The infrared spectra of reactions run in the presence of copper had peaks at 810 and 733 cm.$^{-1}$ that were not accounted for by the 9,10-dihydrophenanthrene or by *sym*-diphenylethane. Phenanthrene has characteristic peaks at these positions. The presence of phenanthrene was verified by the appearance of characteristic ultraviolet peaks at 3295, 3375 and 3455 Å. The rather concentrated sample required cut off at 3200 Å. The phenanthrene concentration as estimated by the base-line technique agreed excellently with that estimated from the infrared curve. That the phenanthrene originated from the diazonium salt of 2-amino-*sym*-diphenylethane and not from that of *cis*-2-aminostilbene present as an impurity was established by the observation that phenanthrene was not produced in all runs.

Quantitative Spectrophotometric Analyses.—Infrared spectra were obtained in carbon disulfide solution in a fixed cell 0.106 mm. thick using a Perkin-Elmer model 21 spectrophotometer equipped with sodium chloride optics. For quantitative work, concentrations were adjusted to give peaks between 15 and 85% transmittance. The curve of the pure solvent was used to obtain the 100% transmission line, and a strong solvent absorption peak was used to give the 0% absorption value. Ultraviolet spectra were obtained with a Cary model 14 spectrophotometer using solvent in the reference beam. The absorbance curve of solvent *vs.* solvent was run after each solution.

A representative calibration analysis of known 3-methylfluorenone and 4-methylbenzophenone mixtures is given in Table IV. The results obtained with mixtures of the other compounds are comparable.

TABLE IV

INFRARED ANALYSIS OF KNOWN MIXTURES OF 3-METHYLFLUORENONE AND 4-METHYLBENZOPHENONE[a]

3-Methylfluorenone taken, %[b]	4-Methylbenzophenone taken, %	3-Methylfluorenone found, %[c]	4-Methylbenzophenone found, %[d]
1.001	0.428	0.939	0.432
1.014	1.044	.984	1.066
0.985	1.438	.989	1.422
.916	0.094	.993	0.086
.351	.356	.404	.351
1.777	.157	1.726	.156

[a] Using the 3-methylfluorenone peaks at 1723 and 765 cm.$^{-1}$ and the 4-methylbenzophenone peaks at 1668 and 1276 cm.$^{-1}$. [b] Concn. in wt. % in CS_2. [c] Std. dev. 0.063. [d] Std. dev. 0.015.

An ultraviolet spectrophotometric assay was made of several samples of 2-(4′-methylbenzoyl)-benzenediazonium bisulfate and showed that the preparation of pure samples of this diazonium salt was readily reproducible.

COLUMBIA, S. C.

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

The Base-promoted Dehydrohalogenation of *cis*- and *trans*-2-Chlorocycloalkyl Aryl Sulfones[1]

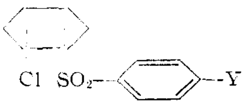
BY HARLAN L. GOERING, DOUGLAS I. RELYEA AND KING L. HOWE[2]

RECEIVED JUNE 29, 1956

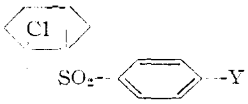
The base-promoted dehydrochlorination of *cis*-(I) and *trans*-2-chlorocyclohexyl aryl sulfones (II), and *cis*-(III) and *trans*-2-chlorocyclopentyl aryl sulfones (IV) in "80%" ethanol has been investigated. Rate constants and activation energies were determined for the least reactive of the four series of compounds, the *trans*-2-chlorocyclohexyl aryl sulfones. The other three series of compounds are too reactive to follow by the sampling technique used in the present work. For these compounds approximate relative reactivities were determined. In each of the four series of chlorocycloalkyl aryl sulfones I–IV, electron-withdrawing substituents in the aryl moiety increase the rate of dehydrochlorination. The following rate sequence for corresponding *p*-substituted 2-chlorocycloalkyl aryl sulfones was observed: *cis*-2-chlorocyclopentyl > *cis*-2-chlorocyclohexyl > *trans*-2-chlorocyclopentyl > *trans*-2-chlorocyclohexyl. The rate of elimination for *trans*-2-chlorocyclohexyl phenyl sulfone is essentially the same as that for *trans*-2-tosyloxycyclohexyl phenyl sulfone. The *trans*-2-chlorosulfones II and IV undergo *cis* elimination, evidently by a two-step process involving abstraction of the C_1-hydrogen followed by conversion of the resulting anion to the elimination product. The first step is rate determining and irreversible under the present conditions (*i.e.*, 80% ethanol containing 0.004 to 0.03 *M* sodium hydroxide). Presumably the *cis*-chlorosulfones I and III undergo a concerted *trans* dehydrohalogenation.

