

Electronic Effects in Elimination Reactions.

V. Bimolecular *cis* Eliminations.

2-Arylcyclopentyl Tosylates

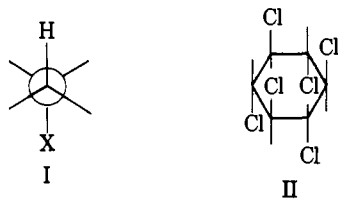
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Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa. Received January 22, 1965

trans-2-Arylcyclopentyl tosylates have been shown to undergo a rapid concerted *cis* E2 reaction when treated with potassium *t*-butoxide in *t*-butyl alcohol. The *trans* E2 reaction in the analogous *cis*-2-arylcyclopentyl tosylate system has been studied in *t*-butyl alcohol and also in ethanol using sodium ethoxide as the base. The *cis* E2 reaction is shown to develop more carbanionic character in its transition state than the *trans* E2 reaction. In its ρ -value (+2.8) and in its response to solvent changes the *cis* E2 transition state resembles that for the *trans* elimination from β -phenylethyl tosylate. Methods of synthesis for *cis*- and *trans*-2-arylcyclopentanol are reported as well as for 1- and 3-arylcyclopentenes.

Introduction

In general, it has appeared to be the case that, given a free choice, bimolecular elimination reactions (E2 reactions³) proceed most rapidly when the leaving groups occupy antiperiplanar positions (I). The evidence for this preferred mode of elimination is well covered in a number of texts and reviews and need not be summarized here.⁴ There are at least three circumstances in which bimolecular *cis* eliminations have been observed. In the first of these cases, in-



vestigated by Cristol and co-workers,⁵ the geometry of the molecule was so arranged that *trans* elimination was impossible. Thus, the β -isomer of benzene hexachloride (II), which contains only *cis* hydrogens and chlorines, undergoes bimolecular elimination under strenuous conditions,⁵ as do a number of bicyclic halides (III).⁶

(1) For a preliminary report of some of this work see C. H. DePuy, R. D. Thurn, and G. F. Morris, *J. Am. Chem. Soc.*, **84**, 1314 (1962).

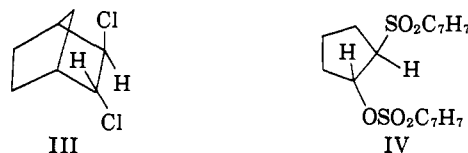
(2) Alfred P. Sloan Fellow, 1960-1964; Department of Chemistry, University of Colorado, Boulder, Colo.

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VIII.

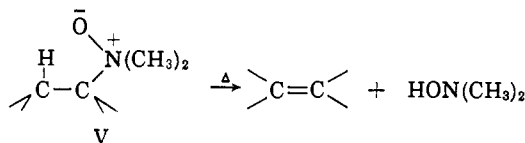
(4) (a) D. Banthrope, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963; (b) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter VIII; (c) D. J. Cram in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter VI; (d) J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, **1**, 225 (1962).

(5) (a) S. J. Cristol, *J. Am. Chem. Soc.*, **69**, 338 (1947); (b) S. J. Cristol, N. L. Hause, and J. S. Meek, *ibid.*, **73**, 674 (1951); S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953).

(6) (a) S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952); (b) S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957); (c) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 3441 (1957).



Bimolecular *cis* eliminations may also be observed in cases where the hydrogen being removed is acidified by an adjacent electron-withdrawing group. The most widely studied of these cases have been those involving cyclohexyl and cyclopentyl tosyloxysulfones of type IV. Here *cis* elimination, toward the acidified hydrogen, is more rapid than unactivated *trans* elimination.⁷ Finally, *cis* eliminations are known to occur in pyrolytic eliminations in which the base, because it is an internal one, can reach only the adjacent *cis* hydrogens. Perhaps the most striking is the Cope elimination of amine oxides (V), since these reactions



proceed readily at moderate temperatures.⁸ Sicher⁹ has recently proposed a *cis* elimination to account for the preponderance of *cis* over *trans* olefin formed in certain Hofmann eliminations.

It now seems quite probable that the *cis* eliminations of the second type, those involving the removal of highly acidified protons, are not truly concerted eliminations at all, but rather involve the rate-determining formation of a carbanion followed by a rapid elimination.¹⁰ Pyrolytic *cis* eliminations do not offer an opportunity to compare *cis* and *trans* modes of reaction in similar molecules. When our interest in pyrolytic *cis* eliminations led us into the whole question of the mechanism of *cis* eliminations in general, it seemed to us, as it has to others, that the study of systems in which *trans* elimination was inhibited would offer the best opportunities for an investigation of *cis* E2 reactions.

In the cases in which *cis* E2 reactions have been studied earlier, they uniformly react slowly, as compared to molecules in which normal *trans* E2 reactions are

(7) (a) J. Weinstock, R. G. Pearson, and F. G. Bordwell, *ibid.*, **76**, 4748 (1954); **78**, 3468 (1956); (b) H. L. Goering, D. I. Relyea, and K. L. Howe, *ibid.*, **79**, 2502 (1957).

(8) (a) A. C. Cope and E. R. Trumbull, *Org. Reactions*, **2**, (1960); (b) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

(9) J. Zauada and J. Sicher, *Proc. Chem. Soc.*, 96 (1963).

(10) (a) J. Hine and P. B. Langford, *J. Org. Chem.*, **27**, 4149 (1962); (b) F. G. Bordwell and E. W. Garbisch, Jr., *ibid.*, **28**, 1765 (1963); (c) F. G. Bordwell, R. L. Arnold, and J. B. Biranowski, *ibid.*, **28**, 2406 (1963); see, however, R. Breslow, *Tetrahedron Letters*, 339 (1964).

possible. In the benzene hexachloride series the β -isomer II, in which *cis* elimination is necessary, reacts 7000 to 24,000 times less rapidly than other isomers in which at least one *trans* elimination is possible.⁶ Among bicyclic compounds *cis* elimination sometimes exceeds *trans* in rate. Nevertheless, the conditions necessary to induce reaction are quite drastic, and it has usually been assumed that in these compounds the *cis* elimination has not been speeded up, but rather the *trans* elimination made more difficult since, by incorporation into a rigid ring system, a coplanar *trans* elimination has been made impossible. A particularly thorough study of the E2 reaction of a number of dihalonorbornanes has been reported recently by LeBel and co-workers.¹¹

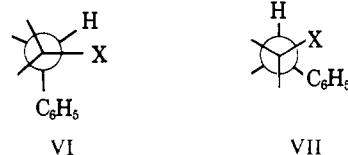
In those reactions in which *cis* eliminations undoubtedly do occur, substantial questions still remain as to mechanism. In the β -benzene hexachloride case Cristol has presented evidence⁵ that intermediate carbanions are involved, and this has found added confirmation in recent work by Hine.¹² In at least one bicyclic case there is good evidence that the elimination is concerted.¹¹ The two results are by no means incompatible, and in this paper we report some studies which, we feel, demonstrate for the first time rapid concerted bimolecular *cis* eliminations in systems which can readily be compared with a variety of other eliminations and which illustrate somewhat more clearly than it has been possible to do before the conformational and electronic effects which are evidently important in determining *cis* E2 rates.

