benzophenone azine: 290, 4.22; 323, 4.20. *p,p,p',p'*-Tetramethoxybenzophenone azine: 278, 4.46; 335, 4.2. Benzophenone hydrazone: 275, 4.09. Benzophenone semicarbazone: 282, 4.32. Benzophenone phenylhydrazone: 293, 338, 4.26. Benzophenone oxime: 250. Fluorenone hydrazone: 330, 5.00.

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

Mechanisms of Elimination Reactions. XXII. Some *cis*- and *trans*-2-Phenylcyclohexyl Derivatives. The Hofmann Elimination[1]

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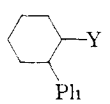
The products and rates of reaction of the *cis* and *trans* isomers of 2-phenylcyclohexyltrimethylammonium ion, 2-phenylcyclohexyldimethylsulfonium ion and 2-phenylcyclohexyl *p*-toluenesulfonate with potassium hydroxide in ordinary ethanol have been investigated. The *cis* and *trans* isomers of the onium compounds differ in elimination reactivity (to give 1-phenylcyclohexene) by factors of 133 (ammonium) and 383 (sulfonium), *trans* elimination being favored over *cis*. A comparison of the rates of reaction with the acyclic (2-phenylethyl) analogs suggests that the *cis* ammonium phenylcyclohexyl isomer is abnormally unreactive, presumably because of conformational difficulties, while the *trans* sulfonium isomer is abnormally reactive. The results are interpreted in terms of a concerted elimination process for the *cis* isomers (*trans* coplanar transition state), and some multistage elimination process (dipolar-ion intermediate) for the *trans* onium compounds (*cis* elimination).

Although a number of bimolecular elimination reactions have been studied in detail regarding the effect of stereochemistry upon rate, generally only qualitative information is available concerning the Hofmann elimination. Several workers[2] have found that this reaction, similar to other bimolecular, base-promoted elimination reactions, shows a preference for *trans* elimination. The present study was undertaken to provide more quantitative information regarding this preference. The *cis* and *trans* isomers in the 2-phenylcyclohexyl system were chosen since the presence of the phenyl group on the β-carbon would activate the β-hydrogen, causing an increase in rate and obviating the necessity for using very high-boiling solvents as is common in work on the Hofmann elimination.

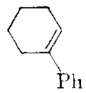
Arnold and Richardson[3] had observed that elimination from *cis*- and *trans*-I gave 1-phenylcylohexene (IV) rather than 3-phenylcyclohexene (V) and Weinstock and Bordwell[4] showed that the base-promoted isomerization of V to IV was slow enough so that IV was not obtained through V as an intermediate, but probably directly from *cis*- and *trans*-I. The isomers of I thus appeared to represent an excellent system for a study of *cis* and *trans* Hofmann eliminations.



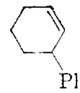
$PhCH_2CH_2Y$

I, Y = $\overset{+}{N}Me_3$
II, Y = $\overset{+}{S}Me_2$
III, Y = OTs

Ia, Y = $\overset{+}{N}Me_3$
IIa, Y = $\overset{+}{S}Me_2$
IIa, Y = OTs



IV



V

At the same time, it appeared worthwhile to study the corresponding sulfonium ions (*cis*- and *trans*-II) as another example of an "onium" system and the corresponding *p*-toluenesulfonates (*cis*- and *trans*-III) as an example of a presumably "normal" system. For further comparison, elimination rates were studied on 2-phenylethyltrimethylammonium bromide (Ia).[5] Data for the corresponding sulfonium compound IIa and *p*-toluenesulfonate IIIa were available from the literature.

Preparation of Materials.—The 2-phenylcyclohexyltrimethylammonium iodides (*cis*- and *trans*-I) were previously prepared and characterized by Arnold and Richardson[3] and by Cope and Bumgardner.[6] A different synthetic route was employed here, in which a mixture of the corresponding amines was prepared and the isomers separated by chromatography on alumina of the N-benzoyl derivatives. The amine mixture was obtained either from the Leuckart reaction on 2-phenylcyclohexanone or from the reduction of the corresponding oxime with lithium aluminum hydride. Based upon the amount of N-benzoyl derivatives formed, the Leuckart reaction gave about seven parts of *trans*-amine to four parts of *cis*-amine while reduction of the oxime gave five parts of *trans* to four parts of the *cis* compound. The latter ratio is in contrast to that reported by Smith, Maienthal and Tipton[7] who obtained only *trans*-amine in the lithium aluminum hydride reduction of some methylcyclohexanone oximes. The N-ben-

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[1] Previous paper in series: S. J. Cristol and R. S. Bly, Jr., THIS JOURNAL, **82**, 142 (1960).

[2] See for example: W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940); N. L. McNiven and J. Read, *J. Chem. Soc.*, 153 (1952); R. D. Haworth, J. McKenna and R. G. Powell, *ibid.*, 1110 (1953); F. E. King and H. Booth, *ibid.*, 3798 (1954); K. Jewers and J. McKenna, *ibid.*, 2209 (1958).

[3] R. T. Arnold and P. N. Richardson, THIS JOURNAL, **76**, 3649 (1954).

[4] J. Weinstock and F. G. Bordwell, *ibid.*, **77**, 6706 (1955).

[5] This compound was kindly supplied by Prof. A. N. Bourns, McMaster University, Hamilton, Ontario.

[6] A. C. Cope and C. L. Bumgardner, THIS JOURNAL, **79**, 960 (1957).

[7] D. R. Smith, M. Maienthal and J. Tipton, *J. Org. Chem.*, **17**, 294 (1952).

zoyl derivatives were hydrolyzed with 20% hydrochloric acid and the resulting hydrochlorides treated with sodium carbonate and methyl iodide in nitromethane to produce the quaternary ammonium compounds, *cis* and *trans*-I.

A solution of 1-phenylcyclohexene in methyl mercaptan was irradiated with ultraviolet light for 12 hours and from this reaction two isomeric 2-phenylcyclohexyl methyl sulfides were isolated. One sulfide was obtained in 95% yield and this was assigned the *cis* structure in accordance with a similar reaction studied by Goering, Relyea and Lawrence.[8] In addition, 2% of the *trans*-sulfide was isolated. Both sulfides were converted to sulfones for further characterization. In order to obtain a larger amount of the *trans*-sulfide, the *cis*-sulfone was epimerized to the *trans*-sulfone by heating at reflux with ethanolic base. The *trans*-sulfone was then reduced to the corresponding sulfide in 79% yield with lithium aluminum hydride, using the procedure of Bordwell and McKellin.[9] The success of the sulfone isomerization indicated that the correct assignment of configuration had been made. The sulfides were converted to the dimethylsulfonium iodides (II) with methyl iodide in nitromethane.