Introduction

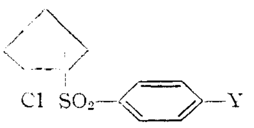
In connection with a study[3,4] of the stereochemistry of radical additions, several *cis*-(I) and *trans*-2-chlorocyclohexyl aryl sulfones (II) and *cis*-(III) and *trans*-2-chlorocyclopentyl aryl sulfones (IV) were prepared. This paper describes the base-promoted dehydrochlorination of these four series of compounds in "80%"[5] ethanol. The effect of the β-sulfone group on the rate of dehydrohalogenation was of interest for comparison with the effect of β-halogen atoms observed in an earlier study.[6] The behavior of the *trans*-2-chlorocycloalkyl aryl sulfones was also of particular interest because of the recent observation by Bordwell and co-workers[7] that in similar systems the β-sulfone group activates the β-hydrogen so that *cis* elimination occurs rather than a concerted *trans* elimination.



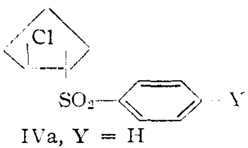
Ia, Y = H
Ib, Y = CH_3
Ic, Y = Cl



IIa, Y = H
IIb, Y = CH_3
IIc, Y = Cl
IId, Y = NO_2



IIIa, Y = H
IIIb, Y = CH_3
IIIc, Y = Cl



IVa, Y = H
IVb, Y = CH_3
IVc, Y = Cl
IVd, Y = NO_2

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(1) This work was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600) 1037.

(2) Socony-Mobil Fellow, 1955–1956.

(3) H. L. Goering, D. I. Relyea and D. W. Larsen, THIS JOURNAL, **78**, 348 (1956).

(4) K. L. Howe and D. I. Relyea, unpublished results.

(5) The solvent was prepared by mixing four volumes of pure ethanol and one volume of water at 25°.

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

(7) (a) J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **76**, 4748 (1954); **78**, 3468, 3473 (1956); (b) F. G. Bordwell and R. J.

Results

The chlorosulfones I-IV were obtained by oxidation (hydrogen peroxide or perbenzoic acid) of the corresponding sulfides. *trans*-2-Chlorocycloalkyl aryl sulfides were prepared by the *trans* addition[3,8] of the appropriate benzenesulfenyl chloride to cyclohexene or cyclopentene. The *cis*-chlorosulfides were obtained by the radical addition of the appropriate thiophenol to 1-chlorocyclohexene or 1-chlorocyclopentene.[3,4] *trans*-2-Tosyloxycyclohexyl phenyl sulfone, which was of interest for comparison of the rate of elimination with that of *trans*-2-chlorocyclohexyl phenyl sulfone, was prepared from the corresponding alcohol which in turn was obtained by oxidation of *trans*-2-hydroxycyclohexyl phenyl sulfide.[3]

The 2-chlorocycloalkyl aryl sulfones I-IV dehydrochlorinate rapidly at 0 to 10° in "80%" ethanol containing 0.004 to 0.03 M sodium hydroxide. That the reactions are indeed base-promoted is clear from the fact that the chlorosulfones do not solvolyze to a detectable extent in 24 hours at 25°, whereas in the presence of 0.03 M sodium hydroxide the least reactive compounds IIa and IIb are about 50% reacted in 2 hours at 10°.

The chlorosulfones dehydrochlorinate so rapidly that only for the least reactive series of compounds, the *trans*-2-chlorocyclohexyl aryl sulfones (II), could accurate rate constants be determined. The specific second-order rate constants (k) for this series of compounds and for *trans*-2-tosyloxycyclohexyl phenyl sulfone are shown in Table I. The reactions were quenched by rapidly delivering aliquots of reaction mixture into excess acid. The extent of reaction at the time of quenching was determined by either (a) titration with base to determine the amount of base consumed during the reaction (method A) or (b) Volhard titration of chloride ion (method B). The values of k given in Table I are the averages and mean deviations of six to ten values calculated by use of the appropriate equation for a second-order reaction. The reactions were followed to about 80% completion and no trends in k were observed. As shown in Table I, values of k were found to be reproducible.