Results

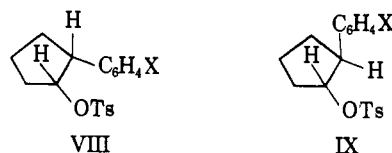
A series of earlier investigations reported from these laboratories¹³ and those of Saunders¹⁴ has measured the rates of elimination of a variety of β -arylethyl compounds including tosylates, halides, and sulfonium and ammonium salts. These rates have, in some cases, been measured in both ethanol and *t*-butyl alcohol solvents, and kinetic isotope effects have been determined for proton removal in several cases^{15a} and for the leaving group in two cases.^{15b,c} Rates have also been reported recently in D₂O.¹⁶ Hammett σ - ρ correlations have been applied to a number of β -arylethyl eliminations. In no other system have so many quantitative E2 studies been carried out and so it was natural, in searching for molecules in which to study bimolecular *cis* eliminations, to choose a derivative of the β -phenylethyl system.

Cristol and Stermitz¹⁷ have investigated the reaction of *cis*- and *trans*-2-phenylcyclohexyl tosylate with KOH in ethanol. They showed that the *trans* E2 reaction was rapid but that no *cis* E2 could be observed. If reaction times are prolonged, the *trans* isomer under-

goes solvolysis rather than elimination. We wished to investigate the possibility that if a concerted *cis* E2 reaction were to be at all rapid the most favorable reaction path would be through a transition state in which the departing proton and leaving group would be *cis* and coplanar (VI).¹⁸ In *trans*-2-phenylcyclohexyl tosylate both substituents are equatorial (VII). Any

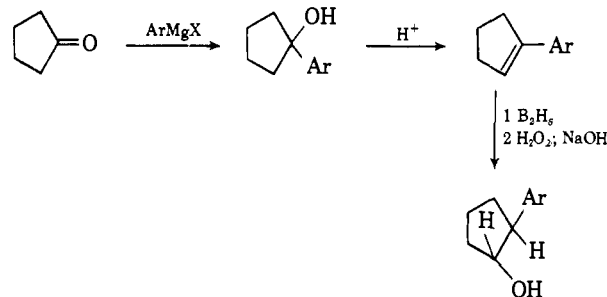


elimination transition state which demands coplanarity would require a boat form for the cyclohexane ring. In smaller rings coplanarity can probably be obtained more readily. We therefore decided to examine the rates of elimination of *cis*- and *trans*-2-arylcyclopentyl tosylates VIII and IX.



The *trans* isomers of the desired 2-arylcyclopentanol are readily available by two methods. Reaction of aryllithium with cyclopentene oxide gives the alcohol directly,¹⁹ but yields are low and not all the requisite aryllithium compounds can be prepared readily. In the preferred method outlined in Chart I, yields are high and the alcohols are quite pure as determined by gas chromatography.

Chart I



The *cis* isomers of 2-arylcyclopentanol are much more difficult to prepare. We first synthesized *cis*-2-phenylcyclopentanol itself by the Raney nickel reduction of 2-phenylcyclopentanone.²⁰ This reduction gives a mixture of 79% *cis*- and 21% *trans*-2-phenylcyclopentanol as determined by g.p.c. analysis. Lithium aluminum hydride reduction of the same ketone affords a 41% *cis*-59% *trans* mixture. Pure *cis* alcohol could be isolated by fractionation through a spinning-band column. A more general synthetic method is outlined in Chart II. 3-Chlorocyclopentene, formed by the addition of HCl to cyclopentadiene,²¹ reacts with

(11) N. A. LeBel, P. D. Bierne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Am. Chem. Soc.*, **85**, 3199 (1963).

(12) J. Hine, R. D. Weimer, Jr., P. B. Langford, and O. B. Ramsey, *ibid.*, **85**, 3894 (1963).

(13) C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2532, 2535 (1960).

(14) W. H. Saunders, C. B. Gibbons, and R. A. Williams, *ibid.*, **80**, 4099 (1958), and earlier papers.

(15) (a) W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960); (b) W. H. Saunders, Jr., and S. Asperger, *ibid.*, **79**, 1612 (1957); (c) G. Ayrey, A. N. Bourns, and V. A. Vyas, *Can. J. Chem.*, **41**, 1759 (1963).

(16) L. J. Steffa and E. R. Thornton, *J. Am. Chem. Soc.*, **85**, 2680 (1963).

(17) S. J. Cristol and F. R. Stermitz, *ibid.*, **82**, 4962 (1960).

(18) F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957), and earlier papers.

(19) W. H. Tallent, *J. Org. Chem.*, **21**, 1862 (1956).

(20) K. Mislow and C. L. Hamermish, *J. Am. Chem. Soc.*, **77**, 1590 (1955).

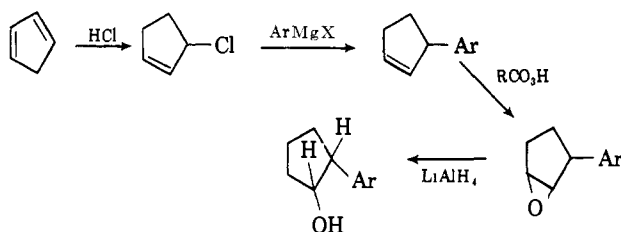
(21) B. Wladislaw, *J. Chem. Soc.*, 4227 (1955).