The *cis*- and *trans*-2-phenylcyclohexyl *p*-toluenesulfonates (III) were prepared by treating a commercial mixture of the alcohols with *p*-toluenesulfonyl chloride in pyridine. The tosylate mixture was then separated by fractional crystallization. Since the *cis* isomer was quite sensitive to base, a pure sample of the *trans*-tosylate could be obtained by recrystallizing the mixture from basic ethanol. This isomer was identical to that prepared from a pure sample of *trans*-2-phenylcyclohexanol. The *cis* isomer was unstable and decomposition could be noted in two days at room temperature. Melting point behavior of both isomers was extremely erratic and dependent upon the method of isolation or crystallization. In subsequent experiments on the *cis*-tosylate, 8–10% of the *trans* isomer was isolated as a residue. It is not known if this was due to isomerization or to the presence of that much *trans* in the *cis* compound originally. Since the *trans* isomer reacted much slower in the reactions studied, it would have only a negligible effect on the results obtained in the *cis*-tosylate rate studies. Treatment of the *trans*-tosylate with sodium methyl mercaptide in ethanol gave the same sulfide as was assigned the *cis* configuration. This is additional structure proof for the *cis*- sulfide since one would expect a direct displacement reaction to produce inversion at the carbon being substituted. Corresponding treatment of the *cis*-tosylate yielded only olefin.

TABLE I

DATA AND SECOND-ORDER RATE CONSTANTS FOR ELIMINATION TO 1-PHENYLCYCLOHEXENE WITH POTASSIUM HYDROXIDE IN ETHANOL[a]

Compound	Temp., °C.	$10^5 k$, l./mole/sec.
cis-III	43.95	23.8 ± 0.1
	63.70	190 ± 9[b]
cis-I	63.71	9.71 ± 0.16
	75.03	40.0 ± 0.1
	86.30	169 ± 1
trans-I	95.80	10.2 ± 0.1
	107.00	36.8 ± 1.4
	116.82	116 ± 2
Ia[c]	33.90	7.12 ± 0.05
	43.95	29.2 ± 0.6
	53.00	93.6 ± 0.7
cis-II	16.98	65.3 ± 0.1
	25.20	209 ± 8
	33.90	667 ± 12
trans-II	33.90	2.75 ± 0.04
	43.95	15.2 ± 0.9
	53.00	70.7 ± 1.3

[a] All experiments were conducted at compound concentrations of 0.006 to 0.01 *M* and potassium hydroxide concentrations of *ca.* 0.2 *M*. Each rate constant given in the table is the average of two or three runs. [b] When the base concentration was dropped to 0.11 *M*, the rate constant was 200 × 10^{-5}. [c] Product is styrene rather than 1-phenylcyclohexene.

Results.—The results of the kinetic measurements are listed in Table I. No data are given for *trans*-2-phenylcyclohexyl *p*-toluenesulfonate since a second-order elimination was not observed. The solvent used was ordinary ethanol (92.6 wt.%) and the base was potassium hydroxide. The rate constants are for elimination to 1-phenylcyclohexene in the case of the 2-phenylcyclohexyl derivatives and to styrene in the case of the 2-phenylethyl compound. The formation of olefin was followed by observing the increase in absorption at 247 mμ and corrections were applied where the yield of olefin was not quantitative or nearly so. A large excess of base was used and the pseudo-first-order rate constant was determined graphically. In order to show that the reactions were also first-order in base, the base concentration was decreased by one-third to one-half in a number of runs. In the case of the *cis*-tosylate, the agreement in *k* was good. In applying this test with the onium compounds, it was necessary to add an inert salt in the amount needed to keep the ionic strength of the solution constant, as decreased ionic strength causes an increase in rate. However, when neutral salt was added, an over-compensation was observed and the rates were 10–50% slower for the five onium compounds investigated. The type of salt added (sodium iodide, sodium perchlorate or potassium iodide) did not result in appreciably different behavior and it is thought possible that the high concentration (about 0.2 molar) of the solutions may be the cause of the discrepancy. It seems, however, that the reactions must be second order and not of a solvolytic type since no solvolysis products are obtained (2-phenylcyclohexyl ethers or alcohols), except with the *trans*-tosylate which was indeed found not to give a strictly second-order rate. Also, solvolysis experiments on the sulfonium iodides gave only a minor amount of elimination from the *cis* isomer and none from the *trans*. The first-order carbonium-ion type mechanism for onium compounds has only been observed in extreme cases such as those

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[8] H. L. Goering, D. I. Relyea and D. W. Lawrence, THIS JOURNAL, **78**, 348 (1956).

[9] F. G. Bordwell and W. H. McKellin, *ibid.*, **73**, 2251 (1951).

reported by Norcross and Openshaw[10] and by McKenna and Slinger.[11]

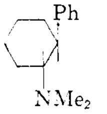
In addition to the study of the kinetics of elimination, a study of the products of the reaction of each substrate under conditions similar to the rate study was made. In most cases, elimination to 1-phenylcyclohexene (IV) represented the principal reaction, but this was not uniformly true (see Table II). It may be noted that all of the *cis* isomers gave largely 1-phenylcyclohexene (IV) as the principal elimination product with small amounts of the 3-phenyl olefin V or substitution products as by-products. The *trans* onium compounds gave substantially greater amounts of substitution products (demethylation to amine VI or thioethers VII and VIII), but the principal elimination product (>90%) was again the 1-phenyl olefin IV. On the other hand, the *trans*-sulfonate III gave large amounts of the 3-phenyl olefin under these conditions. In agreement with the report of Weinstock and Bordwell,[4] it was found that the 3-olefin did not isomerize to IV under the conditions used in the alkaline reactions fast enough to account for the formation of the 1-olefin.

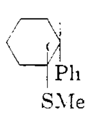
TABLE II

PRODUCTS OF REACTION WITH POTASSIUM HYDROXIDE IN 92.6 WT. % ETHANOL OF SOME ONIUM SALTS AND *p*-TOLUENESULFONATES

		Yield of products, %		
Compound	Temp., °C.	1-Phenyl-cyclohexene	3-Phenyl-cyclo-hexene[a]	Substn. product[a]
trans-I	107	64[a,b]	2	8 VI
cis-I	86	>93[b]	[c]	[c]
Ia	44	100 styrene[b]	..	.....
trans-II	75	20,[a] 23[b]	2	61 VIII
cis-II	75	69,[a] 75[b]	1	7.5 VII
trans-III	75	20	53	7 IX, 10 X
cis-III	75	87,[a] 80[b]	7	

[a] Yields are by isolations. [b] Yields by ultraviolet spectra determinations. [c] Not investigated.


VI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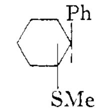
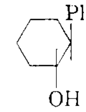
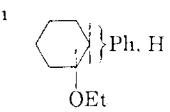

VIII


IX


X

Interpretation of the results on elimination from the *trans*-sulfonate is clouded because it is clear that at least a portion of the reaction with this material is zero order in alkali.

Solvolyses in ordinary ethanol (92.6 wt. %) were performed on the *cis*- and *trans*-sulfonium compounds and *cis*- and *trans*-tosylates. The products isolated from each are given in Table III.

In each case, vapor-phase chromatography indicated that the products listed were the only ones formed in each reaction. Hence, low total yields are believed to be the result of losses in reaction work-up and not failure to isolate some additional product. The approximate solvolysis rate was checked. In the case of the *cis*- and *trans*-sulfonium compounds and the *cis*-tosylate, the rate was too slow to interfere with the rate of base-promoted elimination. This was not true of the *trans*-tosylate.

TABLE III

PRODUCTS OF SOLVOLYSIS OF SOME SULFONIUM AND SULFONOXY COMPOUNDS IN 92.6 WT. % ETHANOL

	Yield of product, %		
Compound	1-Phenyl-cyclohexene	3-Phenyl-cyclohexene	Substn. product
trans-II	..	..	85 VIII
cis-II	13	1	74 VII
trans-III	29	30	12 IX 16 X
cis-III	50[a]	2[a]	
trans-III (+0.4 *M* KOH)	20	53	7 IX 16 X

[a] Losses in isolation procedure; sole products formed; ratio probably correct.

