyclohexane molecules such as are present in bicycloheptanes and bicyclooctanes. Accordingly, solvolysis rates were studied in 85% ethanol with certain β-chlorothioethers, including *exo*-2-thiocresoxy-*endo*-3-chloronorbornane (III), *exo*-2-thiocresoxy-*endo*-3-chloro-5-norbornene (IV), and *cis*- (V) and *trans*-11-*p*-thiocresoxy-12-chloro-9,10-dihydro-9,10-ethanoanthracene (VI). The rate constants for the compounds studied are given in Table II.

It should be noted that all of the β-chlorosulfides reacted very slowly, even at 116°, the reactivities being roughly equivalent to those of bornyl chloride[8] (*endo* chlorine) or *endo*-norbornyl chloride.[9] No large difference was noted between the *cis* and *trans* isomers studied; the *trans* isomer reacted only four times as fast as the *cis* isomer. The relative inertness of our compounds may also be compared with the reactivity reported for *trans*-2-chlorocyclohexyl phenyl thioether.[10] This compound solvolyzes completely in 30 minutes at 100° in 80% ethanol.

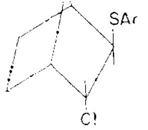
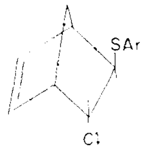
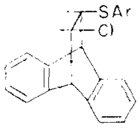
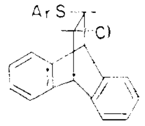
The normal mode of solvolysis of a β-chlorothioether may be presumed[11] to be



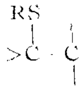
$$>\overset{\text{RS:}}{\overset{|}{\text{C}}}-\underset{\text{Cl}}{\underset{|}{\text{C}}}< \xrightarrow{\text{slow}} \underset{+\text{Cl}^-}{>\text{C}\overset{\overset{\text{R}}{|}}{\overset{\text{S}}{\overset{\diagup\oplus\diagdown}{}}}\!\!-\!\!\text{C}<} \xrightarrow[-\text{H}^+]{\text{ROH}} >\overset{\text{RS}}{\overset{|}{\text{C}}}-\underset{\text{OR}}{\underset{|}{\text{C}}}<$$

TABLE II

RATES OF SOLVOLYSIS OF SOME β-CHLOROTHIOETHERS IN 85% ETHANOL AT 116.5°

Compound[a] Ar = *p*-tolyl	Halide, *M*		*k*, sec.$^{-1}$
 III	0.009		2.5×10^{-5}
	.004		2.8×10^{-5}
		Av.	2.6×10^{-5}
 IV	0.005		6.3×10^{-6}
	0.004		7.0×10^{-6}
		Av.	6.6×10^{-6}
 V	0.003		1.2×10^{-6}
	0.003		0.9×10^{-6}
		Av.	1.1×10^{-6}
 VI	0.002		5.9×10^{-6}
	0.001		5.6×10^{-6}
		Av.	5.8×10^{-6}

with rate enhancement of about 10^7 over the corresponding simple alkyl halide due to neighboring-group participation of the β sulfur atom.[11] No such rate enhancement is noted in our compounds, and it therefore appears that the formation of the sulfonium intermediate cannot be a part of the rate-determining step, but rather that a simple carbonium ion of type



$$>\overset{\text{RS}}{\overset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}^{+}}}$$

is being formed. The most reasonable explanation for these results appears to us to be a definite stereochemical requirement for *trans*-coplanarity in neighboring-group assistance of solvolysis and that this requirement cannot be met in the rigid geometry of these bicycloheptanes and bicyclooctanes.

It may be further noted that the norbornene chlorothioether was somewhat less reactive than the norbornane analog. This is consistent with observations made on the corresponding *endo* chlo-

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(5) H. L. Goering and H. H. Espy, THIS JOURNAL, **78**, 1454 (1956).

(6) D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 44 (1956).

(7) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, THIS JOURNAL, **74**, 1113 (1952).

(8) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952).

(9) J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

(10) H. L. Goering, D. I. Relyea and D. W. Larson, *ibid.*, **78**, 348 (1956).

(11) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

rides[9] and *endo-p*-bromobenzenesulfonates.[12] Rate data further indicate that there is little driving force toward solvolysis by participation of the π electrons of the benzene ring in solvolysis of the ethanodihydroanthracenes. Some participation might have been anticipated by analogy with the participation observed in *exo*-dehydronorbornyl systems, although the analogous bicyclo[2.2.2]octenyl systems have not been studied and may indeed show no such participation.[13]

Acknowledgments.—The authors are indebted to the Office of Naval Research, U. S. Navy, and to the National Science Foundation for support of this work.

Experimental

Preparation of Compounds.—The preparation of the materials used in these studies will be reported elsewhere. In general the chlorosulfides were prepared by addition of *p*-toluenesulfenyl chloride to the corresponding olefin or of thiocresol to the chloroölefin. The sulfones were prepared by oxidation of the chlorothioether with hydrogen peroxide.

Rate constants for elimination were measured as follows.