Table I. Rates of Elimination of 2-Phenylcyclopentyl and Cyclohexyl Tosylates in Potassium *t*-Butoxide-*t*-Butyl Alcohol at 50°

Tosylate	Type of elimination	k_{E2} , l. mole ⁻¹ sec. ⁻¹	$k_{trans E2}/k_{cis E2}$
<i>cis</i> -2-Phenylcyclopentyl	<i>trans</i>	26.4×10^{-4}	9.1
<i>trans</i> -2-Phenylcyclopentyl	<i>cis</i>	2.9×10^{-4}	
<i>cis</i> -2-Phenylcyclohexyl	<i>trans</i>	1.92×10^{-4}	$>10^4$
<i>trans</i> -2-Phenylcyclohexyl	<i>cis</i>	No reaction	

aryl Grignard reagents to form 3-arylcyclopentenes.²² Epoxidation with monoperoxyphthalic acid furnishes a mixture of epoxides which, on reduction with lithium aluminum hydride, gives a mixture of arylcyclopentanols from which the desired *cis*-2-arylcyclopentanols may be separated by fractional distillation.

Chart II



We found immediately that the attempted *cis* elimination of *trans*-2-phenylcyclopentyl tosylate with sodium ethoxide in ethanol was complicated by a competing solvolysis reaction. In an attempt to reduce the importance of solvolysis we began an investigation of the elimination using the base potassium *t*-butoxide in *t*-butyl alcohol as solvent, since this solvent-base system had already been extensively used in studies of β -arylethyl eliminations. Under these conditions, a smooth reaction took place at 50° generating 1-phenylcyclopentene as the main product, and good second-order kinetics were observed. *cis*-2-Phenylcyclopentyl tosylate, under identical conditions, reacted more rapidly but only by a factor of 9. Here was clearly a case in which a *cis* E2 reaction appeared to be relatively rapid and nearly as fast as a *trans* E2 reaction in the same system.

When an investigation of elimination from the *cis*- and *trans*-2-phenylcyclohexyl tosylates was carried out, it was discovered that, as was the case in ethanol, *cis*-2-phenylcyclohexyl tosylate underwent a ready E2 reaction in *t*-butyl alcohol. In marked contrast to the results in the cyclopentyl system, *trans*-2-phenylcyclohexyl tosylate was completely inert to potassium *t*-butoxide in *t*-butyl alcohol and was recovered unchanged after 22 days at 50°. The pertinent data are summarized in Table I. The results given in this table seem to confirm the view that a *cis* E2 reaction is more rapid in a system in which coplanarity is possible. We wished next to prove conclusively that the reaction under investigation was indeed a *cis* elimination and to investigate electronic requirements for this elimination.

(22) F. Winternitz and N. Mausseron, *Bull. soc. chim. France*, 713 (1949).

A major difficulty soon arose; rate constants were not always reproducible using different batches of potassium *t*-butoxide-*t*-butyl alcohol. This problem is not without precedent. In an earlier study of the rate of elimination of 2-phenylethyl tosylate with potassium *t*-butoxide in *t*-butyl alcohol¹³ we had obtained rate constants significantly larger than those reported by Saunders and Edison.¹⁵ The major source of the difficulty was traced mainly to impurities in the potassium metal. Good reproducibility was obtained when the metal was purified before use, and each batch of base was checked before use by determining the rate at which it induced the elimination from β -phenylethyl tosylate. In addition, as many rates as possible were carried out using the same batch of base. Despite the fact that the absolute rates reported here are faster than those reported in our earlier communication,¹ relative rates, and functions like ρ which are ratios of rates, have not been affected to any large degree. The rates reported in this paper are those determined spectrophotometrically but these have, in nearly every case, been duplicated titrimetrically. We therefore feel that while the ultimate "best" value for some of these rate constants may still be in some doubt, relative rates and values which depend upon relative rates, e.g., Hammett ρ -values and deuterium isotope effects, are not likely to be appreciably wrong. For instance, despite the much larger rate constants reported here, ρ for the *cis* E2 reaction and k_{cis}/k_{trans} are not much different from the value reported by us earlier.¹ It may also be seen in Table IV that ρ -values calculated from three independent sets of rate data all agree well, again indicating that relative values are likely to be more accurate than individual rate constants.

We have applied three criteria to show that the formation of 1-phenylcyclopentene from *trans*-2-phenylcyclopentyl tosylate in base is a true *cis* elimination. In order to rule out the possibility of a *trans* elimination to form 3-phenylcyclopentene followed by a rapid base-catalyzed isomerization of the double bond, we prepared some 3-phenylcyclopentene by pyrolysis of *cis*-2-phenylcyclopentyl acetate (Table II). The product of this pyrolysis was 94% unconjugated olefin. When a 0.05 *N* solution of this olefin was allowed to react for 48 hr. with a 0.12 *N* solution of potassium *t*-butoxide in *t*-butyl alcohol at 50°, no isomerization could be detected. Unconjugated olefin is therefore stable to the reaction condition.

Table II. Composition of Phenylcyclopentenes Formed in the Pyrolysis of 2-Phenylcyclopentyl Acetates at 500°

Acetate	Olefin composition, %	
	3-Phenyl	1-Phenyl
<i>cis</i>	94	6
<i>trans</i>	14	86

If a *cis* elimination were indeed under observation, replacement of the benzylic hydrogen by deuterium should reduce the rate. This deuterated compound was prepared readily by reaction of 1-phenylcyclopentene with B_2D_6 , formed from lithium aluminum deuteride. As shown in Table III, the deuterated compound did indeed react slowly, giving a deuterium isotope effect

Table III. Rate Constants for Eliminations from a Variety of Tosylates in 0.1 *N* Potassium *t*-Butoxide-*t*-Butyl Alcohol Solution

Y	Z	E2 type	Temp., °C.	$k_{E2} \times 10^4$, l. mole ⁻¹ sec. ⁻¹	1-Olefin, ^a %
<i>p</i> -CH ₃	H	<i>cis</i>	50.0	1.20 ± 0.04	82
H	H	<i>cis</i>	30.3	0.47 ± 0.16	
H	H	<i>cis</i>	50.0	3.10 ± 0.11	91
H	H	<i>cis</i>	70.0	17.50 ± 0.40	
H	D	<i>cis</i>	50.0	0.55 ± 0.02	70
<i>p</i> -Cl	H	<i>cis</i>	50.0	13.60 ± 0.20	
<i>m</i> -Cl	H	<i>cis</i>	50.0	35.40 ± 1.00	
<i>p</i> -CH ₃		<i>trans</i>	50.0	13.40 ± 0.40	
H		<i>trans</i>	30.3	5.90 ± 0.10	100
H		<i>trans</i>	50.0	29.10 ± 0.10	
<i>p</i> -Cl		<i>trans</i>	50.0	50.40 ± 2.30	
<i>m</i> -Cl		<i>trans</i>	50.0	93.60 ± 0.10	
H		<i>trans</i>	50.0	1.93 ± 0.05	73
H		<i>trans</i> ^b	50.0	110.00 ± 4.00 ^c	100