The remaining three series of compounds (I, III and IV) dehydrochlorinate too rapidly even at 0° to be followed by conventional sampling techniques. Approximate relative reactivities for these compounds at 0° were determined from the lengths of time required for solutions 0.02 M in substrate and 0.01 M in sodium hydroxide in "80%" ethanol containing brom thymol blue to reach the same color as that of a slightly alkaline buffered solution of the indicator. From the relative reactivities thus obtained, together with the approximate second-order rate constant of 0.35 l. mole^{-1} sec.$^{-1}$ for the dehydrochlorination of *trans*-2-chlorocyclopentyl *p*-chlorophenyl sulfone (IVc) at 0°,[9] the reactivities of I, III and IV relative to *trans*-2-chlorocyclohexyl phenyl sulfone (IIa) can be calculated. The results are presented in Table II. As indicated in Table II, the relative reactivities measured in this way are reproducible to within 10%.

TABLE I

RATES OF SECOND-ORDER ELIMINATION FOR *trans*-2-CHLOROCYCLOHEXYL ARYL SULFONES AND *trans*-2-TOSYLOXYCYCLOHEXYL PHENYL SULFONE IN "80%" ETHANOL

trans-2-Chloro-cyclohexyl-sulfone	Method[a]	Temp. °C.	RX 10^3M	NaOH 10^3M	10^3k, l. mole^{-1} sec.$^{-1}$	E_a, kcal.
p-Tolyl		0.0			2.6[b]	16.6
(IIb)	B	8.36	9.8	19.8	6.44 ± 0.02	
	A	19.86	17	28	21.2 ± .3	
	B	20.05	9.9	9.4	21.0 ± .1	
Phenyl		0.0			4.5[b]	15.7
(IIa)	B	8.36	9.5	19.7	10.7 ± 0.2	
	A	9.95	11	13	11.5 ± .3	
	A	9.95	23	25	11.0 ± .2	
	A	19.86	16	27	34.3 ± 1.2	
	B	20.05	9.3	9.5	32.8 ± 0.1	
p-Chloro-		0.0			10.1[b]	16.5
phenyl	A	1.35	16	27	11.0 ± 0.1	
(IIc)	A	1.35	15	29	10.9 ± .2	
	B	8.36	9.5	9.6	24.7 ± .4	
	A	9.95	12	8.1	25.3 ± 1.2	
	A	9.95	11	24	25.8 ± 2.0	
	B	20.05	10	8.8	79.4 ± 0.8	
	B	20.05	6.3	9.4	81.0 ± 0.7	
p-Nitro-		0.0			57.7[b]	15.4
phenyl	B	8.36	4.5	4.6	134 ± 3	
(IId)	B	8.36	4.4	9.5	134 ± 2	
	B	20.05	3.0	3.6	401 ± 12	
	B	20.05	4.9	5.1	404 ± 10	
trans-2-		0.0			3.7[b]	
Tosyloxy-	A	1.35	7.5	18	4.5 ± 0.4	
cyclo-	A	1.35	4.3	18	5.0 ± .5	
hexyl	A	9.95	4.4	18	14.6 ± .3	
phenyl	A	9.95	5.5	18	14.7 ± .7	
sulfone						

[a] Method A, reaction followed by determination of amount of base consumed; method B, reaction followed by determination of amount of chloride ion produced. [b] Determined by extrapolation.

TABLE II

APPROXIMATE RELATIVE REACTIVITIES OF BASE-PROMOTED DEHYDROCHLORINATION OF *cis*-2-CHLOROCYCLOHEXYL ARYL SULFONES (I) AND *cis*- (III) AND *trans*-2-CHLOROCYCLOPENTYL ARYL SULFONES (IV) IN "80%" ETHANOL AT 0°

Compound	Rel. rate
trans-2-Chlorocyclohexyl phenyl sulfone (IIb)	1
cis-2-Chlorocyclohexyl aryl sulfones	
p-Tolyl (Ib)	280
Phenyl (Ia)	490[a]
p-Chlorophenyl (Ic)	1600
trans-2-Chlorocyclopentyl aryl sulfones	
p-Tolyl (IVb)	21
Phenyl (IVa)	31
p-Chlorophenyl (IVc)	78
p-Nitrophenyl (IVd)	550
cis-2-Chlorocyclopentyl aryl sulfones	
p-Tolyl (IIIb)	760
Phenyl (IIIa)	1200[a]
p-Chlorophenyl (IIIc)	3700[a]

[a] This value is the average of two independent experiments which differed by the following percentage: Ia, 4%; IIIa, 8%; IIIc, 8%.

Kern, THIS JOURNAL, 77, 1141 (1955); (c) F. G. Bordwell and M. L. Peterson, *ibid.*, 77, 1145 (1955).