The products of solvolysis of the *trans*-tosylate in the presence of 0.4 *N* ethanolic potassium hydroxide are also recorded in Table III.

As a larger amount of the 3-olefin was found here as compared to the solvolysis experiment, it was thought that isomerization in the latter case might be occurring because of the acid which is formed. However, heating 3-phenylcyclohexene at 63.70° with *p*-toluenesulfonic acid for 44 hours in ethanol showed no increase in ultraviolet absorption at 247 mμ.

Rough first-order rate constants for solvolysis in ordinary ethanol for the *cis*- and *trans*-tosylates at 63.7° were 3.6×10^{-5} and 0.06×10^{-5} sec.$^{-1}$, respectively. Thus the compound with the *cis*-phenyl group is about 60 times more reactive than the *trans* compound.[12]

Discussion of Results.—Table IV summarizes data on all of the compounds studied, giving extrapolated or interpolated rate constants for elimination from the phenylcyclohexyl compounds to 1-phenylcyclohexene and from the β-phenyl-

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(10) G. Norcross and H. T. Openshaw, *J. Chem. Soc.*, 1174 (1949).

(11) J. McKenna and J. B. Slinger, *ibid.*, 2759 (1958).

(12) It is of some interest that solvolysis of *trans*-III gave unrearranged olefins and substitution products, while it has been reported that deamination of *trans*-2-phenylcyclohexylamine gives only the ring-contracted cyclopentylphenylcarbinol[13] and dehydration with phosphoric acid gives largely benzylcyclopentene and benzalcyclopentane.[14,15] Infrared spectra on our products, vapor-phase chromatography and infrared spectra on the fractions indicated, by comparison to reported peaks,[15] that there were little or no ring-contracted products formed. This obviously represents another case in which presumably similar cationic intermediates lead to different products or to different mixtures of products.[16–19] Conformational differences do not appear significant[14,20] in explaining the results, and it is difficult to involve phenyl neighboring-group participation[21] in a solvolysis where a *cis*-phenyl group induces greater reactivity than a *trans*-phenyl group (even though stereochemical results would favor this interpretation). We hope to investigate these reactions more completely in the future.

(13) D. V. Nightingale and M. Maienthal, THIS JOURNAL, **72**, 4823 (1950).

(14) H. J. Schaeffer and C. J. Collins, *ibid.*, **78**, 124 (1956).

(15) E. L. Eliel, J. W. McCoy and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1957).

(16) J. G. Burr, Jr., and L. S. Ciereszko, THIS JOURNAL, **74**, 5426, 5431 (1952).

(17) D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954).

(18) D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).

(19) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 2888 (1957).

(20) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

(21) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948); S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948); S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *ibid.*, **74**, 1113 (1952).

ethylammonium compound to styrene, as well as entropies and Arrhenius energies of activation for these processes. In addition, data from the literature[22,23] are given for elimination from β-phenylethyldimethylsulfonium ion and β-phenylethyl *p*-toluenesulfonate. The values in this table have been compared in Table V in such a fashion as to give in the first column the ratio of the rate of elimination from the *cis* isomer to that from the *trans*, in the second column the ratio of elimination from the open-chain analog to that of the *cis* isomer and in the third, that of the acyclic analog to that of the *trans* isomer.

TABLE IV

RATE CONSTANTS AND QUANTITIES OF ACTIVATION FOR ELIMINATION TO 1-PHENYLCYCLOHEXENE OR TO STYRENE WITH POTASSIUM HYDROXIDE IN 92.6% ETHANOL

Compound	$k_{25°}$, l./mole/sec.	E_{act}, kcal./mole	$\Delta S,^\ddagger$ cal./deg.
cis-I	2.69×10^{-7a}	30.3	11.2
trans-I	2.02×10^{-9a}	33.4	11.9
Ia	2.15×10^{-5a}	25.5	3.7
cis-II	1.98×10^{-3}	24.3	8.7
trans-II	5.17×10^{-6}	33.8	28.8
IIa	2.54×10^{-3b}	23.9^b	7.7^b
cis-III	$4.60 \times 10^{-5a,c}$	22.4	−6.4
IIIa	$3.9 \times 10^{-5c,d}$	..	...

[a] Extrapolated. [b] Determined by Saunders and Williams[22] using sodium ethoxide in absolute ethanol; the rate constant would be expected to be somewhat lower in ordinary ethanol. [c] 30.10°. [d] Determined by DePuy and Froemsdorf[23] using sodium ethoxide in absolute ethanol.

It may be seen that while *trans* elimination (*cis* isomer) is favored over *cis* elimination (*trans* isomer) in both onium series, the difference in reactivity is only 133 for the ammonium compounds and 383 for the sulfonium salts. These small differences may be compared with much larger differences observed with alkyl halides, as for example, the benzene hexachlorides,[24] where ratios in reactivity between isomers undergoing *trans* and *cis* eliminations are above 10,000.

One might suggest that these lowered ratios reflect a difference simply between elimination in neutral compounds and those in onium compounds, and thus might reflect differences in intimate mechanisms between Hofmann eliminations of onium compounds and other eliminations.[22,23] However, comparisons of the cyclic compounds with each other and with their acyclic analogs (Table V) are particularly instructive and argue against a simple common interpretation. They show that while the differences between the rates of *trans* and *cis* elimination are not very large and are about the same whether the leaving group is trimethylamine or dimethyl sulfide, the reasons for this similarity are quite different. The data suggest that when the departing group is the trimethylamine group, elimination from the *cis* compound (*trans* elimination) is inordinately slow compared with the acyclic compound, while that from the *trans* isomer (*cis* elimination) is consistent with data which we have found previously in *cis* and *trans* eliminations. On the other hand, when the departing group is the dimethyl sulfide molecule or the *p*-toluenesulfonate ion, the *cis* isomer (*trans* elimination) eliminates at the same rate as the acyclic analog. The discrepancy with the sulfonium compounds is that the *trans* isomer (*cis* elimination) appears more reactive than anticipated.

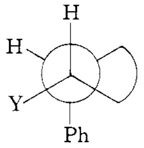
TABLE V

RELATIVE RATES OF ELIMINATION FROM THE *cis* AND *trans* ISOMERS OF 2-PHENYLCYCLOHEXYLTRIMETHYLAMMONIUM ION, 2-PHENYLCYCLOHEXYLDIMETHYLSULFONIUM ION, 2-PHENYLCYCLOHEXYL *p*-TOLUENESULFONATE AND THE CORRESPONDING 2-PHENYLETHYL COMPOUNDS

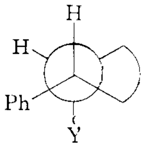
Leaving group	k_{cis}/k_{trans}	$k_n{}^a/k_{cis}$	k_n/k_{trans}
NMe_3	133	80	10,700
SMe_2	383	1.28	491
OTs^-	..	0.85	....

[a] k_n = rate of elimination of the 2-phenylethyl compound.