^a As determined by gas chromatography. ^b Presumably. ^c From ref. 13.

of approximately five. Finally, the observation of a large substituent effect on the rate of reaction also argues for an elimination directly toward the aromatic ring. The rates of elimination from a number of cyclopentyl and cyclohexyl tosylates in *t*-butyl alcohol are given in Table III, together with the rate of elimination from 2-phenylethyl tosylate for comparison. In Table IV, Hammett ρ -values and energies and entropies of activation for the *cis* and *trans* E2 reaction of 2-arylcyclopentyl tosylates are given, together with values for 2-phenylethyl tosylate determined earlier. It should be noted that ρ -values from three independent series of rate determinations agree excellently, and that energies and entropies of activation are in fair agreement.

trans E2 reactions in *cis*-2-arylcyclopentyl tosylates proceed readily in ethanol-sodium ethoxide solution, and the rate data for these reactions are recorded in Table V. We did investigate the rate of the *cis* E2 reaction of *trans*-2-(*m*-chlorophenyl)cyclopentyl tosylate in pure ethanol. This compound was chosen because it underwent the most rapid E2 reaction, and hence the E2/S_N1 ratio would be maximized. The rate of appearance of conjugated olefin in pure ethanol-sodium ethoxide was about 0.01 that in *t*-butyl alcohol-potassium *t*-butoxide. This was considerably faster than the rate of appearance of conjugated olefin in pure ethanol in the absence of base.

Discussion

Given the fact that a *cis* E2 reaction does indeed occur in *trans*-2-phenylcyclopentyl tosylate induced by potassium *t*-butoxide in *t*-butyl alcohol solution, we may next ask about the steric and electronic characteristics of its transition state. Incorporating the β -phenylethyl system into a cyclopentane ring serves to reduce the rate of *trans* elimination (Table III) by a factor of 2 in *t*-butyl alcohol solution.²³ In ethanol solution the rate increases by a factor of nearly 10 (Table V). The Hammett ρ -value (Table IV) for the *trans* elimination in the cyclic system is greater in *t*-butyl alcohol ($\rho = 1.5$) than it is in ethanol ($\rho = 1.0$), and both of these values are smaller than those for β -phenylethyl tosylate ($\rho = 3.4$ and 2.3, respectively). These ρ -values and relative rates are in accord with the view expressed earlier¹³ that eliminations in *t*-butyl alcohol have a transition state with less double-bond character than eliminations in ethanol. Attachment of alkyl groups to the double bond slows down the rate in *t*-butyl alcohol by an inductive effect and in ethanol increases the rate by stabilization of the double bond being generated. We would then place the *trans* E2 elimination in the arylcyclopentyl series toward the E1 end of the E2 scale of eliminations,^{4d} and give a relatively large importance to C-O bond breaking. These same *trans* eliminations in *t*-butyl alcohol will have moved somewhat back along the E2 scale so that C-H bond breaking assumes more importance.

cis Eliminations from *trans*-2-arylcyclopentyl tosylates clearly have a transition state in which C-H bond breaking has become of greater importance, *i.e.*, the reaction is closer to the E1_{CB} end of the E2 scale.^{4d} This is shown by the fact that the ρ -values are larger for *cis* ($\rho = 2.8$) than for *trans* ($\rho = 1.5$) elimination and by the fact that the rate of *cis* E2 reaction is much slower in pure ethyl alcohol than it is in pure *t*-butyl alcohol. In fact, in most respects the *cis* E2 reaction in the cyclic system resembles the open-chain elimination from the primary 2-phenylethyl tosylate. The ρ -values for the two eliminations are comparable and they respond similarly to solvent changes. The *trans* E2 elimination in *cis*-2-arylcyclopentyl tosylates, on the other hand, appears to have a transition state with significantly more double-bond character and so responds differently, particularly to change in solvent.

Although the *cis* E2 reactions studied appear to have E1_{CB} character, there is no indication that the reaction is two step and that the benzylic hydrogen is completely removed before C-O bond breaking begins. In the first place the conditions appear much too mild to permit the formation of a benzyl carbanion. Secondly, the ρ -value for the reaction appears too small for a carbanionic mechanism. ρ -Values of as much as +4 have been observed for eliminations in the β -phenylethyl series and Szwarc has observed a ρ of +5 in a reaction in which benzyl carbanions seem surely to be involved.²⁴ A ρ of +2.8 hardly seems large enough for an E1_{CB} reaction.

The *cis* E2 reaction exhibits a kinetic isotope effect k_H/k_D of 5.6 at 50°. This isotope effect is close to the

(23) A statistical correction of two must be applied to the β -phenylethyl system since there are two protons available for removal.

(24) M. Shima, D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 1306 (1963).

Table IV. Hammett Correlations of Rates and Enthalpies and Entropies of Activation for the β -Elimination of *cis*- and *trans*-2-Arylcyclopentyl Tosylates

Compd.	E2 type	Base	Solvents	ρ , ^a at 50°	ΔH , kcal. mole ⁻¹	S, cal. mole ⁻¹ deg. ⁻¹
<i>trans</i> ^b	<i>cis</i>	0.1 <i>N t</i> -BuOK	<i>t</i> -BuOH	2.76 ± 0.04	17.6	-18.1
<i>trans</i> ^c	<i>cis</i>	0.1 <i>N t</i> -BuOK	<i>t</i> -BuOH	2.77 ± 0.03	17.6	-17.5
<i>trans</i> ^c	<i>cis</i>	0.3 <i>N t</i> -BuOK	<i>t</i> -BuOH	2.69 ± 0.05	16.4	-21.5
<i>cis</i> ^c	<i>trans</i>	0.1 <i>N t</i> -BuOK	<i>t</i> -BuOH	1.48 ± 0.09	15.1	-21.7
<i>cis</i> ^c	<i>trans</i>	0.2 <i>N</i> EtONa	EtOH	0.99 ± 0.06		
β -Phenylethyl	<i>trans</i>	0.1 <i>N t</i> -BuOK	<i>t</i> -BuOH	3.39 ± 0.29 ^d	14.7	-25.2
β -Phenylethyl	<i>trans</i>	0.1 <i>N</i> EtONa	EtOH	2.27 ± 0.08	20.4	-11.2

^a Calculated by the method of least squares. ^b Calculated from bimolecular rates determined titrimetrically. ^c Calculated from pseudo-first-order rates determined spectrophotometrically. ^d From ref. 13.

