always less than 0.05, and coupling constants were accurate to ±0.05 Hz.[44]

(44) Edgell, *et al.*, have recently published an infrared study of a series of inorganic salts in THF which provide additional insight into the structure of ion pairs in solution: W. F. Edgell, J. Lyford, R. Wright, W. Risen, and A. Watts, *J. Amer. Chem. Soc.*, **92**, 2240 (1970).

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Chloride-Induced Elimination from 2-Phenylcyclopentyl, 2-Phenylcyclohexyl, and 2-Norbornyl Brosylates in Acetone

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Abstract: *cis*- and *trans*-2-phenylcyclopentyl and 2-phenylcyclohexyl *p*-bromobenzenesulfonates by reaction with *n*-Bu_4NCl in acetone give variable amounts of olefinic products. The cis isomers (fraction of elimination F_E = 0.81–0.99) show a preference for Saytzeff elimination to the extent of 99.7% 1-phenylcyclopentene and 99.5% 1-phenylcyclohexene. The trans isomers (F_E = 0.55–0.22) have a >90% preference for Hofmann products, 3-phenylcyclopentene and 3-phenylcyclohexene. The ratio k_{cis}/k_{trans} of second-order rate constants for elimination at 50° is 48 for cyclopentyl derivatives and 1140 for cyclohexyl derivatives. *exo*-2-Norbornyl *p*-bromobenzenesulfonate under the same conditions gives, besides *endo*- and *exo*-norbornyl chlorides, nortricyclene and norbornene (F_E = 0.70) with nortricyclene largely predominant. Kinetic measurements show that, while nortricylene and norbornene are formed in a 9:1 ratio in ionization processes, the halide-induced elimination gives them in the ratio 99.4:0.6. *endo*-2-Norbornyl *p*-bromobenzenesulfonate reacts with *n*-Bu_4NCl to give mainly *exo*-2-norbornyl chloride with no endo chloride and a small amount of elimination products (F_E = 0.05).

Several years ago it was discovered that halide ions in acetone are effective in promoting elimination reactions.[3] Since then, a number of papers on the subject have been published. The substrates investigated were alkyl tosylates, brosylates, and halides; while primary derivatives give little or no elimination,[4] and tertiary derivatives present fractions of elimination close or equal to unity,[4-6] secondary substrates are more flexible in giving a blend of substitution and elimination products.[3,4,7] The most useful solvent–salt system for the study of these reactions seems to be acetone containing tetra-*n*-butylammonium halides, although other salts and dipolar aprotic solvents have been used.[3,8]

An interpretation of the halide-induced elimination has been advanced that requires an interaction of the halide ion with both α-carbon and β-hydrogen atoms at the transition state (E2C-like transition state).[7,9] However, this suggestion has not been generally accepted,[5,6,10,11] and the whole question seems to be far from being solved.

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(3) S. Winstein, D. Darwish, and N. J. Holness, *J. Amer. Chem. Soc.*, **78**, 2915 (1956).
(4) S. Winstein, "Chimica teorica," Accademia naz. Lincei, Rome, 1965, p 327.
(5) J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, **35**, 76 (1970).
(6) D. J. McLennan and R. J. Wong, *Tetrahedron Lett.*, 881 (1970).
(7) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 115 (1970).
(8) R. A. Bartsch, *J. Org. Chem.*, **35**, 1023 (1970).
(9) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968).
(10) D. Eck and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 3099 (1969).
(11) See, however, D. Cook and A. J. Parker, *Tetrahedron Lett.*, 4901 (1969).

As a contribution to the understanding of the mechanism of this reaction, we present results obtained on 2-phenylcyclopentyl brosylates (I), 2-phenylcyclohexyl brosylates (II), and 2-norbornyl brosylates (III) reacting with *n*-Bu_4NCl in acetone.