[8] A. J. Havlik and N. Kharasch, *ibid.*, 78, 1207 (1956).

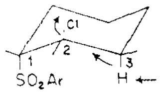
[9] Dr. Robert Jagow, University of Wisconsin, unpublished results.

As shown in Table I electron-withdrawing substituents in the aryl moiety of *trans*-2-chlorocyclohexyl aryl sulfone (II) increase the rate of base-promoted dehydrochlorination. The kinetic data for the four members of this series give an excellent fit with the Hammett equation[10] and ρ at 0° is 1.42 ± 0.01. The data in Table II show that ρ is also positive for *cis*-2-chlorocyclohexyl aryl sulfone (I) and *cis*-(III) and *trans*-2-chlorocyclopentyl aryl sulfone (IV).

Discussion

In both the *cis* and *trans* isomers the β-sulfone group has a large accelerating effect on the rate of the base-promoted dehydrohalogenation. For example, *trans*-2-chlorocyclohexyl *p*-tolyl sulfone (IIb), the least reactive member of the least reactive series, is about 10^6 times as reactive as cyclohexyl chloride.[11] *cis*-2-Chlorocyclohexyl phenyl sulfone is about 10^9 times as reactive as cyclohexyl chloride.

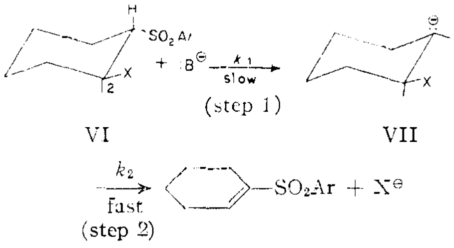
From the much greater reactivities of the *trans*-chlorosulfones than of cyclohexyl chloride it is apparent that a *cis* dehydrohalogenation is involved. Clearly the sulfone group in II could not accelerate a concerted *trans* elimination involving the C_3-hydrogen (V) or an SN2 displacement (at C_2) by a factor of 10^6. In fact the sulfone group would be expected to retard the rates of these processes. The axial conformation (with chlorine in an axial position) is required for a concerted E2 elimination[6,12] and preferred for an SN2 displacement.[13] Not only would the sulfone group tend to shift the conformational equilibrium toward the equatorial form (as compared to the conformational equilibrium for cyclohexyl chloride) which would retard the rate,[14] but in addition the axial sulfone group in the reactive conformation would retard both of these processes by shielding the C_3-axial hydrogen and the back side of C_2. The *cis* dehydrohalogenation of the *trans*-2-chlorocycloalkyl sulfones is not surprising and in fact would be expected in view of the observations by Bordwell, *et al.*,[7] that *cis* elimination is more rapid than *trans* if the *cis*-β-hydrogen is activated by a sulfone or similar group.



V

The most informative observation concerning the mechanism of the *cis* elimination is the nearly identical rates of elimination for *trans*-2-chlorocyclohexyl phenyl sulfone (IIa) and *trans*-2-tosyloxycyclohexyl phenyl sulfone (VI, X = $OSO_2C_6H_4CH_3$). Ordinarily, *p*-toluenesulfonates are much more reactive than the corresponding chlorides for second-order elimination reactions; *e.g.*, cyclohexyl *p*-toluenesulfonate[14] reacts with base—presumably the main reaction is an E2 elimination—more rapidly than cyclohexyl chloride[15] in absolute ethanol (75°) by a factor of 180.

The similar rates for IIa and the corresponding *p*-toluenesulfonate, the high reactivity of IIa and the effect of substituents on the rate are consistent with the two-step process illustrated below. This mechanism, which involves the removal of the β-proton by lyate ion ($:B^{\ominus}$) followed by conversion of the anion VII to product, has previously been suggested[16] for the dehydrohalogenation of β-benzene hexachloride.



(step 1)

VI VII

(step 2)

Although certain details of this mechanism are not known, *e.g.*, the reactive conformation of the anion VII, etc., the present data show that step 1 is rate-determining and irreversible. Thus the second-order constants in Table I correspond to k_1 in step 1. Presumably the *trans*-2-chlorocyclopentyl aryl sulfones, which obviously undergo a *cis*-elimination, also react by this so-called E1cB[12] mechanism.