Table V. Rate Constants for Elimination from *cis*-2-Arylcyclopentyl Tosylates in Sodium Ethoxide-Ethanol Solution at 50°

Y	E2 type	$k_{E2} \times 10^4$, ^a l. mole ⁻¹ sec. ⁻¹
<i>p</i> -CH ₃	<i>trans</i>	19.3
H	<i>trans</i>	24.2
<i>p</i> -Cl	<i>trans</i>	47.5
<i>m</i> -Cl	<i>trans</i>	62.8
β -Phenylethyl	<i>trans</i>	3.8 ^b

^a Calculated from pseudo-first-order rates followed spectrophotometrically. ^b Calculated from the data of ref. 13.

theoretical maximum at that temperature.²⁵ If a carbanion were involved one might expect a lower value since the proton would be substantially completely transferred to the alkoxide, and O-H bond making would compensate for C-H bond breaking.²⁶

Finally we must consider why *cis* elimination is possible in the cyclopentyl system and not in the cyclohexyl. Steric effects do not seem responsible since in both *cis* and *trans* eliminations the hydrogen being attacked by the base is an axial one. If the *cis* E2 reaction proceeds through a carbanionic intermediate there seems no reason why there should be such large differences in rate between five- and six-membered rings. It seems reasonable to assume that there is a conformational preference involved for *cis* eliminations as well as for *trans*. The most reasonable assumption would seem to be that *cis* coplanar eliminations are most favorable.

Experimental²⁷

1-Arylcyclopentenes. The 1-arylcyclopentenes were prepared from the corresponding Grignard reagents and cyclopentanone followed by an acid-catalyzed dehydration of the 1-arylcyclopentanol. A 0.5 *M* Grignard reagent was prepared under an anhydrous nitrogen atmosphere in the usual way and cyclopentanone was added. After acidification and extraction the ether

(25) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(26) Deuterium isotope effects may, however, be quite ambiguous: see F. Westheimer, *ibid.*, **61**, 265 (1961); K. B. Wiberg and E. L. Motell, *Tetrahedron*, **19**, 2009 (1963).

(27) Melting and boiling points are uncorrected. Analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich. Gas chromatographic analyses were performed on a Perkin-Elmer Model 154D instrument. Ultraviolet spectra were determined on a Beckman DK-2A spectrophotometer. We are grateful to the National Science Foundation for a grant to the Chemistry Department for the purchase of this instrument.

was replaced by benzene, 1 g. of *p*-toluenesulfonic acid was added, and the solution was heated at reflux for 2 hr. The benzene solution was washed with sodium bicarbonate solution and with water and dried, and the solvent was removed. The 1-arylcyclopentenes were purified by distillation and obtained in 60–80% yield. 1-Phenylcyclopentene had b.p. 27° (0.6 mm.), lit.¹⁹ 118° (25 mm.); 1-(*p*-methylphenyl)cyclopentene had b.p. 76° (0.6 mm.); 1-(*p*-chlorophenyl)cyclopentene had b.p. 85° (0.6 mm.); and 1-(*m*-chlorophenyl)cyclopentene had b.p. 81° (0.6 mm.).

***trans*-2-Arylcyclopentanol.** These alcohols were prepared by hydroboration and oxidation using Brown's procedure.²⁸ Under a dry nitrogen atmosphere 0.05 mole of sodium borohydride was dissolved in 45 ml. of diglyme (bis(2-methoxyethyl) ether) with 0.04 mole of the proper 1-arylcyclopentene. After cooling to 0°, 0.075 mole of boron trifluoride etherate in 10 ml. of diglyme was added and the reaction was stirred for 12 hr. at room temperature. The solution was again cooled to 0° and 15 ml. of water was added cautiously. Sodium hydroxide (40 ml. of a 10% solution) was added rapidly and then 30 ml. of a 30% hydrogen peroxide solution was added dropwise. Stirring was continued for 6 hr., during which time the reaction mixture was allowed to warm to room temperature. Working up in the usual way gave, after distillation, *trans*-2-arylcyclopentanol in yields of 60–80%. *trans*-2-Phenylcyclopentanol had b.p. 80° (0.2 mm.), lit.¹⁸ 110–113° (2 mm.); *trans*-2-(*p*-methylphenyl)cyclopentanol had b.p. 90° (0.2 mm.); *trans*-2-(*p*-chlorophenyl)cyclopentanol had b.p. 110° (0.2 mm.); and *trans*-2-(*m*-chlorophenyl)cyclopentanol had b.p. 106° (0.2 mm.).

***trans*-2-Deuterio-2-phenylcyclopentanol.** This was prepared by a modification of Sondheimer's procedure²⁹ for hydroboration. Lithium aluminum deuteride (1 g., 0.024 mole) was dissolved in a solution of 40 ml. of anhydrous ether containing 0.071 mole of 1-phenylcyclopentene. After this mixture was stirred at room temperature for 4 hr. it was cooled to 0° and a solution of 0.048 mole of boron trifluoride etherate in 80 ml. of ether was added cautiously. The reaction mixture was stirred at room temperature for 24 hr. and cooled again to 0°, and 10 ml. of a saturated sodium sulfate solution was slowly added. Anhydrous sodium sulfate (5 g.) was added and the mixture was stirred vigorously and then filtered into 50 ml. of tetrahydrofuran which had

(28) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

(29) S. Wolfe, M. Nussin, Y. Mazeir, and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959); F. Sondheimer and M. Nussin, *ibid.*, **26**, 630 (1961).

been freshly distilled from lithium aluminum hydride. The ether was removed by distillation until the distillate temperature reached 55°. The tetrahydrofuran solution was made basic with 25 ml. of a 10% sodium hydroxide solution and oxidized at 0° by the slow addition of 15 ml. of 30% hydrogen peroxide. After stirring at room temperature for 6 hr. the reaction was worked up in the usual way to give, after distillation, *trans*-2-deuterio-2-phenylcyclopentanol, b.p. 80° (0.2 mm.). Its n.m.r. spectrum indicated that it was greater than 95% deuterated in the 2-position.