Results

Rate coefficients k_{E+S} for the total reaction were obtained by adding the observed rates of chloride ion consumption and acid production. The ratio of acid produced to reacted substrate gave the fraction of elimination F_E. In some cases F_E was directly determined from product glc analysis. Rate coefficients k_E for elimination and k_S for substitution were calculated from the values of k_{E+S} and F_E. Results are given in Table I. Product analyses, by glc, gave the results summarized in Tables II and III.

Solvolyses, in the absence of chloride ion, were also studied, usually both in terms of rates and products. The results are gathered in Tables IV and V. An upward drift of first-order coefficients k_1 was observed during the kinetic runs of compounds *cis*-I, *cis*-II, and *trans*-II, which was attributed to salt effects. A positive salt effect was ascertained for *exo*-III, by working at different concentrations of *n*-Bu_4NClO_4. The intervention of solvolysis in the reaction with chloride ion was estimated by comparing k_1 values, corrected for salt effect, with the rates of bimolecular reactions, expressed as pseudo-first-order coefficients $k' = k_{E+S} \times$ average $[Cl^-]$. Considerable intervention of solvolysis was found only in the case of *exo*-2-norbornyl brosylate (see later).

***cis*- and *trans*-2-Phenylcyclopentyl Brosylates.** The cis isomer (*cis*-I) is the most reactive with *n*-Bu_4NCl of

Table I. Rates of Elimination (k_E) and Substitution (k_S) Reactions with n-Bu_4NCl in Acetone

Compound[a]	Temp, °C	10^2M salt	10^2F_E	10^4k_{E+S}, M^{-1} sec^{-1}	10^4k_S, M^{-1} sec^{-1}	10^4k_E, M^{-1} sec^{-1}
cis-2-Phenylcyclopentyl-OBs	15.0	3.34	80.6 ± 0.5	28.8 ± 0.4	5.6	23.2
(*cis*-I)	30.0	3.36	81.4 ± 1.1	165 ± 3	31	134
trans-2-Phenylcyclopentyl-OBs (*trans*-I)	49.6	3.41	55.2 ± 0.2[b]	40.8 ± 0.6	18.3	22.5
cis-2-Phenylcyclohexyl-OBs	20.0	3.55	96 ± 1	19.6 ± 0.4	0.8	18.8
(*cis*-II)	35.0	3.70	99.4 ± 0.3	112 ± 2	1	111
trans-2-Phenylcyclohexyl-OBs (*trans*-II)	50.0	3.14	21.7 ± 0.3[b]	2.18 ± 0.04	1.71	0.47
exo-2-Norbornyl-OBs	50.0	2.34	74.6 ± 1.0[c]	6.52	1.66	4.86
(*exo*-III)		6.47	69.4 ± 0.7	6.77	2.07	4.70
endo-2-Norbornyl-OBs (*endo*-III)	50.0	4	5[c]	1.63[d]	1.55	0.08

[a] OBs is *p*-bromobenzenesulfonate. Substrates are 0.016–0.020 *M*. Acetone contains 0.025–0.031 *M* 2,6-lutidine. [b] Extrapolated to zero time. [c] Determined by glc. [d] G. Biale, Ph.D. Thesis, University of California, Los Angeles, 1963.

Table II. Saytzeff *vs.* Hofmann Products from Bimolecular Elimination Reactions of I and II

Compd[a]	Temp, °C	10^2M n-Bu_4NCl	Elim products, %	No. of half-lives
cis-I	50.0	4.50	99.7 (IV); 0.3 (V)	17, 650, 2000
trans-I	50.0	3.92	17.8 (IV); 82.2 (V)	34
			19.7; 80.2	49
			23.9; 76.1	66
			32.7; 67.3	170
			44.6; 55.4	560
cis-II	20.0	3.55	99.5 (VI); 0.5 (VII)	20
	35.0	3.70	99.5; 0.5	15, 35
trans-II	50.0	3.14	59.7(VI); 40.3 (VII)	20
			70.2; 29.8	42