It is clear from the present and earlier[7] studies that in systems such as II, IV and VI, the β-sulfone group increases the acidity of the C_1-hydrogen (or in other words stabilizes the anion VII)[17] so that *trans* elimination does not compete with proton abstraction (step 1). It is interesting to note that a *trans*-β-halogen atom does not activate the *cis*-hydrogen atom sufficiently for *cis* elimination to be important as compared to *trans* elimination, *e.g.*, *trans*-1,2-dihalocyclohexanes give primarily 3-halocyclohexene as the initial product.[6] In systems where *trans* elimination is not possible (*e.g.*, β-benzene hexachloride) β-halogen atoms are sufficiently activating so that *cis* dehydrochlorination can be realized.[16] The latter observation, together with the fact that under certain conditions *trans*-1,2-dihalocyclohexanes give some 1-halocyclohexene[6,7] indicates that a *trans*-β-halogen is almost sufficiently activating for proton abstraction (*cis* elimination) to compete with the E2 reaction. This suggests that in the cyclohexyl system *cis* dehydrohalogenation will predominate if a *trans* substituent is present with a larger electron-withdrawing effect than that of a halogen atom.

The almost identical rates for IIa and the corresponding *p*-toluenesulfonate show that the leaving group is not involved in the rate-limiting step. This also shows that step 1 is irreversible. Undoubtedly k_2 in step 2 is larger for the *p*-toluene-

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[10] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. VII.

[11] Extrapolation of the second-order rate constants for the dehydrohalogenation of cyclohexyl chloride in "80%" ethanol at 80 and 100° (ref. 6) gives a value of 5×10^{-9} *l. mole*$^{-1}$ sec.$^{-1}$ for 10°.

[12] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, Chapt. VIII.

[13] E. L. Eliel and R. S. Ro, *Chemistry & Industry*, 251 (1956).

[14] S. Winstein and N. J. Holnes, THIS JOURNAL, **77**, 5562 (1955).

[15] E. D. Hughes, C. K. Ingold and J. B. Rose, *J. Chem. Soc.*, 3839 (1953).

[16] S. J. Cristol, THIS JOURNAL, **69**, 338 (1947); (b) S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951); (c) S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953).

[17] W. von E. Doering and L. K. Levy, *ibid.*, **77**, 509 (1955).

TABLE III

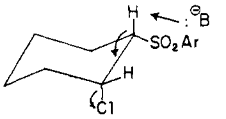
PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR *trans*-2-CHLOROCYCLOPENTYL AND *trans*-2-CHLOROCYCLOHEXYL ARYL SULFIDES

2-Chlorocyclo sulfide	B.p. °C.	Mm.	$n^{25}\mathrm{D}$	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Pentyl *p*-tolyl	122–123	0.1	1.5711	$C_{12}H_{15}ClS$	63.56	63.53	6.67	6.58
Pentyl phenyl	102–103	.5	1.5783	$C_{11}H_{13}ClS$	62.10	62.33	6.16	6.34
Pentyl *p*-chlorophenyl	125–126	.1	1.5894	$C_{11}H_{12}Cl_2S$	53.45	53.21	4.90	4.70
Pentyl *p*-nitrophenyl	51.8–52.8 (m.p.)			$C_{11}H_{12}ClNO_2S$	53.03	53.15	5.19	5.28
Hexyl *p*-tolyl	155–157	.3	1.5736	$C_{13}H_{17}ClS$	64.84	64.75	7.11	6.91
Hexyl *p*-chlorophenyl	160–162	.3	1.5890	$C_{12}H_{14}Cl_2S$	55.18	55.40	5.40	5.16
Hexyl *p*-nitrophenyl	64.4–65.6 (m.p.)			$C_{12}H_{14}ClNO_2S$	51.27	51.70	4.70	4.76

sulfonate than for the chloride by a factor of about 200. Thus if step 1 were reversible, step 2 would be in competition with this reverse reaction and the *p*-toluenesulfonate would undergo elimination faster than the chloride.

The observation that the first step in the *cis* elimination is irreversible in the present case suggests that the absence of deuterium exchange[18] does not necessarily rule out the possibility of a carbanion intermediate.[18] This observation also parallels that of Cristol and Fix[16c] that in the *cis* dehydrochlorination of benzene hexachloride, presumably by a two-step process similar to the one shown above, step 2 is 150 times as fast as the reverse of step 1.

Evidently the *cis*-chlorosulfones react by a concerted *trans* (E2) elimination (VIII). In the cyclohexyl system the *cis*-chlorosulfones are more reactive than the corresponding *trans* isomers by factors of 400 to 500. For the cyclopentyl system the factors are smaller, the *cis* isomers being more reactive than the corresponding *trans* isomers by factors of 40 to 50.