2-Phenylcyclopentanone. A solution of 2-chlorocyclopentanone³⁰ (35 g., 0.30 mole) in 400 ml. of dry ether was added to a well stirred, ice-cold solution of phenylmagnesium bromide, prepared from 8.5 g. of magnesium and 55 g. of bromobenzene in 700 ml. of dry ether. The ether was removed by distillation and replaced by 150 ml. of dry xylene. The dark red reaction mixture was heated at 150–170° for 2 hr., cooled, treated with ice and dilute hydrochloric acid, and extracted with benzene. After washing with dilute sodium bicarbonate and water and drying, the solvent was removed and the product was recovered by distillation. 2-Phenylcyclopentanone distilled at 140° (10 mm., 29% yield). Recrystallization from petroleum ether (b.p. 60–80°) gave 22 g. of crystalline ketone, m.p. 35–36° (lit.¹⁹ m.p. 35–36°). It was stored under nitrogen in the cold.

***cis*-2-Phenylcyclopentanol.** 2-Phenylcyclopentanone (10 g.) in 100 ml. of absolute ethanol was reduced at room temperature and a slight pressure of hydrogen using freshly prepared W-2 Raney nickel as catalyst. After 4 hr. the theoretical amount of hydrogen had been absorbed. Gas chromatographic analysis showed the product to be a mixture of 79% *cis*- and 21% *trans*-2-phenylcyclopentanol. The residues from two such reductions were combined and distilled through a 30-in. spinning-band column at reduced pressure to give pure *cis*-2-phenylcyclopentanol, b.p. 63–63.7° (0.1 mm.), n_D^{25} 1.5444. It was free from the *trans* isomer as determined by gas chromatography. *Anal.* Calcd. for C₁₁H₁₄O: C, 81.41; H, 8.64. Found: C, 81.28; H, 8.33.

3-Chlorocyclopentene. Freshly distilled cyclopentadiene (188 g.) was cooled to –15° and anhydrous hydrogen chloride was bubbled through the diene as fast as possible without loss of hydrogen chloride or rise in temperature. The addition was stopped as soon as any color developed in the solution. The solution was warmed slightly while dry nitrogen was bubbled through the solution to remove any excess hydrogen chloride. Last traces of HCl were removed under vacuum. The product could be distilled, b.p. 37° (37 mm.), lit.²¹ b.p. 27–29° (20 mm.), but it was better used without distillation.

3-Arylcyclopentenes. 3-Chlorocyclopentene was diluted with an equal volume of dry ether and added dropwise to an equimolar amount of the appropriate aryl Grignard reagents. The reaction was carried out at 0° and the resulting solution was stirred for 1 hr. after addition was complete and then poured onto ice and acidified with 10% hydrochloric acid. After working up in the usual way, the ether was removed and the

residual olefins were run through a 100 × 40 mm. column of silica gel using chloroform as a solvent and eluent. The chloroform was removed and the products were vacuum distilled to give 3-arylcyclopentenes in yields of 70–80%. They were uncontaminated with 1-arylcyclopentenes as shown by g.p.c. analysis. 3-Phenylcyclopentene had b.p. 50° (2 mm.), lit.²² 94° (15 mm.); 3-(*p*-methylphenyl)cyclopentene had b.p. 71° (2 mm.); 3-(*p*-chlorophenyl)cyclopentene had b.p. 84° (2 mm.); and 3-(*m*-chlorophenyl)cyclopentene had b.p. 84° (2 mm.).

***cis*-2-Arylcyclopentanol.** *cis*-2-Arylcyclopentanol were prepared from the 3-arylcyclopentenes by epoxidation with monoperoxyphthalic acid in ether followed by lithium aluminum hydride reduction of the 3-arylcyclopentene oxides in refluxing tetrahydrofuran. This procedure yielded a mixture of alcohols (*cis*- and *trans*-2 and *cis*- and *trans*-3) which were separated on a spinning-band distillation column. The distillation was monitored by g.p.c. using a 1-m. Ucon LB550X (1:4) on 60/80 mesh Chromosorb at a temperature of 150–170°. The properties of the *cis* alcohols are: *cis*-2-phenylcyclopentanol, b.p. 65° (0.15 mm.); *cis*-2-(4-methylphenyl)cyclopentanol, b.p. 74–75° (0.1 mm.); *cis*-2-(4-chlorophenyl)cyclopentanol, b.p. 85° (0.2 mm.); and *cis*-2-(3-chlorophenyl)cyclopentanol, b.p. 90–91° (0.1 mm.). The n.m.r. spectrum of each alcohol was consistent with the structure.

***trans*-2-Phenylcyclohexanol.** To a solution of phenyllithium (from 0.2 mole of bromobenzene and 0.44 g.-atom of lithium in 400 ml. of anhydrous ether) was added 19.6 g. (0.2 mole) of cyclohexene oxide (Arapahoe Chemical Co.) at 0°. The solution was warmed to room temperature, followed by a 3-hr. reflux period, and allowed to stand overnight. Addition of 100 ml. of water, separation of the ether layer, drying over anhydrous magnesium sulfate, and solvent removal and distillation yielded 22.3 g. (69%) of *trans*-2-phenylcyclohexanol, b.p. 148–150° (20 mm.). The distillate solidified and was recrystallized from hexane, m.p. 56.5–57.5° (lit.³¹ m.p. 56–57°).

***trans*-2-Phenylcyclohexyl *p*-Toluenesulfonate.** This tosylate was prepared by Tipson's³² procedure and recrystallized from hexane or ether-chloroform, m.p. 134.5–135° (lit.¹⁷ m.p. 130–131°).

***cis*-2-Phenylcyclohexyl *p*-Toluenesulfonate.** A mixture of *cis*- and *trans*-2-phenylcyclohexanols (11.0 g., 0.063 mole; K & K Laboratories) was dissolved in 100 ml. of pyridine and cooled to 0°. To this solution was added 19 g. (0.1 mole) of *p*-toluenesulfonyl chloride and the solution was kept at –10° for 3 days. The mixture (containing solid pyridinium chloride) was poured into ice water. Crystallization occurred and the mixture was filtered. The crystals were washed with ice water and ice-cold dilute hydrochloric acid and air dried. The gummy crystals were washed again with ether and the remaining solid was found to be almost pure *trans*-2-phenylcyclohexyl *p*-toluenesulfonate, m.p. 129–132°.