Two explanations offer themselves to rationalize these results. First, the *cis* compounds may have two conformations XI and XII depending upon



XI



XII

whether the substitute Y and the phenyl take up equatorial and axial positions, respectively, as in XI or *vice versa* as in XII. For facile elimination to take place, the substituent Y should have the axial conformation in the transition state since then the β-hydrogen is also axial, *trans* and coplanar. Although some steric interactions with the axial hydrogens occur if the phenyl, tosylate or dimethylsulfonium groups are in the axial position, these, as evidenced by models, can be made negligible by rotating the group slightly. However, with the trimethylammonium group the interactions are much more severe and cannot be minimized by rotation. In this regard, it is quite similar to the *t*-butyl group, whose effects on conformation have been discussed by Winstein and Holness[20] and by Eliel and his co-workers.[25] Conceivably then, the slower rate of elimination with the *cis*-quaternary compound could be the result of the increase in energy of activation necessary to force the ammonium group into the axial position or to cause the elimination to proceed before the most favorable stereochemistry had been achieved.

If the *cis*-ammonium compound had eliminated at about the same rate as the 2-phenylethyl analog, then *trans* elimination would have been favored over *cis* elimination by a factor of about 10^4. Thus, the apparent difference between the Hofmann elimination from ammonium compounds and other eliminations as regards the dependence of rate upon stereochemistry may be entirely due to the conformational problem just discussed.

On the other hand, the rate and product data could be rationalized upon the basis of a competi-

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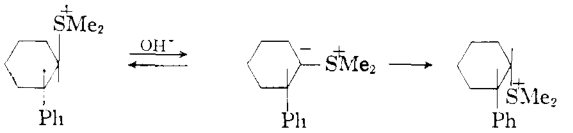
(22) W. H. Saunders and R. A. Williams, THIS JOURNAL, **79**, 3712 (1957).

(23) C. H. DePuy and D. H. Froemsdorf, *ibid.*, **79**, 3710 (1957).

(24) S. J. Cristol, *ibid.*, **69**, 338 (1947); S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951).

(25) E. L. Eliel and R. G. Haber, *ibid.*, **81**, 1249 (1959), and preceding papers.

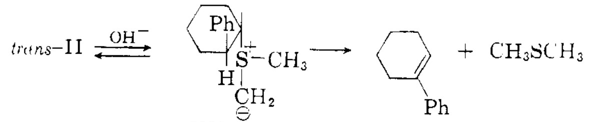
tion between β-elimination and α-exchange accompanied by isomerization of *trans* to *cis* isomer. For example, the *trans*-sulfonium (or ammonium) ion could react with base to give the zwitterion (ylide) XIII as



trans II XIII *cis*-II

Any rearrangement of *trans* isomer to *cis* would of course lead to elimination to 1-phenylcyclohexene, as the *cis* compounds are much more reactive than their *trans* isomers. Thus the apparent rates of elimination of *trans*-I or *trans*-II might be the rate of isomerization of *trans* to *cis* isomer and the *cis* elimination observed may be an artifact. Exchange in the α-position in onium compounds is known,[26–28] and is likely to be much more rapid with sulfonium (II) than with ammonium compounds (I).[26] The possibility of such epimerization is fortunately amenable to test by deuterium exchange, and we have begun work on this test.

An alternative mechanism for *cis* elimination also involving an ylide intermediate XIV, may be written as

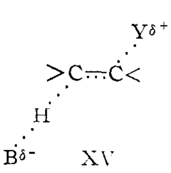


XIV

This mechanism finds analogy in the work by Wittig[29] on elimination from cyclooctyltrimethylammonium bromide with phenyllithium and the high temperature decomposition of ethyltrimethylammonium hydroxide,[30] which mechanism has been termed[29] an α',β-elimination. Such a mechanism could, of course, explain why 1-phenylcyclohexene, rather than 3-phenylcyclohexene, is the principal product. This mechanism is also amenable to test with isotopic labels in our systems.

One of the latter two mechanisms seems appealing for elimination from the *trans* isomer of the sulfonium compound to explain its relatively rapid rate of reaction, and of course might also be involved with the *trans*-ammonium compound.[31]

The rate data thus appear consistent with the idea that *trans* elimination, even with onium compounds, prefer a concerted mechanism *via* a transition state such as XV, where the atoms involved must be *trans* and coplanar, while those eliminations which are sterically unable to produce a transition state such as XV, or where another path is energetically favorable, react *via* a carbanion intermediate or rearrangement process.[32] These interpretations find support in the work of Professor A. N. Bourns[33] of McMaster University on nitrogen kinetic isotope effects on the quaternary ammonium ions we have studied kinetically and product-wise.



XV

Acknowledgments.—The authors are indebted to the Office of Naval Research, the National Science Foundation and the Eastman Kodak Co. for support of this work.

Experimental

All melting points are corrected. The purity of the isomers prepared below was tested by observing diagnostic bands in the infrared which were present in one isomer but not the other. Such bands were found in each isomer, with the possible exception of the *cis*-2-phenylcyclohexyl *p*-toluenesulfonate. In this compound, shoulders were always present at the same points where the *trans* isomer showed strong absorption. As discussed, this may have been due to some of the *trans* isomer present in the *cis* compound. All infrared spectra of solid compounds were taken in potassium bromide pressings and the spectra of liquids were taken of the pure compounds in sodium chloride cells.

Preparation of *cis*- and *trans*-2-Phenylcyclohexyltrimethylammonium Iodides.—One procedure used to prepare a mixture of the amines was *via* a Leuckart reaction, adapted from that of Kost and Grandberg.[34] 2-Phenylcyclohexanone[35] (50.0 g., 0.29 mole) was added in portions to a hot mixture of 80 ml. of 90% formic acid, 60 g. of formamide and 0.3 g. of Raney nickel. The mixture was kept at 110–117° during the addition, which was over a period of 50 minutes. The mixture was then stirred for an additional 2 hours, maintaining the temperature at the same level. After it had cooled slightly, it was poured into 500 ml. of concentrated hydrochloric acid. This was then allowed to evaporate to dryness under an air jet while being kept warm. The residue was dissolved in 600 ml. of water, made strongly basic and extracted with ether. The ethereal solution was dried over anhydrous magnesium sulfate and the ether was removed by distillation. The oily residue was treated with base and benzoyl chloride to yield 53.9 g. of a mixture of *cis*- and *trans*-N-benzoyl-2-phenylcyclohexylamine, m.p. 123–165°. No attempt was made to analyze the isomer mixture accurately, but subsequent purifications indicated a *trans/cis* ratio of about seven to four.

In a second method, 2-phenylcyclohexanone oxime (10.0 g., 53.5 mmoles) was dissolved in 500 ml. of dry ether containing 20 ml. of dry benzene and this solution was added to a slurry of 5 g. of lithium aluminum hydride in 100 ml. of dry ether at a rate causing slow reflux. The mixture was then heated for 18 hours. After the complex was decomposed with wet ether and aqueous acid, the aqueous layer was separated, made basic and extracted with ether. The solu-

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(26) W. v. E. Doering and A. K. Hoffman, This Journal, **77**, 521 (1955).

(27) V. J. Shiner, Jr., and M. L. Smith, *ibid.*, **80**, 4095 (1958).

(28) T. Masamune, *Bull. Chem. Soc. Japan*, **30**, 491 (1957); *C. A.*, **52**, 6311i (1958).

(29) G. Wittig and R. Polster, *Ann.*, **612**, 102 (1958).

(30) F. Weygand, H. Daniel and H. Simon, *Chem. Ber.*, **91**, 1691 (1958).