[a] Substrates are 0.016–0.021 *M*. Acetone contains 0.03 *M* 2,6-lutidine.

seems to be very little dependent on temperature. Calculated values of 10^4k_S and 10^4k_E at 50° are 250 and 1070, respectively. Glc analysis showed that 1-phenylcyclopentene (IV) is mainly produced together with a small amount of 3-phenylcyclopentene (V); IV and V were in the ratio 99.7:0.3 (Table II). A third peak, whose area was 21.5% of the total area, was also revealed. Retention times, at a column temperature of 175° and at a flow rate around 100 ml/min, were: V, 3.6 min; IV, 6.5 min; third peak, 12.2 min. While IV and V were identified by the use of authentic samples, the third peak was assumed to be the product of SN2 substitution, *i.e.*, *trans*-2-phenylcyclopentyl chloride. The nature of the products and their relative yields were independent of the length of the experiment (Table

Table III. Products of Reactions of *exo*-III and *endo*-III in the Presence of n-Bu_4NCl in Acetone at 50.0°

Compd[a]	10^2M n-Bu_4NCl	% of total reaction VIII	IX	*exo*-X	*endo*-X	10^2F_E (glc)	No. of half-lives
exo-III	2.34	2.5	72.1	2.2	23.2	74.6	10
	3.41	1.7	67.2	3.1	28.0	68.9	15, 22
	6.47	1.2	68.3	2.6	27.9	69.5	6, 14
	11.5	1.0	67.2	2.7	29.1	68.2	20
endo-III	3.15	1.7	3.8	94.5		5.5	6, 12
	10.5	1.8	2.2	96.0		4.0	6

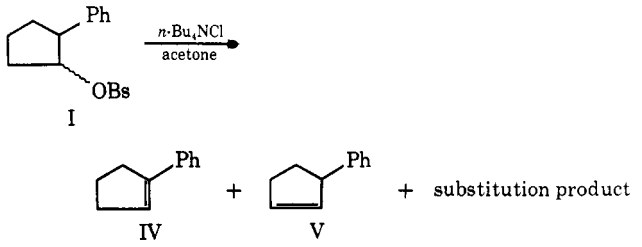
[a] Substrates are 0.02 *M*. Acetone contains 0.02–0.03 *M* 2,6-lutidine.

Table IV. Rates and Olefinic Products from Solvolysis of I and II in Acetone, in the Presence of n-Bu_4NClO_4

Compd[a]	Temp, °C	10^2M n-Bu_4NClO_4	10^6k_1, sec^{-1}	Olefinic products,[b] %
cis-I	50.0	3.80	1.88[c]	*d*
	75.0	3.26	*d*	91.0 (IV); 9.0 (V)
trans-I	50.0	3.82	0.937 ± 0.002	*d*
	75.0	3.76	1.70 ± 0.2	93.3 (IV); 6.7 (V)
cis-II	50.0	3.55	0.181[c]	*d*
trans-II	75.0	3.31	0.184[c]	*d*

[a] Substrates are 0.017–0.020 *M*. Acetone contains 0.027–0.030 *M* 2,6-lutidine. [b] The only products, apart from a few per cent of unknown impurities. [c] Initial rate. [d] Not determined.

all the compounds examined. From rate coefficients k_{E+S} at 15 and 30° (Table I) an apparent activation energy of 20.2 kcal mol^{-1} was obtained, and the rate coefficient at 50° was calculated to be 10^4k_{E+S} = 1320 M^{-1} sec^{-1}. The fraction of elimination is 0.81 and II). Solvolysis of *cis*-I accounts for less than 0.1% of the products.