Evaporation of the ether washings left an oily crystalline mass which was a mixture of the alcohols and tosylates.

(31) J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936).

(32) R. S. Tipson, *J. Org. Chem.*, 9, 235 (1944).

(30) H. W. Wanzlick, G. Gollmer, and H. Miiz, *Ber.*, 88, 69 (1955).

The original aqueous layer contained an oily film on the surface which subsequently crystallized. Filtration yielded 1.5 g. of *cis*-2-phenylcyclohexanol, m.p. 41–44°. This was again subjected to the tosylation reaction at room temperature for several days. The usual work-up yielded white crystals which were recrystallized from ether–chloroform to yield *ca.* 2 g. of *cis*-2-phenylcyclohexyl *p*-toluenesulfonate, m.p. 100–100.5° dec. (lit.¹⁷ m.p. 102°). Further crystallizations did not change the melting point.

Subsequent work (kinetics) showed that this *cis*-2-phenylcyclohexyl *p*-toluenesulfonate was contaminated with 17% of the *trans* isomer.

cis- and *trans*-2-Arylcyclopentyl Tosylates. These tosylates were prepared by Tipson's procedure,³² recrystallized five times from an ether–pentane mixture, and dried *in vacuo* at room temperature for 8 to 12 hr. before being used for kinetic runs.

trans-2-Phenylcyclopentyl *p*-toluenesulfonate had m.p. 68–69°. *Anal.* Calcd. for C₁₈H₂₀O₃S: C, 68.32; H, 6.37; S, 10.14. Found: C, 68.39; H, 6.31; S, 10.11.

trans-2-Deuterio-2-phenylcyclopentyl *p*-toluenesulfonate showed m.p. 68–69°.

trans-2-(3-Chlorophenyl)cyclopentyl *p*-toluenesulfonate had m.p. 55–56°. *Anal.* Calcd. for C₁₈H₁₉ClO₃S: C, 61.61; H, 5.46. Found: C, 61.23; H, 5.35.

trans-2-(4-Chlorophenyl)cyclopentyl *p*-toluenesulfonate showed m.p. 92–93°. *Anal.* Calcd. for C₁₈H₁₉ClO₃S: C, 61.61; H, 5.46. Found: C, 61.50; H, 5.42.

trans-2-(4-Methylphenyl)cyclopentyl *p*-toluenesulfonate had m.p. 88–89°. *Anal.* Calcd. for C₁₉H₂₂O₃S: C, 69.06; H, 6.71. Found: C, 68.68; H, 6.67.

cis-2-Phenylcyclopentyl *p*-toluenesulfonate had m.p. 97–98°. *Anal.* Calcd. for C₁₈H₂₀O₃S: C, 68.32; H, 6.37; S, 10.14. Found: C, 68.18; H, 6.25; S, 9.97.

cis-2-(3-Chlorophenyl)cyclopentyl *p*-toluenesulfonate showed m.p. 81–82°. *Anal.* Calcd. for C₁₈H₁₉ClO₃S: C, 61.61; H, 5.46. Found: C, 61.81; H, 5.68.

cis-2-(4-Chlorophenyl) *p*-toluenesulfonate had m.p. 108°. *Anal.* Calcd. for C₁₈H₁₉ClO₃S: C, 61.61; H, 5.46. Found: C, 61.75; H, 5.44.

cis-2-(4-Methylphenyl)cyclopentyl *p*-toluenesulfonate showed m.p. 89–90°. *Anal.* Calcd. for C₂₀H₂₂O₃S: C, 69.06; H, 6.71. Found: C, 68.81; H, 6.70.

2-Phenylethyl *p*-toluenesulfonate had m.p. 38–39° (lit.⁶ m.p. 38.5–39°).

Anhydrous Ethanol. Absolute ethanol was distilled and the middle fraction was collected. Freshly cut sodium (5 g.) was treated with the ethanol and the middle fraction was collected from a second distillation. The method of Manske was employed to remove the last trace of water from the ethanol.³³ The center cut of the distillation from sodium ethoxide and diethyl phthalate was distilled again from sodium.

*Anhydrous *t*-Butyl Alcohol.* *t*-Butyl alcohol (Eastman Kodak White Label) was fractionally distilled, a sharp fraction being taken, b.p. 83° (1 atm.). This sample was then distilled at least four times from clean metallic sodium under anhydrous conditions with only the

(33) R. H. Manske, *J. Am. Chem. Soc.*, **53**, 1106 (1931).

middle fraction being carried over to the next distillation. The metallic sodium (approximately 5 g./l. of *t*-butyl alcohol) was cleaned of all oxides and washed with pentane and warm *t*-butyl alcohol before being placed in the partially purified *t*-butyl alcohol. The all glass distillation apparatus was washed with 5% HF solution and water and dried at 110° before use. No grease was used on this apparatus.

*Potassium *t*-Butoxide.* Potassium metal was cut clean of all oxides and washed in pentane twice. This clean potassium was cut into 0.5-g. cubes and these were melted in hot *t*-butyl alcohol. After reacting approximately 30 sec. in the hot *t*-butyl alcohol the potassium "ball" was removed with a porcelain spoon and frozen in *t*-butyl alcohol at 25°. The "balls" of potassium metal were rinsed in purified *t*-butyl alcohol and placed in the pure, anhydrous *t*-butyl alcohol and allowed to dissolve under anhydrous conditions.

After most of these rate data were taken the following simplified procedure for purification of potassium metal was discovered. Rates obtained by the two methods are the same but reproducibility is better by the following procedure. The potassium metal was cut into small cubes and melted under purified heptane (washed with concentrated sulfuric acid, then water, and dried over anhydrous magnesium sulfate and distilled) at reflux temperature of the heptane. A nitrogen atmosphere was maintained during the entire operation. After the potassium had melted the mixture was gently agitated by hand swirling and then allowed to cool and the heptane (with impurities floating on the surface) was pipetted off. This procedure was repeated a total of three times. The potassium was placed in a small volume of purified *t*-butyl alcohol and allowed to react for a few seconds to remove surface impurities. It was immediately transferred to the sample of purified *t*-butyl alcohol and allowed to dissolve at 25–30°.