(31) Dr. D. I. Davies of this Laboratory (unpublished work) has demonstrated that an ylide related to XIII cannot be an intermediate with *trans*-I.

(32) A comparison of the products of solvolysis of the *trans*-tosylate III in ethanol with and without added 0.4 *M* potassium hydroxide (Table III) suggests that bimolecular elimination in this case (as opposed to *trans*-I and II—*cf.* Table II) gives largely 3-phenylcyclohexene (V) and not 1-phenylcyclohexene (I). A similar result obtains with methyl mercaptide ion. This seems to indicate that base is promoting an E2 elimination using the *trans*-hydrogen from carbon three rather than the *cis* hydrogen from the activated 1-position. Thus, *trans*-elimination is favored over *cis* elimination even though the latter receives considerable assistance from the presence of the phenyl group. In this case, of course, there would be no large stabilization of an anionic charge by a full positive charge, and the normal preference[24] for *trans*, coplanar concerted elimination is apparently demonstrated.

(33) G. Ayrey and A. N. Bourns, private communication.

(34) A. N. Kost and I. I. Grandberg, *Zhur. Obshchei Khim.*, **25**, 1432 (1955).

(35) M. S. Newman and M. D. Farbman, This Journal, **66**, 1550 (1944).

tion was dried and the ether removed, leaving a residue which was converted as before with benzoyl chloride to 8.2 g. (55%) of a mixture of the N-benzoylamides, m.p. 128–160°. Later purification indicated a *trans/cis* ratio of about five to four.

In order to obtain pure isomers for subsequent use, the mixtures were separated by chromatography on neutral alumina. A solvent mixture containing 35% benzene in petroleum ether (b.p. 60–70°) eluted the *cis* isomer, while a mixture containing 60% benzene was used to elute the *trans* isomer. Due to the limited solubility of the compounds in such solvents, the mixture was powdered and placed on top of the prepared alumina column prior to eluting with large volumes of eluent. This procedure gave *cis*-N-benzoyl-2-phenylcyclohexylamine, m.p. 125–126°,[34] and *trans*-N-benzoyl-2-phenylcyclohexylamine, m.p. 181–182°.[36]

Preparation of *cis*- and *trans*-2-Phenylcyclohexylamine Hydrochloride.—The N-benzoyl derivatives were heated 6 hours with 20% hydrochloric acid in sealed tubes at 170–180°. The resulting amine hydrochlorides were purified by recrystallization from water. This procedure gave an 80.4% yield of *trans*-2-phenylcyclohexylamine hydrochloride, m.p. 249–251°,[37] and a 65.2% yield of the previously unreported *cis*-2-phenylcyclohexylamine hydrochloride, m.p. 205–207°.

Anal. Calcd. for $C_{12}H_{18}ClN$: C, 68.08; H, 8.56. Found: C, 67.97; H, 8.57.

Preparation of *cis*- and *trans*-2-Phenylcyclohexyltrimethylammonium Iodide.—The procedure used was essentially that of Cope and Bumgardner.[6] Since the amine hydrochlorides were used directly, anhydrous sodium carbonate was added to the reaction mixture to free the amine. This procedure gave 59% of the *trans* quaternary iodide, recrystallized from absolute ethanol or water to m.p. 232–234°, and 58.5% of the *cis* isomer, m.p. 215–216°.

Preparation of *cis*- and *trans*-2-Phenylcyclohexyl *p*-Toluenesulfonate.—The *trans*-2-phenylcyclohexanol used was prepared by the method of Eliel, McCoy and Price.[15] For use in preparing both *cis*- and *trans*-tosylates, 2-phenylcyclohexanol (stereochemistry or content of isomers unspecified) was purchased commercially from Matheson, Coleman and Bell.

trans-2-Phenylcyclohexanol (0.30 g., 1.70 mmoles) was dissolved in 10 ml. of pyridine and *p*-toluenesulfonyl chloride (0.30 g., 1.83 mmoles) was added. The mixture was allowed to stand at 25° for 24 hours. It was then poured into water and the precipitate was filtered and washed well with water. The precipitate was then dried overnight at reduced pressure to yield 0.33 g. (1.00 mmoles or 60%) of *trans*-2-phenylcyclohexyl *p*-toluenesulfonate, m.p. 157–158° dec.

Anal. Calcd. for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71. Found: C, 69.03; H, 6.76.

Recrystallization of the *trans*-tosylate from ethanol gave needles of m.p. 130–131° dec. The infrared spectrum and analysis of this material was identical to that melting at 157–158°. The material melting at 130– 131° could be dissolved in pyridine and precipitated by adding water to give the solid melting at 157–158°.

2-Phenylcyclohexanol (Matheson, Coleman and Bell, 100 g., 0.568 mole) was dissolved in 400 ml. of pyridine and 114 g. (0.600 mole) of *p*-toluenesulfonyl chloride was added. The solution was allowed to stand at 25° for 20 hours. A precipitate of white needles had formed and this was filtered, washed and dried to give 69.0 g. (37%) of essentially pure *trans*-tosylate, m.p. 126–128°. Water was added to the filtrate and the precipitated material was filtered to yield 47.0 g. (25%) of tosylate, m.p. 95–115°. Fractional crystallization from benzene or ethanol showed this to be about 3 parts *trans* to 2 parts *cis*. An analytical sample of the *cis*-2-phenylcyclohexyl *p*-toluenesulfonate had m.p. 102–103° dec.

Anal. Calcd. for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71. Found: C, 69.18; H, 6.86.

The *cis*-tosylate showed the same behavior as the *trans*. A portion dissolved in pyridine and reprecipitated with water had m.p. 123–127°. This could be recrystallized from ethanol to give the material of m.p. 102–103°. Analyses and infrared spectra of the two materials were identical.

Preparation of *cis*- and *trans*-2-Phenylcyclohexyl Methyl Sulfides and Sulfones.—1-Phenylcyclohexene (31.8 g., 0.20 mole) and methyl mercaptan Eastman Kodak Reagent Grade, (50.0 g., 1.04 mmoles) were placed in a 125-ml. Vycor flask and the solution was irradiated for 12 hours. A large Dry Ice cold finger was attached to the flask. After irradiation, the excess mercaptan was removed *in vacuo* and the residue was chromatographed on 350 g. of acid-washed alumina. Twelve fractions (100 ml.) with petroleum ether (b.p. 60–70°) and two fractions using 50% benzene in petroleum ether as eluents yielded a total of 39.5 g. (95%) of *cis*-2-phenylcyclohexyl methyl sulfide, b.p. 114–116° (1 mm.). An analytical sample prepared by vapor-phase chromatography at 210° on a silicone oil column had refractive index at 23° of 1.5610.

Anal. Calcd. for $C_{13}H_{18}S$: C, 75.67; H, 8.79. Found: C, 75.54; H, 8.97.

The *cis*-sulfide was converted with hydrogen peroxide in acetic acid[38] to *cis*-2-phenylcyclohexyl methyl sulfone, m.p. 172–174°.

Anal. Calcd. for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.57; H, 7.71.

In continuing the above chromatography of the reaction product from the addition of methyl mercaptan to 1-phenylcyclohexene, two additional fractions using 50% benzene in petroleum ether followed by two using a 50–50 mixture of benzene and ethyl ether yielded a total of 0.88 g. (2%) of *trans*-2-phenylcyclohexyl methyl sulfide, b.p. 84–86° (0.1 mm.), refractive index at 22° of 1.5612.