VIII

The large effect of the sulfone group in VIII on the rate of dehydrohalogenation is illustrated by comparing the rates for the *cis*-chlorosulfones I (Table II) with that for cyclohexyl chloride.[11] This comparison shows that the *trans* elimination in VIII is about 10^9 times faster than it would be if the sulfone group were replaced by hydrogen. The equatorial sulfone group in VIII has a considerably larger effect than a similarly located halogen atom; *cis*-1,2-dichlorocyclohexane dehydrohalogenates (to give 1-chlorocyclohexene) about 100 times faster than cyclohexyl chloride.[6] It is interesting to note that substituents in the aryl moiety have about the same effect in all four series of compounds.

Experimental

***trans*-2-Chlorocyclopentyl and *trans*-2-Chlorocyclohexyl Aryl Sulfides.**—These series of compounds were prepared by the *trans* addition[3,8] of the corresponding sulfenyl chlorides to cyclopentene[19] and cyclohexene according to the general method of Lecher and Stocklin.[20] Benzene-, *p*-toluene- and *p*-chlorobenzenesulfenyl chloride were prepared by chlorinolysis of the corresponding thiophenols.[21] *p*-Nitrobenzenesulfenyl chloride was prepared by the chlorinolysis of 4,4′-dinitrodiphenyl disulfide.[22] The preparation of *trans*-2-chlorocyclohexyl phenyl sulfide was described in an earlier paper.[3] The properties of the *trans*-2-chlorocycloalkyl aryl sulfides prepared by this procedure are shown in Table III.

***cis*-2-Chlorocyclopentyl and *cis*-2-Chlorocyclohexyl Aryl Sulfides.**—These series of compounds were prepared by the radical (photoinitiated) addition[3] of the corresponding thiophenol to 1-chlorocyclopentene[23] and 1-chlorocyclohexene,[3] according to the method described below for the preparation of *cis*-2-chlorocyclohexyl phenyl sulfide. A mixture of 77 g. (0.70 mole) of thiophenol (Eastman Kodak Co. White Label, redistilled) and 81.5 g. (0.70 mole) of 1-chlorocyclohexene in a Vycor flask was stirred for 10 days. During this period the solution was kept under nitrogen and irradiated with a Hanovia (type S100) mercury arc lamp placed 10 cm. from the reaction flask. Distillation of the reaction mixture gave 78 g. (49%) of crude ***cis*-2-chlorocyclohexyl phenyl sulfide**, b.p. 121–125° (0.5 mm.), $n^{25}\mathrm{D}$ 1.5838, which solidified almost completely. After recrystallization from hexane the product melted at 38–39°.[24]

Anal. Calcd. for $C_{12}H_{15}ClS$: C, 63.56; H, 6.67. Found: C, 63.79; H, 6.78.

cis-2-Chlorocyclohexyl *p*-tolyl sulfide and *cis*-2-chlorocyclohexyl *p*-chlorophenyl sulfide were prepared in the same manner. In each case the crude reaction product, *i.e.*, product containing diaryl disulfide, was used for the preparation of the sulfones. The chlorosulfides were separated from the disulfide by chromatography using a column packed with Alcoa F-20 activated alumina. Pentane solutions of the crude products were passed through the column and the material was eluted with *n*-pentane. In each case the diaryl disulfide was eluted first and the disulfide was cleanly separated from the chlorosulfide.

The solid ***cis*-2-chlorocyclohexyl *p*-tolyl sulfide** remaining after evaporation of the pentane, melted at 34–35° (pentane).

Anal. Calcd. for $C_{13}H_{17}ClS$: C, 64.84; H, 7.11. Found: C, 65.23; H, 7.23.

Pure ***cis*-2-chlorocyclohexyl *p*-chlorophenyl sulfide**, m.p. 34.5–35.0° (pentane), was obtained in a similar manner.

Anal. Calcd. for $C_{12}H_{14}Cl_2S$: C, 55.18; H, 5.40. Found: C, 55.14; H, 5.62.

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[18] See P. S. Skell and C. R. Hauser, THIS JOURNAL, **67**, 1661 (1945); D. G. Hill, B. Stewart, S. W. Kantor, W. A. Judge and C. R. Hauser, *ibid.*, **76**, 5129 (1954); see also ref. 16c.

[19] B. B. Corson and V. N. Ipatieff, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 152.

[20] H. Lecher and P. Stocklin, *Ber.*, **58**, 414 (1925).

[21] H. Lecher, *ibid.*, **58**, 409 (1925).

[22] M. T. Bogert and A. Stull, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1941, p. 220.