All solutions of potassium *t*-butoxide in *t*-butyl alcohol were protected by a drying tube containing Drierite and Ascarite to prevent entry of moisture and carbon dioxide vapors. Solutions prepared by either of these methods and protected as indicated remained clear and colorless for an indefinite time at temperatures between 20 and 50°.

Attempted Isomerization of Cyclopentenes. 3-Phenylcyclopentene (0.3108 g., 0.043 mole) was weighed into a 50-ml. volumetric flask and dissolved in 50 ml. of 0.1 *N* potassium *t*-butoxide in *t*-butyl alcohol and maintained at 50°. A 5-ml. aliquot was withdrawn at the beginning of the heating period and diluted with 95% ethanol, and its ultraviolet spectrum was determined. Another 5-ml. aliquot was withdrawn after 36 hr. and diluted with ethanol, and its ultraviolet spectrum was identical with that determined initially. 3-Phenylcyclopentene showed $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ 263 m μ (ϵ 432) and 1-phenylcyclopentene gave $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ 256.5 m μ (ϵ 14,700).

Ultraviolet Spectra of 1-Arylcyclopentenes. Molar extinction coefficients were determined in 95% ethanol as follows: 1-phenylcyclopentene, 14,710 (256.5 m μ); 1-(4-methylphenyl)cyclopentene, 17,820 (258.9 m μ); 1-(4-chlorophenyl)cyclopentene, 17,680³⁴ (261.3 m μ); and 1-(3-chlorophenyl)cyclopentene, 14,680 (259.5 m μ).

(34) This value is low. From infinity points the correct value can be estimated to be 20,000.

Second-Order Base-Catalyzed Elimination Reactions. A solution, 0.05 *M* in *p*-toluenesulfonate and approximately 0.1 *M* in base, was prepared in the following manner. The desired compound (0.0025 mole) was weighed accurately into a 50-ml. volumetric flask. After equilibration at the reaction temperature, it was diluted to the calibration mark of the volumetric flask with 0.1 *M* base also equilibrated at the same temperature. The flask was shaken until homogeneity was obtained. Kinetic runs were made at 30, 50, and 70°, and all solutions were equilibrated and pipetted at those temperatures.

The kinetics were measured by quenching a 5-ml. aliquot in 50 ml. of distilled water and titrating the excess base with standard hydrochloric acid. Infinity points were taken experimentally and checked well with calculated values. The base was standardized by this procedure at each reaction temperature.

All rates were second order and the integrated form of the second-order rate equation was applied to the data. Rates were calculated from each experimental point.

Pseudo-First-Order Base-Catalyzed Elimination Reactions. A solution, 0.005 *M* in desired compound and 0.1 or 0.3 *M* in base, was prepared in the following

manner. The proper *p*-toluenesulfonate (0.00025 mole) was weighed accurately into a 50-ml. volumetric flask and placed in the constant temperature bath. After equilibration of base at the reaction temperature, the volumetric flask was filled to the calibration mark and shaken until homogeneity was observed. The kinetics were followed by quenching a 5-ml. aliquot in 40 ml. of 95% ethanol in a 50-ml. volumetric flask. After diluting to the calibration mark and shaking, the solution was diluted 1:10 with 95% ethanol in a 50-ml. volumetric flask. The olefin concentration of this dilution was measured.

The pseudo-first-order rate constants were obtained from the measured absorbances by use of the following equation

$$k = \frac{2.303}{t} \log \frac{A_{\infty} - A_0}{A_{\infty} - A_t}$$

wherein A_{∞} is the measured infinity absorption after 10 or more half-lives, A_0 is the absorbance at $t = 0$, and A_t is the absorbance at time t . In each kinetic run at least eight points were determined and the rate constant is the numerical average of six or more points. In almost all cases, the runs were duplicated and errors listed are the standard deviation between runs.

Extraordinary Dipositive Carbonium Ions. A Re-examination of the Evidence for Their Formation in Sulfuric Acid¹

R. J. Gillespie² and E. A. Robinson

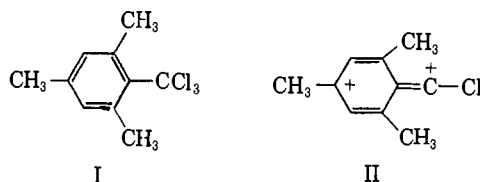
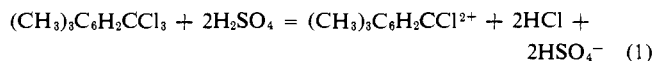
Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, and the Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada. Received January 29, 1965

Cryoscopic and conductometric studies of solutions of trichloromethylmesitylene and mesitoyl chloride in sulfuric acid show that in each case reaction occurs to give five particles in solution ($\nu = 5$), two of which are hydrogen sulfate ions ($\gamma = 2$). Conductometric titrations with dilute oleum and proton n.m.r. measurements have also been carried out for solutions of both solutes. The n.m.r. and ultraviolet spectra of solutions of mesitoyl chloride in sulfuric acid show that the mesitoyl cation is formed quantitatively. It is concluded that mesitoyl chloride and trichloromethylmesitylene react with sulfuric acid according to eq. 3 and 7. Thus trichloromethylmesitylene gives rise to a monopositive carbonium ion rather than a dipositive ion as has been claimed previously. The almost quantitative reaction of hydrogen chloride with sulfuric acid according to eq. 2 is confirmed by cryoscopic and conductometric measurements on dilute solutions of HCl in sulfuric acid.

(1) For a preliminary communication see R. J. Gillespie and E. A. Robinson, *J. Am. Chem. Soc.*, **86**, 5676 (1964).

(2) Department of Chemistry, McMaster University, Hamilton, Ontario.

Hart and Fish³⁻⁵ have presented evidence that trichloromethylmesitylene (I) ionizes in sulfuric acid with the formation of the dicarbonium ion II (eq. 1)



and that pentamethyltrichloromethylbenzene and trichloromethylprehnitene behave in a similar manner. They claim that all three compounds give a fivefold depression of the freezing point of sulfuric acid, that conductance measurements show the formation of two hydrogen sulfate ions from each molecule of solute,

(3) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **80**, 5894 (1958).

(4) H. Hart and R. W. Fish, *ibid.*, **82**, 5419 (1960).

(5) H. Hart and R. W. Fish, *ibid.*, **83**, 4460 (1961).