Anal. Calcd. for $C_{13}H_{18}S$: C, 75.67; H, 8.79. Found: C, 75.87; H, 8.82.

The *trans*-sulfide was converted with hydrogen peroxide in acetic acid[38] to the *trans*-sulfone, m.p. 108–109°.

Anal. Calcd. for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.38; H, 7.57.

Isomerization of *cis*-2-Phenylcyclohexyl Methyl Sulfone.—*cis*-2-Phenylcyclohexyl methyl sulfone (10.0 g., 41.9 mmoles) was heated at reflux with 400 ml. of approximately 2 *N* sodium ethoxide in absolute ethanol for 48 hours. The solution was acidified and then concentrated *in vacuo* to about 200 ml. About 50 ml. of water was then added and the white precipitate which had formed was filtered off to yield 9.9 g. (99%) of *trans*-2-phenylcyclohexyl methyl sulfone.

Reduction of *trans*-2-Phenylcyclohexyl Methyl Sulfone.—An adaptation of the method of Bordwell and McKellin[9] was used. In a one-liter 3-neck flask was placed *trans*-2-phenylcyclohexyl methyl sulfone (21.4 g., 89.9 mmoles) and lithium aluminum hydride (15 g., 366 mmoles). To this mixture was then carefully added from a dropping funnel 150 ml. of butyl ethyl ether. After addition was completed, the mixture was heated at reflux with stirring for 24 hours. The reaction mixture was then treated with ice, water and finally dilute hydrochloric acid. The suspension was extracted with ether and the ethereal solution was dried over anhydrous magnesium sulfate. The ether was removed *in vacuo* to leave 17.5 g. of a viscous liquid which was chromatographed on 150 g. of acid-washed alumina. From benzene-petroleum ether (b.p. 60–70°) fractions was obtained 14.6 g. (79%) of *trans*-2-phenylcyclohexyl methyl sulfide. In addition, 2.06 g. (10%) of the *trans*-sulfone starting material was recovered.

Reaction of *cis*- and *trans*-2-Phenylcyclohexyl *p*-Toluenesulfonate with Sodium Methyl Mercaptide.—In the thimble of a Soxhlet extractor was placed *trans*-2-phenylcyclohexyl *p*-toluenesulfonate (7.6 g., 22 mmoles) and extraction was accomplished into an approximately 0.7 *N* solution of sodium methyl mercaptide in absolute ethanol by heating at reflux for 64 hours. The precipitated sodium *p*-toluenesulfonate was removed by filtration and, after adding 100 ml. of water, the mixture was extracted with ether. From the ethereal solution was isolated a yellow oil which was chromatographed on 100 g. of acid-washed alumina. This gave a yield of 3.2 g. (73%) of *cis*-2-phenylcyclohexyl methyl sulfide. No olefin or *trans*-sulfide was found. In a subsequent experiment on a larger scale, 39% *cis*-sulfide and 35% 3-phenylcyclohexene were isolated. The reaction was not

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(36) D. V. Nightingale and V. Tweedie, This Journal, **66**, 1968 (1944).

(37) J. V. von Braun, H. Gruber and G. Kirschbaum, *Ber.*, **55**, 3664 (1922).

(38) S. J. Cristol, R. P. Arganbright, G. D. Brindell and R. M Heitz, This Journal, **79**, 6035 (1957).

further investigated to determine the reason for varying results.

In the thimble of a Soxhlet extractor was placed *cis*-2-phenylcyclohexyl *p*-toluenesulfonate (7.1 g., 21.2 mmoles) and extraction was accomplished into an approximately 0.6 *N* solution of sodium methyl mercaptide in absolute ethanol by heating at reflux for 22 hours. The work-up was performed as with the *trans*-tosylate reaction and resulted in the isolation of 2.9 g. (87%) of 1-phenylcyclohexene and 0.1 g. (4%) of *trans*-2-phenylcyclohexyl *p*-toluenesulfonate.

Preparation of *cis*- and *trans*-2-Phenylcyclohexyldimethylsulfonium Iodide.—*trans*-2-Phenylcyclohexyl methyl sulfide (6.4 g., 31.0 mmoles) and methyl iodide (55 g., 387 mmoles) were dissolved in about 60 ml. of nitromethane. The solution was then allowed to stand in a stoppered flask for 65 hours at 25°. The solution, which had become deep red in color, was concentrated *in vacuo* leaving a red solid. This was dissolved in a mixture of about 250 ml. of water, 50 ml. of ether and 20 ml. of ethanol. The layers were separated and the aqueous layer was filtered and evaporated *in vacuo* to leave a pale yellow solid. This was slurried with 25 ml. of absolute ethanol and filtered to yield 6.8 g. (63%) of *trans*-2-phenylcyclohexyldimethylsulfonium iodide, m.p. 124–126° dec. Recrystallization from absolute ethanol or a mixture of absolute ethanol and absolute ether did not change the melting point. A second crop of 0.2 g. (5%), m.p. 123–125° dec., was obtained.

Anal. Calcd. for $C_{14}H_{21}IS$: C, 48.28; H, 6.08. Found: C, 48.07; H, 5.99.

In a similar manner, from *cis*-2-phenylcyclohexyl methyl sulfide (3.10 g., 15.0 mmoles), was obtained 3.01 g. (58%) of *cis*-2-phenylcyclohexyldimethylsulfonium iodide, m.p. 111–113° dec.

Anal. Calcd. for $C_{14}H_{21}IS$: C, 48.28; H, 6.08. Found: C, 47.99; H, 6.07.

Reaction of *trans*-2-Phenylcyclohexyltrimethylammonium Iodide with Ethanolic Potassium Hydroxide.—*trans*-2-Phenylcyclohexyltrimethylammonium iodide (1.04 g., 3.02 mmoles) was dissolved in 13 ml. of 0.3 *N* ethanolic potassium hydroxide and the solution was sealed in a Pyrex tube. The tube was heated at 107° for 24 hours. After cooling, the tube was opened and the contents were washed into a separatory funnel containing 10 ml. of dilute hydrochloric acid. This was extracted with two 5-ml. portions of cyclohexane. The cyclohexane solution was dried over anhydrous magnesium sulfate, and filtered; the filtrate was evaporated to about 5 ml. The solution was then analyzed by vapor-phase chromatography using a silicone oil column at 197°. Besides the cyclohexane peak, two other peaks in the ratio of 30:1 were found. The large peak was identified by infrared as 1-phenylcyclohexene. Sufficient material was not obtained from the small peak for infrared analysis, but its retention time was identical to that of 3-phenylcyclohexene. Analysis of infinity samples by ultraviolet during the rate determinations showed the yield of 1-phenylcyclohexene to be 65%; hence the yield of 3-phenylcyclohexene would be about 2%. The aqueous acid layer which had been extracted with cyclohexane was evaporated to about 5 ml., at which point a precipitate had formed. This was filtered to yield 0.13 g. (12.5%) of starting material (*trans*-iodide, m.p. 215–220°), identified by infrared spectrum.

The filtrate from the *trans*-iodide was made basic and extracted with ether. Dry hydrogen chloride was passed into the ether extract and the mixture was evaporated to dryness leaving a gummy residue. This was recrystallized from benzene to yield 34 mg. of white crystals of *trans*-2-phenylcyclohexyldimethylamine hydrochloride, m.p. 174–177°. A second crop of 20 mg., m.p. 170–175°, was obtained to make a total yield of 54 mg. (7.6%).