The *trans*-I isomer is less reactive than *cis*-I both in substitution and in elimination, according to k_S and k_E values (Table I). The value of 0.552 for the fraction of elimination was estimated by extrapolation to time zero, because F_E varied with time due to a secondary reaction, probably elimination from the substitution product. Disregarding the correction for the secondary reaction and averaging F_E values along the

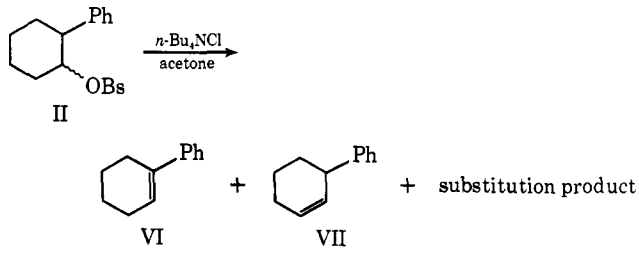
Table V. Rates and Products from Solvolysis of *exo*-III and of *endo*-III in Acetone at 50.0°

Compd[a]	Salt	$10^2 M$ salt	$10^6 k_1$, sec^{-1}	% of total reaction VIII	IX	Other products
exo-III			3.0 ± 0.3[b]	7.4	69.6	23.0 (*exo*-XI)
	n-Bu_4NClO_4	4.55	4.4 ± 0.3	7.2	69.4	*c*
		8.15	5.3 ± 0.2	7.3	69.5	*c*
endo-III			0.13 ± 0.01	1.9[d]	76.1[d]	*c*

[a] Substrates are 0.01–0.02 *M*. Acetone contains 0.02–0.03 *M* 2,6-lutidine. [b] Under the same conditions, the first-order polarimetric rate coefficient, k_α, is 27×10^{-6} sec^{-1}. [c] Not determined. [d] At 100°.

run, a value of 0.558 was obtained. Olefinic products were IV and V, only the former markedly increasing with time. A third peak with a retention time of 17.2 min was observed; its area amounted to 34.2% of the total area at 34 half-lives and decreased to 3.1% at 560 half-lives. At this time, a fourth peak (1.4% of the total area) with the retention time previously attributed to *trans*-2-phenylcyclopentyl chloride was observed. The third peak was assumed to correspond to *cis*-2-phenylcyclopentyl chloride; its disappearance roughly accounts for the increasing amount of olefin IV, which changes the ratio IV:V as shown in Table II. Calculations based on the corrected F_E value gave an approximate ratio IV:V = 9:91 for the original olefinic product from *trans*-I. Solvolysis of *trans*-I accounts for <0.8% of the products.

***cis*- and *trans*-2-Phenylcyclohexyl Brosylates.** Isomer *cis*-II was kinetically studied at 20 and 35°; an apparent activation energy of 20.9 kcal mol^{-1} was obtained from the rate coefficients k_{E+S}. The value of $10^4 k_{E+S}$ at 50° was calculated to be 548 M^{-1} sec^{-1}. After taking into account the gas-chromatographic results the difference between the F_E values at 20 and 35° (Table I) was not considered significant, so an average value of 0.977 was taken. Values of $10^4 k_S$ and $10^4 k_E$ at 50° equal to 13 and 535 M^{-1} sec^{-1}, respectively, were calculated. By glc analysis 1-phenylcyclohexene (VI) and 3-phenylcyclohexene (VII) were identified as products on the basis of their retention times,[12] and found to be in a ratio VI:VII = 99.5:0.5. A third peak, having an area 1.0–1.7% of the total, was thought to correspond to *trans*-2-phenylcyclohexyl chloride. Retention times under the standard conditions were: VII, 6.0 min; VI, 9.2 min; third



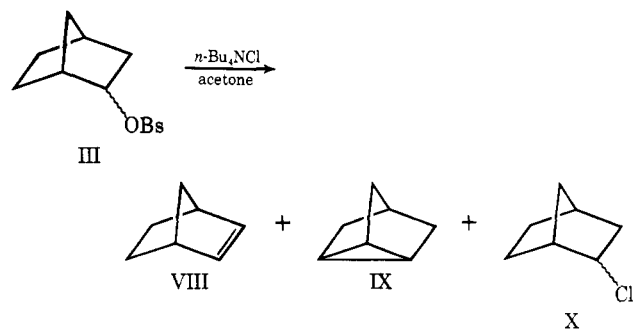
peak, 20.5 min. All products were found to be stable. Solvolysis was negligible (<0.02%).