[23] 1-Chlorocyclopentene, b.p. 103.0–103.5°, $n^{25}\mathrm{D}$ 1.4364, was prepared according to the method of E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951). Contrary to the report of these workers, this product was found to be unreactive toward aqueous alcoholic silver nitrate.

[24] The liquid sample of *cis*-2-chlorocyclohexyl phenyl sulfide described in reference 3, prepared by irradiation with a specially constructed high-intensity Hanovia lamp (type SC-2537) which was in contact with the reaction mixture, has been found to contain significant amounts of diphenyl disulfide. In the present work it has been found that less intense irradiation, *e.g.*, a Hanovia (type 30600) lamp placed 10 cm. or more from the reaction mixture, reduces considerably the amount of disulfide formed in the addition of thiophenol, *p*-thiocresol and *p*-chlorothiophenol.

TABLE IV

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR 2-CHLOROCYCLOALKYL ARYL SULFONES

2-Chlorocyclosulfone	Method of prepn.[a]	M.p., °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
			A. *Trans* series				
Pentyl *p*-tolyl	B	46.4–48.4	$C_{12}H_{15}O_2ClS$	55.70	55.68	5.84	5.71
Pentyl phenyl	B	84.2–84.8	$C_{11}H_{13}O_2ClS$	53.98	54.45	5.35	5.61
Pentyl *p*-chlorophenyl	B	59.0–59.8	$C_{11}H_{12}O_2Cl_2S$	47.33	47.48	4.33	4.12
Pentyl *p*-nitrophenyl	B	96.8–97.6	$C_{11}H_{12}O_4ClNS$	45.60	45.73	4.17	4.15
Hexyl *p*-tolyl	A	43.2–44.2	$C_{13}H_{17}O_2ClS$	57.23	57.24	6.28	6.21
Hexyl *p*-chlorophenyl	A	74.0–74.6	$C_{12}H_{14}O_2Cl_2S$	49.15	49.56	4.81	4.57
Hexyl *p*-nitrophenyl	A	142.0–142.8	$C_{12}H_{14}O_4NClS$	47.45	47.81	4.65	4.56
			B. *Cis* series				
Pentyl *p*-tolyl	A	95.9–96.5	$C_{12}H_{15}O_2ClS$	55.70	55.82	5.84	5.94
Pentyl phenyl	A	94.6–95.3	$C_{11}H_{13}O_2ClS$	53.98	53.88	5.35	5.24
Pentyl *p*-chlorophenyl	A	95.4–96.2	$C_{11}H_{12}O_2Cl_2S$	47.33	47.32	4.33	4.09
Hexyl *p*-tolyl	A	74.5–75.0	$C_{13}H_{17}O_2ClS$	57.23	56.79	6.28	6.03
Hexyl *p*-chlorophenyl	A	135.7–136.2	$C_{12}H_{14}O_2Cl_2S$	49.15	49.08	4.81	4.88

[a] A = oxidation of sulfide with 30% hydrogen peroxide in acetic acid; recrystallization from acetic acid–water (2:1). B = Oxidation of sulfide with perbenzoic acid in chloroform; recrystallization from chloroform–hexane (1:9).

The *cis*-2-chlorocyclopentyl aryl sulfides were prepared in the same way.[4] These samples, which contained about 10% of the corresponding diaryl disulfides, were not purified further but were converted directly to the corresponding sulfones.

Conversion of Sulfides to Sulfones.—The *cis*- and *trans*-2-chlorocycloalkyl aryl sulfides were converted to the corresponding sulfones by oxidation with hydrogen peroxide in acetic acid[25] or perbenzoic acid in chloroform.[26] The properties of the sulfones, with the exception of *cis*- and *trans*-2-chlorocyclohexyl phenyl sulfone which were reported previously,[3] are shown in Table IV together with the analytical data.

***trans*-2-Tosyloxycyclohexyl Phenyl Sulfone.**—*trans*-2-Hydroxycyclohexyl phenyl sulfide[3] was oxidized with hydrogen peroxide in acetic acid (see above) to ***trans*-2-hydroxycyclohexyl phenyl sulfone**, m.p. 102–103° (aqueous acetic acid).

Anal. Calcd. for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 59.72; H, 6.86.