Anal. Calcd. for $C_{14}H_{22}ClN$: C, 70.12; H, 9.25. Found: C, 70.18; H, 9.11.

Reaction of *trans*-2-Phenylcyclohexyldimethylsulfonium Iodide with Ethanolic Potassium Hydroxide.—*trans*-2-Phenylcyclohexyldimethylsulfonium iodide (2.93 g., 8.41 mmoles) was heated at reflux in 25 ml. of approximately 0.3 *N* ethanolic potassium hydroxide for 92 hours. The solution was evaporated to dryness *in vacuo* and the residue slurried with cyclohexane. The cyclohexane washes were evaporated *in vacuo* to leave 1.33 g. of an oily liquid. Vapor-phase chromatography through a silicone oil column at 165° showed the liquid to be a mixture of three compounds which were subsequently identified by infrared analysis. The products and yields, based upon analysis of the chromatography curves according to Eastman,[39] were 3-phenylcyclohexene, 0.02 g. (1.7%), 1-phenylcyclohexene, 0.26 g. (19.3%); and *trans*-2-phenylcyclohexyl methyl sulfide, 1.05 g. (60.8%). Ultraviolet analysis of infinity samples during the rate determinations indicated that the yield of 1-phenylcyclohexene was 23%.

Reaction of *cis*-2-Phenylcyclohexyldimethylsulfonium Iodide with Ethanolic Potassium Hydroxide.—*cis*-2-Phenylcyclohexyldimethylsulfonium iodide (2.72 g., 7.82 mmoles) was heated at reflux with 50 ml. of approximately 0.4 *N* potassium hydroxide for 20 hours. The solution was then evaporated *in vacuo* to about 25 ml. and water and dilute hydrochloric acid was added. The resulting suspension was extracted with ether. The ethereal solution was washed with dilute sodium thiosulfate solution to remove the orange-red color and was then dried over anhydrous magnesium sulfate. Removal of the ether left 0.98 g. of an oily liquid. Vapor-phase chromatography through a silicone oil column at 203° gave three compounds which were identified by infrared analysis. The products and yields, calculated as before, were 3-phenylcyclohexene, 0.01 g. (0.8%); 1-phenylcyclohexene, 0.85 g. (68.7%); and *cis*-2-phenylcyclohexyl methyl sulfide, 0.12 g. (7.5%). Ultraviolet analysis of infinity samples during the rate determinations indicated that the yield of 1-phenylcyclohexene was 76–77%.

Reaction of *trans*-2-Phenylcyclohexyl *p*-Toluenesulfonate with Ethanolic Potassium Hydroxide.—*trans*-2-Phenylcyclohexyl *p*-toluenesulfonate (9.28 g., 28.1 mmoles) was heated at reflux in 200 ml. of approximately 0.4 *N* ethanolic potassium hydroxide for 8 days. Some of the tosylate did not dissolve and the mixture was filtered hot to yield 1.65 g. (5.0 mmoles) of *trans*-tosylate, m.p. 134–138°. The filtrate was cooled and filtered to yield 2.39 g. of *trans*-tosylate, m.p. 142–143°. The filtrate was evaporated *in vacuo* to leave a red oil. This was taken up in 15 ml. of cyclohexane and washed with water to remove the red color. The cyclohexane solution was dried and evaporated *in vacuo* to leave a slightly yellow liquid, 2.67 g. Vapor-phase chromatography and subsequent infrared analysis showed the following compounds, appearing in the following order from the column: 3-phenylcyclohexene, 1.27 g. (28.6%); 1-phenylcyclohexene, 0.49 g. (11.0%); 2-phenylcyclohexyl ethyl ether, 0.49 g. (8.5%)[40]; and *trans*-2-phenylcyclohexanol, 0.18 g. (3.6%). The structure of the alcohol was proved by comparison of infrared spectra and by conversion to a tosylate, m.p. 130–134°, having the identical infrared spectrum as the known tosylate. The ether had strong absorption in the infrared from 1050 to 1120 cm.$^{-1}$ with the peak at 1106 cm.$^{-1}$. It had refractive index at 23° of 1.5240.

Reaction of *cis*-2-Phenylcyclohexyl *p*-Toluenesulfonate with Ethanolic Potassium Hydroxide.—*cis*-2-Phenylcyclohexyl *p*-toluenesulfonate (2.00 g., 6.05 mmoles) was heated at reflux for 36 hours in approximately 0.25 *N* ethanolic potassium hydroxide. The solution was cooled and filtered to yield 0.2 g. (0.6 mmole or 10%) of *trans*-tosylate, m.p. 148–153°. Further work-up essentially as above for the *trans*-tosylate yielded 0.96 g. of oily liquid. Vapor-phase chromatography and infrared analysis showed the products: 3-phenylcyclohexene, 0.065 g. (6.8%); 1-phenylcyclohexene, 0.84 g. (87.3%). These yields plus that of recovered tosylate add to 104%. The yield of 1-phenylcyclohexene indicated by ultraviolet analysis during the rate determinations was 67%.

Solvolysis of *trans*-2-Phenylcyclohexyldimethylsulfonium Iodide.—*trans*-2-Phenylcyclohexyldimethylsulfonium iodide, 1.85 g., (5.30 mmoles) was dissolved in 25 ml. of ethanol (92.5 wt.%) and the solution was heated at reflux for 92 hours. It then stood at 25° for an additional 72 hours. The solution was concentrated *in vacuo* to about 5 ml. and water and ether were then added. The ether layer was washed with water and dilute sodium thiosulfate solution, dried and evaporated to leave 0.92 g. (85%) of *trans*-2-phenylcyclohexyl methyl sulfide. Vapor-phase chromatography showed only one peak and the crude material had an infrared spectrum identical to that of the pure sulfide.

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[39] R. H. Eastman, THIS JOURNAL, **79**, 4243 (1957).

[40] The elemental analysis on this compound indicated that there was about 15–20% of a hydrocarbon contaminant, presumably some 1-phenylcyclohexene.

Solvolysis of *cis*-2-Phenylcyclohexyldimethylsulfonium Iodide.—*cis* - 2 - Phenylcyclohexyldimethylsulfonium iodide (3.1 g., 8.9 mmoles) was heated at reflux in 40 ml. of ethanol for 52 hours. The solution then stood at 25° for an additional 24 hours. Isolation of products was as for the solvolysis of the *trans* isomer. A crude residue of 1.57 g. was obtained which was found to contain 3-phenylcyclohexene, 0.019 g. (1.3%); 1-phenylcyclohexene, 0.185 g. (13.1%); and *cis*-2-phenylcyclohexyl methyl sulfide, 1.36 g. (74.2%).

Solvolysis of *trans*-2-Phenylcyclohexyl *p*-Toluenesulfonate.—*trans*-2-Phenylcyclohexyl *p*-toluenesulfonate (3.30 g., 10.0 mmoles) was heated at reflux in 300 ml. of ethanol for 120 hours. The solution then stood at 25° for 72 additional hours. The solution was cooled to precipitate 0.9 g. (27.2 %) of *trans*-tosylate, m.p. 128°. The filtrate was concentrated to 25 ml. and cooled to yield an additional 0.2 g. (6.1%) of *trans*-tosylate. The filtrate was evaporated to yield 0.93 g. of a slightly yellow liquid. Product determination as before showed this to contain 3-phenylcyclohexene, 0.292 g. (18.4%); 1-phenylcyclohexene, 0.283 g. (17.9%); 2-phenylcyclohexyl ethyl ether, 0.199 g. (9.7%); and *trans*-2-phenylcyclohexanol, 0.126 g. (7.2%). The ether was the same as that described above under the reaction of *trans*-tosylate with base.