trans-II is less reactive than the corresponding cis isomer. Dissection of k_{E+S} into k_S and k_E values was made using a value of F_E (0.217) extrapolated to time zero for the same reason as for the cyclopentyl derivative. The uncorrected mean value was F_E = 0.236. Peaks observed during glc analysis were those of olefins VI and VII together with a third one (retention time 24.5 min under standard conditions) assumed to correspond to *cis*-2-phenylcyclohexyl chloride. The amount of the latter decreased with time, while olefin VI increased. Using the corrected F_E value, calculations give an approximate ratio VI:VII = 8:92 for the original mixture of olefins from *trans*-II. The intervention of solvolysis can account for no more than 0.2% of the products.

***exo*- and *endo*-2-Norbornyl Brosylates.** Compound *exo*-III is more reactive than epimer *endo*-III toward *n*-Bu_4NCl, as shown by k_{E+S} values (Table I). Fractions of elimination are remarkably different in the two cases, being F_E = 0.70 for the exo and *ca.* 0.05 for the endo isomer. From Tables I and III it appears that F_E values decrease slightly with increasing concentration of chloride ion.

The reaction of *exo*-III, followed by glc analysis, gave the following products, identified by comparison with authentic samples: norbornene (VIII), nortricyclene (IX), and the endo and exo epimers of 2-norbornyl chloride (X). With decane as internal standard, the observed retention times were: decane, 21.5 min; *exo*-X, 75 min; *endo*-X, 79 min. Control experiments showed that when *exo*-X is kept at 75° for 48 hr in the presence of a threefold excess of *n*-Bu_4NCl and of 2,6-lutidine, neither elimination nor substitution products are detectable. Also, the other products were stable under the reaction conditions. Quantitative analysis (Table III) showed that the sum of IX and *endo*-X accounts for 95–96% of the initial substrate and that the relative amounts do not change much with chloride ion concentration. On the other hand, the percentage of norbornene is small and sensitive to changes in *n*-Bu_4NCl concentration.

The reaction of *endo*-III was found to give *exo*-X as the predominant product, plus VIII and IX in small amounts. No *endo*-X was observed; it was established that 0.5% of *endo*-X could have been detected in the presence of 99.5% of *exo*-X.



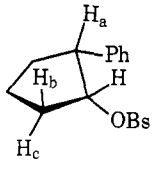
In the run of *endo*-III *n*-Bu_4NCl (Table I), solvolysis intervenes to the extent of *ca.* 2.7% as expressed by the ratio of first-order coefficients k_1/k'. Reaction

(12) L. S. McNamara and C. C. Price, *J. Org. Chem.*, 27, 1230 (1962).

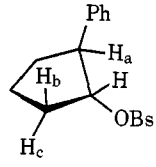
of *exo*-III with chloride ion is accompanied by the following extents of solvolysis, depending on chloride ion concentration: k_1/k' is equal to 0.29 at 2.34×10^{-2} *M* initial salt concentration, and to 0.12 at 6.47×10^{-2} *M*. Solvolysis products were examined in detail for a run of *exo*-III without salt addition (Table V), and found to be the elimination products VIII and IX, besides *exo*-2-norbornyl alcohol (XI). No endo-XI was found, while control experiments showed that 0.2–0.3% could have been detected. In the other runs the difference from 100 of the sum of the percentages of VIII and IX is almost the same (Table V), and probably is to be attributed to the presence of the same by-product. Formation of *exo*-XI is attributed to the presence of water which originates from self-condensation of acetone. Control experiments have confirmed that at 50° lutidinium brosylate catalyzes the condensation of acetone to give some mesityl oxide, thereby indicating the formation of water.