A weighed amount of the β-chlorosulfone, from 0.1 to 0.8 mmole, was placed in a 100-ml. volumetric flask and 50 ml. of dioxane, measured at the temperature of the run, was added. About 40 ml. of 92.6% (by wt.) ethanol was then added, and the flask was placed in a 12.1° rate bath thermostatically controlled to a ±0.05°. After solution was complete and the contents had come to the temperature of the bath, a measured amount of ethanolic sodium hydroxide (normality calculated at 12.1°) was added followed by enough 92.6% ethanol (kept at 12.1°) to bring the volume up to the mark on the flask. The flask was removed from the bath and was shaken vigorously for several seconds. It was immediately replaced in the bath and, because the rates were fast, the first sample usually was taken almost immediately thereafter.

Since room temperature, in the case of the 12.1° runs, was about 20°, an asbestos-wrapped 10-ml. pipet was used for sampling. The samples were pipetted directly into 5 ml. of 3 N nitric acid contained in a 100-ml. erlenmeyer flask, the time being recorded the instant the sample started to flow from the pipet. The same pipet was used for all samples. The tip of the pipet was blown out to allow rapid drainage. The samples were analyzed for chloride ion by the Volhard procedure. Calculations of rate constants were made as described previously.[1,4]

The rate studies at 0° were run similarly except that an ice-water bath was employed in a room held at 2°.

Rate constants for solvolysis were measured as follows:

A sample of the β-chlorothioether (about 0.2 mmole) was weighed into a 50-ml. volumetric flask and 50 ml. of 85% (by wt.) ethanol[14] was added at room temperature. After solution of the thioether had occurred, nine 5.5-ml. samples were removed and placed in 15 × 125 mm. Pyrex test-tubes which were then sealed. All tubes in any particular run were then placed in an oil-bath thermostatically maintained at 116.5 ± 0.05°. Tubes were removed at measured time intervals and were placed in a cold chest until the run was finished. The tubes were then opened and warmed to 20° and exactly 5 ml. was pipetted out of each into flasks for titration. Each sample was diluted with 25 ml. of ordinary ethanol, 2 drops of a mixed indicator (0.075% brom cresol green and 0.05% methyl red in ethanol) was added and the sample was titrated with aqueous 0.01 N sodium hydroxide. The first-order rate constants fell off with time, presumably due to reaction of ethanol with the hydrochloric acid produced in the solvolysis. The first-order plots were straight lines for the initial period of the reaction, however, and the straight-line portions were used to calculate the rate constants. It has been estimated that these results are accurate to ±30%.

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[12] S. Winstein, H. M. Walborsky and K. Schreiber, THIS JOURNAL, **72**, 5795 (1950).

[13] For a discussion of the corresponding saturated systems, see H. M. Walborsky, *Experientia*, **9**, 209 (1953).

[14] This solvent was chosen, in place of the more customary 80% ethanol, in order to effect solubility of the difficultly soluble ethanoanthracene derivatives.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORIES, HARVARD UNIVERSITY]

The Relative Stabilities of *cis* and *trans* Isomers. III. The Cyclodecenes

BY NORMAN L. ALLINGER[1,2]

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The equilibrium constant for the reaction *trans*-cyclodecene ⇄ *cis*-cyclodecene has been determined to be >200 (25°). The dipole moments and other physical properties of the isomers were measured, and the relationships between these various quantities are discussed.

Introduction

It has long been a goal of organic chemists to be able to predict which of the various possible stereoisomeric structures exists in a given compound, either by a consideration of the reactions used to prepare the compound, or by an examination of its physical properties. Thus far no really general methods for accomplishing these purposes have been found. There have been evolved instead numerous rules for determining which of the various stereochemically possible products will result from a given reaction[3] and other rules which may be used to determine structure from physical properties.[4] Among the rules of the latter type, that of von Auwers was the earliest[4a] and it saw considerable service. It became clear at an early date however that exceptions to von Auwers rule existed,[5] nevertheless a great many structures were assigned using this rule some of which subsequently have been shown to be incorrect. When these incorrect assignments were uncovered several workers restated the rule in modified forms in an attempt to obtain a really useful

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[1] Department of Chemistry, Wayne State University, Detroit 2, Mich.

[2] National Science Foundation Post-doctoral Fellow, 1955–1956.

[3] For a recent discussion of this subject see P. B. D. de la Mare in W. Klyne, "Progress in Stereochemistry," Butterworths Scientific Publications, London, 1954, pp. 90–125.

[4] (a) K. von Auwers, *Ann.*, **420**, 84 (1920); (b) L. H. Darling, A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 1364 (1953); (c) S. Siegel, THIS JOURNAL, **75**, 1317 (1953); (d) W. E. Bachmann, A. Ross, A. S. Dreiding and P. A. S. Smith, *J. Org. Chem.*, **19**, 222 (1954); (e) F. R. Hewgill, P. R. Jefferies and A. K. Macbeth, *J. Chem. Soc.*, 699 (1954); (f) N. L. Allinger, *Experientia*, **10**, 328 (1954).

[5] (a) A. Skita, *Ber.*, **56**, 1014 (1923); (b) K. von Auwers and B. Ottens, *ibid.*, **57**, 437 (1924).