Solvolysis of *cis*-2-Phenylcyclohexyl *p*-Toluenesulfonate.—*cis*-2-Phenylcyclohexyl *p*-toluenesulfonate (2.00 g., 6.05 mmoles) was heated at reflux in 100 ml. of ethanol for 36 hours. The solution was evaporated *in vacuo*. Ether was added and crystals which did not dissolve were filtered off to give a total of 0.083 g. (4.2%) of *trans*-tosylate, m.p. 108–112°, which was identified by infrared spectrum. The filtrate was evaporated to leave 0.50 g. of an oil which was found to contain 3-phenylcyclohexene, 0.02 g. (2.1%), and 1-phenylcyclohexene, 0.48 g. (50.3%).

Isomerization of 3-Phenylcyclohexene.—To test base-catalyzed isomerization, one-fiftieth of a solution of 0.1134 g. (0.717 mmole) of 3-phenylcyclohexene in 50 ml. of ethanol was heated in a sealed tube together with 1.00 ml. of 0.4188 *N* ethanolic sodium hydroxide at 107° for 16 hours. The contents were poured into dilute acid and extracted with cyclohexane. The extracts were diluted to 50.00 ml. and showed the typical ultraviolet spectrum of 1-phenylcyclohexene with an absorption maximum at 247 mμ, optical density 0.360. A 1.00-ml. portion of the original solution of the 3-olefin, diluted to 50.00 ml., had an optical density at 247 mμ of 0.198. From the known extinction coefficients[41] at 247 mμ (1-phenylcyclohexene ϵ 12,940 and 3-phenylcyclohexene ϵ 634) it was calculated that 4.6% isomerization had occurred.

To test the acid-catalyzed isomerization, the following procedure was used. In 50.00 ml. of ethanol equilibrated at 63.70° were dissolved 0.0533 g. (0.337 mmole) of 3-phenylcyclohexene and 0.0406 g. (0.236 mmole) of *p*-toluenesulfonic acid. The solution was kept at 63.70° and aliquots withdrawn at varied times. The olefin was extracted into cyclohexane as above and diluted to 50.00 ml. The results were:

Sample	Time, hr.	Optical density At 247 mμ	At 253 mμ
1	0.0	0.192	0.210
2	24.5	.207	.217
3	42.5	.205	.213

The absorption at 253 mμ is the maximum absorption of 3-phenylcyclohexene. Thus, no isomerization to 1-phenylcyclohexene was observed under these conditions.

Rate Procedures. a. ***cis*- and *trans*-2-Phenylcyclohexyltrimethylammonium Iodides.**—Standard solutions of the salts were made up in ethanol (92.6 wt. %) and a known amount was pipetted into alkali-resistant glass tubes. To each was added a measured amount of standard ethanolic potassium hydroxide; the tubes were sealed and immersed in an oil-bath held at the desired temperature to within 0.02°. The rates were measured at temperatures causing sufficiently slow reaction so that the amount of reaction occurring before the tubes reached thermal equilibrium would be insignificant. At appropriate intervals, a tube was removed from the bath, immersed in ice-water, opened, and the contents washed into a separatory flask containing water to which five drops of 6 *N* hydrochloric acid had been added. The suspension was extracted with three portions of distilled cyclohexane, which were combined, dried over anhydrous magnesium sulfate and filtered into a 50-ml. volumetric flask. If necessary, dilutions were made with cyclohexane in order to give readings of from 0.2 to 0.9 optical density at 247 mμ on a Beckman DU ultraviolet-spectrophotometer. The absorption peak at 247 mμ for 1-phenylcyclohexene has an extinction coefficient of 12,940.[41] A large excess of base was used and the pseudo-first-order rate constants determined graphically. Corrections for solvent expansion were made. The *cis* compound showed straight line behavior over the range of reaction studied (6 to 68%) and nine spectral determinations on infinity samples gave values ranging from 91.0 to 93.7% elimination to 1-phenylcyclohexene. Since the *trans* compound did not give a quantitative yield of 1-phenylcyclohexene (four infinity samples gave yields of from 62.1 to 65.4%), but when corrected to give a rate constant for elimination to 1-phenylcyclohexene, the *trans* compound also showed straight line behavior over the range of reaction studied (12 to 84%). The second- order rate constant for elimination was obtained by dividing the first-order constant by the difference between the concentration of base and the total amount of the compound reacting to give 1-olefin.

b. ***cis*- and *trans*-2-Phenylcyclohexyldimethylsulfonium Iodides.**—The compound was weighed into a volumetric flask and a known amount of equilibrated ethanol was added. Equilibrated ethanolic potassium hydroxide was added and the flask shaken. Aliquots were removed at desired intervals and quenched in dilute hydrochloric acid. The balance of the procedure was as described above. The *cis* compound showed straight line behavior over the reaction range studied (7 to 82%) and seven spectral determinations on infinity samples gave values from 74.0 to 77.4% elimination to 1-phenylcyclohexene. The same was true for the *trans* compound which was studied from 4 to 83% reaction. Two spectral determinations on infinity samples gave values of 23.2 and 23.0% elimination to 1-phenylcyclohexene. For the *trans* compound, it was necessary to make an additional correction for the large amount of *trans*-2-phenylcyclohexyl methyl sulfide which was extracted along with olefin. The sulfide was determined to have a molar extinction coefficient of 536 at 247 mμ. Since the sulfide was formed in 61% yield, it was calculated that a 9% correction in optical density was to be applied.

c. 2-Phenylethyltrimethylammonium Bromide.—The rates were run in an identical manner to those for the sulfonium compounds. Elimination to styrene was followed by observing the absorption peak at 248 mμ whose extinction coefficient in cyclohexane was determined to be 16,700. Two spectral determinations on infinity samples gave values of 99.9 and 100.4% styrene formed. No polymerization of the styrene was observed during the time of the rate runs, which were not continued as long as the other eliminations in order to avoid this possibility. The range studied was from 4 to 52% reaction and again straight line behavior was observed.

d. ***cis*- and *trans*-2-Phenylcyclohexyl *p*-Toluenesulfonates.**—The rates of elimination from the *cis*-tosylate with base were determined in the same manner as for the sulfonium compounds. The range studied was from 12 to 61% and again straight line behavior was observed. Two spectral determinations on infinity samples gave values of 66.7 and 67.5% of 1-phenylcyclohexene formed. This was in contrast to a yield of around 80% from the isolation experiment. Some rates were also determined for the *cis*- and *trans*-tosylate reactions with base by following the amount of *p*-toluenesulfonic acid formed. In these runs, comparable amounts of base and tosylate, with base always somewhat in excess, were used. Aliquots were quenched in water and titration with standardized dilute hydrochloric acid showed the amount of base unreacted. In the solvolysis experiments, the aliquots were quenched in a standard basic solution. The excess base was then titrated with standard dilute hydrochloric acid.

BOULDER, COLO.

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[41] R. Y. Mixer and W. G. Young, THIS JOURNAL, **78**, 3379 (1956).