Discussion

Solvolytic reactions of compounds I and II are of negligible importance under the conditions of the halide-induced elimination; therefore, reaction products can be considered as coming entirely from the second-order processes. In *cis*-I the brosylate group is trans to both phenyl-activated H_a and nonactivated H_b hydrogens; H_aOBs is eliminated with a 99.7% preference to give the most stable (Saytzeff) olefin, in agreement with previous observations about halide-induced eliminations.[4,7] For the *trans*-I isomer the competition is between anti elimination of H_bOBs and syn elimination of H_aOBs, neglecting the syn elimination of H_cOBs; the predominance of 3-phenylcyclopentene (Hofmann olefin) over 1-phenylcyclopentene by approximately 91:9 shows that an anti nonactivated elimination is preferred to a syn activated one.



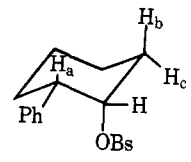
cis-I



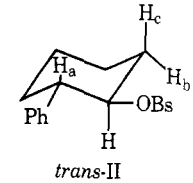
trans-I

Rate coefficients for the formation of olefins IV and V by independent parallel paths can be obtained by dissecting k_E values with the aid of the above olefin ratios. The following values of k_S, k_E^{IV}, and k_E^{V} at 50° are thus available (in M^{-1} sec^{-1}): for *cis*-I, $10^4k_S = 250$, $10^4k_E^{IV} = 1067$, $10^4k_E^{V} = 3$; for *trans*-I, $10^4k_S = 18.3$, $10^4k_E^{IV} = 2.0$, $10^4k_E^{V} = 20.5$. Elimination of the phenyl-activated H_a is therefore 1067/2.0 = 534 times faster when the process is anti than when it is syn. This ratio can be compared with the results obtained by DePuy, *et al.*,[13] on the reaction of 2-phenylcyclopentyl tosylates with *tert*-butoxide ion in *tert*-BuOH, where the activated anti elimination was faster than the syn by a factor of only 14. Since the preference for anti elimination observed with chloride ion is much higher than that observed with *tert*-butoxide ion, and since chloride ion in acetone is a good nucleophile toward saturated carbon, then a possible explanation of this result is the existence of an E2C-like transition state for the halide-induced elimination. In fact, in *cis*-I the chloride ion approaching H_a could also interact with the α-carbon from the opposite side of the leaving OBs group, while in *trans*-I such an interaction would be possible only from the same side of the leaving group, and therefore be unfavorable.

The structure of cyclohexyl derivatives II is obviously affected by the conformational free-energy differences between equatorial and axial positions for Ph and OBs substituents. On the basis of literature data,[14] isomer *cis*-II may be calculated to have 98% of that conformer having an equatorial phenyl group, while *trans*-II should have 99.8% of the conformer with both groups in the equatorial position, at equilibrium.



cis-II (preferred conformation)



trans-II (preferred conformation)

Eliminations of H_aOBs and H_bOBs from *cis*-II are both anti diaxial processes (anti-aa). The former has a 99.5% preference since H_a is an activated hydrogen. The *trans*-II isomer can eliminate either H_bOBs by an anti diequatorial (anti-ee) process or H_aOBs by a syn-ae elimination (the possibility that the Hofmann olefin is produced by syn-ae elimination of H_cOBs is disregarded). The ratio 92:8 of 3-phenylcyclohexene to 1-phenylcyclohexene in the kinetically controlled product shows that the anti-ee elimination involving a nonactivated hydrogen is preferred over the syn-ae process with the activated H_a.