A solution of 14.40 g. (0.060 mole) of *trans*-2-hydroxycyclohexyl phenyl sulfone in 60 ml. of dry pyridine was treated with 19.06 g. (0.100 mole) of *p*-toluenesulfonyl chloride. After standing for one week at room temperature the reaction mixture was decanted from the pyridine hydrochloride and the excess *p*-toluenesulfonyl chloride was hydrolyzed by addition of 20 ml. of water in small portions. The solution was poured into cold water and the mixture extracted with chloroform. The combined chloroform extracts were washed with 20% sulfuric acid and dried over sodium sulfate. Evaporation of the chloroform left 15 g. (63%) of light yellow solid, m.p. 115–116°. Recrystallization from acetone–pentane (15:85) gave pure *trans*-2-tosyloxycyclohexyl phenyl sulfone as white needles, m.p. 119.0–119.5°.

Anal. Calcd. for $C_{19}H_{22}O_5S_2$: C, 57.85; H, 5.62. Found: C, 58.13; H, 5.65.

Kinetic Experiments. Method A.—This method was used for determining the rates of elimination of the *trans*-2-chlorocyclohexyl aryl sulfones and *trans*-2-tosyloxycyclohexyl phenyl sulfone. A typical experiment was carried out as follows. A solution of an accurately weighed 0.6-g. sample of IIa in 75 ml. of "80%" ethanol[5] was thermostated at 9.95°. At zero time 50 ml. of 0.07305 *M* sodium hydroxide in "80%" ethanol (previously thermostated at 9.95°) was added and the resulting solution was rapidly and thoroughly agitated by swirling the reaction vessel in the thermostat. At appropriate time intervals (*ca.* every 10% reaction to 80% completion) 10-ml. aliquots were withdrawn and rapidly delivered into 5 ml. of 0.06041 *M* hydrochloric acid to stop the reaction. The percentage reaction at the time of sampling was determined by titration of the excess acid to the brom thymol blue end-point with 0.05594 *M* sodium methoxide in methanol. Specific second-order rate constants were calculated by use of the appropriate equation. Seven to ten values were determined for each kinetic experiment and the averages of these, together with the mean deviations, are given in Table I.

Method B.—In this method, the reaction was followed by titration of chloride ion. In a typical experiment, 0.37 g. of IIb in 75 ml. of "80%" ethanol was thermostated at 8.36°; 50 ml. of 0.02535 *N* sodium hydroxide in "80%" ethanol was weighed and thermostated in a tared stoppered flask. At zero time, the sodium hydroxide solution was quickly poured (in 1–2 seconds) into the flask containing the solution of sulfone and mixed thoroughly by swirling. The exact amount of sodium hydroxide solution used was determined by weighing the empty flask after the transfer. At appropriate time intervals, 10-ml. aliquots were withdrawn and rapidly delivered into 5 ml. of 3 *M* nitric acid at 0° to quench the reaction. The automatic pipet used for this purpose was wrapped with asbestos and kept in a large test-tube immersed in the thermostat. The amount of chloride ion in the nitric acid solution was determined by the Volhard method using 0.02 *M* standard silver nitrate and potassium thiocyanate solutions.

Determination of Approximate Relative Reactivities of *cis*- and *trans*-2-Chlorocyclopentyl and *cis*-2-Chlorocyclohexyl Aryl Sulfone.—The dehydrochlorinations of these chlorosulfones were too fast to follow by the method described above. Approximate relative reactivities for these compounds at 0° were determined from the relative lengths of time required for solutions 0.02 *M* in substrate and 0.00845 *N* in sodium hydroxide in "80%" ethanol containing brom thymol blue to reach the same color as that of a slightly alkaline buffer solution containing the indicator. The buffer solution was prepared by mixing 9 ml. of 0.1 *N* sodium hydroxide, 10 ml. of 0.1 *M* potassium dihydrogen phosphate, 1 ml. of water and 20 ml. of absolute ethanol; 15 ml. was then placed in an 8" × 1.25" test-tube and 2 drops of 0.05% brom thymol blue indicator (in ethanol) was added to give a bluish-green reference color. In a typical experiment a solution of 0.0777 g. (0.300 mmole) of *cis*-2-chlorocyclohexyl phenyl sulfone in 10.00 ml. of "80%" ethanol was prepared in an 8" × 1.25" test-tube and 2 drops of 0.05% brom thymol blue indicator was added and the solution thermostated at 0°. At zero time, 5 ml. of 0.02535 *M* sodium hydroxide in "80%" ethanol, previously thermostated at 0°, was added with an automatic pipet. The automatic pipet used for this purpose was wrapped with asbestos and stored in a large test-tube immersed in ice. The test-tube was tightly stoppered and swirled. The color of the solution gradually changed from a rich blue to green, and finally to yellow. The time at which the color of the solution first became indistinguishable from the bluish-green color of the reference buffer solution was found to be 1251 seconds.

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