Dissection of k_E values gave the following values of k_S, k_E^{VI}, and k_E^{VII} at 50° (in M^{-1} sec^{-1}): for *cis*-II, $10^4k_S = 13$, $10^4k_E^{VI} = 532$, $10^4k_E^{VII} = 3$; for *trans*-II, $10^4k_S = 1.71$, $10^4k_E^{VI} = 0.04$, $10^4k_E^{VII} = 0.43$. Elimination of the activated H_a is $532/0.04 = 1.3 \times 10^4$ times faster for the anti-aa process than for the syn-ae. A similar result was obtained in the kinetic study of the chloride-induced elimination of menthyl and neomenthyl tosylates in acetone, where elimination involving the same tertiary hydrogen is more than 22,500 times faster in an anti-aa than in a syn-ae process.[7]

In the case of 2-phenylcyclohexyl tosylates the reaction of the trans isomer with strong bases in alcoholic solvents was found to be immeasurably slow[13,15] and the ratio k_{cis}/k_{trans} at 50° was estimated to be $>10^4$. Therefore, the formation of the most stable olefin by a coplanar anti-aa process is enormously easier than by a syn process, independent of the base–solvent system, in the examples given. However, the reactivity ratio is much lower for 2-phenylcyclohexyldimethylsulfonium and trimethylammonium substrates.[15]

A comparison of k_E^{VII} values for *cis*-II and *trans*-II indicates that the elimination involving the nonacti-

(13) C. H. DePuy, R. D. Thurn, and G. F. Morris, *J. Amer. Chem. Soc.*, **84**, 1314 (1962); C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *ibid.*, **87**, 2421 (1965).

(14) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 44.

(15) S. J. Cristol and F. R. Stermitz, *J. Amer. Chem. Soc.*, **82**, 4692 (1960).

vated hydrogen H_b is seven times faster from the cis than from the trans isomer. The reactivity ratio is about the opposite of that found for the cyclopentyl derivatives (k_E^V coefficients) and represents the stronger tendency for anti-aa than for anti-ee elimination. In the case of menthyl and neomenthyl tosylates[7] the analogous ratio was 13.

Nucleophilic substitution is about 14 times faster for *cis*-I than for *trans*-I, while the analogous ratio is about 8 in the case of compounds II. Both the higher stability of ground states and the greater crowding of transition states for trans isomers may be responsible for these findings.

Ionization processes must be carefully taken into account when the reactions of compound *exo*-III are considered. Nortricyclene, *i.e.*, the product of 1,3 elimination, exceeds norbornene by a 90:10 ratio in the solvolysis in acetone (Table V). The prevalence of nortricyclene over norbornene is a common feature for the elimination products from solvolysis of *exo*-2-norbornyl brosylate and tosylate both in hydroxylic and in dipolar aprotic solvents; a nortricyclene to norbornene ratio of 98:2 was found in the acetolysis of *exo*-III,[16] and similar values have been obtained by us in the following solvents at 50°: acetonitrile, 95:5; dimethylformamide, 90:10; pyridine, 84:16. Similar observations have been made for the reaction of *exo*-2-norbornyl tosylate with K^+*tert*-BuO^- in *tert*-BuOH under E1 conditions.[17] The great tendency for the elimination product to be nortricyclene instead of norbornene is, among others, an indication that a nonclassical structure is preferred by norbornyl cation since the bridged ion is structurally related to nortricyclene.

On the other hand, norbornene is the prevalent product in E2 eliminations of *exo*-2-norbornyl sulfonates and bromide with strong bases.[17,18] However, this does not seem to be the case for the chloride-induced elimination of *exo*-III in acetone. When considering the reactions of *exo*-III in the presence of *n*-Bu_4NCl, the detailed product analysis (Table III) allowed the dissection of k_{E+S} into four terms, corresponding to the formation of *endo*- and *exo*-2-norbornyl chlorides, of nortricyclene, and of norbornene, in the overall reaction. This has been done for each value of the initial chloride concentration, and the second-order rate coefficients of the eliminations were converted into pseudo-first-order coefficients by using the average chloride ion concentration of each run. Rate coefficients of solvolysis, corrected for salt effect, were similarly divided into terms corresponding to formation of VIII and IX from the product analysis given in Table V. By difference, pseudo-first-order rate coefficients for the pure bimolecular elimination were obtained and finally converted into second-order rate coefficients k_E^{VIII} and k_E^{IX}. Values substantially independent of initial chloride concentration were obtained; on the average $10^4 k_E^{VIII} = 0.023$ and $10^4 k_E^{IX} = 3.77$ M^{-1} sec^{-1} at 50°. According to this calculation, the chloride-induced 1,3 elimination to give nortricyclene prevails over the β elimination to produce norbornene in the ratio 99.4:0.6.

A further result of the previous calculation is that, under the conditions of the runs, norbornene derives predominantly from an unassisted E1 path (81% at 2.34×10^{-2} M *n*-Bu_4NCl), whereas the formation of nortricyclene occurs mainly through the chloride-induced process (73% at the same salt concentration). As the chloride ion concentration increases, bimolecular processes are favored over solvolysis and this explains why the fraction of VIII in the product becomes increasingly smaller and the value of F_E slightly decreases.

It remains somewhat obscure why chloride ion should exhibit such a high preference for hydrogen in position 6 instead of position 3 as expressed by the ratio $k_E^{IX}:k_E^{VIII}$ in the bimolecular elimination. Most likely initial ionization of the substrate plays a significant role even in the chloride-induced process. *exo*-III ionizes very readily in acetone; in the absence of salt the polarimetric rate coefficient, k_α, exceeds the titrimetric coefficient, k_1, by a factor of 9. If preliminary ionization of the substrate to a bridged ion occurs, attack by chloride ion involves partially or fully developed charged species, and the product tends to be nortricyclene instead of norbornene, by analogy with the E1 process.

endo-III solvolyzes more slowly than *exo*-III; k_1(exo)/k_1(endo) = 23 at 50° so that ionization is less important for this epimer with respect to bimolecular processes. Only 5% of the initial substrate undergoes an elimination reaction; the rest of the product is *exo*-2-norbornyl chloride which is formed mainly by direct displacement. A comparison of the rates of nucleophilic substitution for *endo*-III and *exo*-III, to give the products of inverted configuration, shows that attack from the exo side occurs at nearly the same rate as from the endo side. The small amount of *exo*-X produced from *exo*-III is to be attributed to the ionization path.

Elimination from *exo*-2-norbornyl brosylate shows that a second-order reaction very "E1 like" is possible also in the field of halide-induced eliminations.

Experimental Section

Materials. Acetone was dried, 2,6-lutidine purified, and dry *n*-Bu_4NCl prepared according to standard procedures. Brosylates were obtained from the corresponding alcohols in the usual way;[19] their melting points were: *cis*-I, 80.5–82.5° dec; *trans*-I, 111–113° dec; *cis*-II, 103.5–105° dec; *trans*-II, 130–132° dec; *exo*-III, 54.5–55° (lit.[19] 55.7–57°); *endo*-III 61° (lit.[19] 60–61.7°). *cis*-2-Phenylcyclohexanol was prepared by hydrogenation of *o*-phenylphenol in the presence of Ni Raney and NaOH, and purified through its 3,5-dinitrobenzoate: mp 44–45° (from pentane) (lit.[20] 42–44°). Other alcohols were available.

Kinetic Measurements. Runs at temperatures $\leq 35°$ were carried out by the aliquots procedure and those at higher temperature by the sealed ampoules technique. Acid was determined by pouring the sample in cold acetone (compounds I and II) or in pyridine (compounds III) and quickly titrating with sodium methoxide in methanol. *p*-Hydroxyazobenzene and Thymol Blue were used as indicators. For reactions with *n*-Bu_4NCl a second sample was poured into pentane and extracted with water; the aqueous extracts were titrated for chloride ion by the Volhard method.

Average values of first-order (k_1) and second-order (k_{E+S}) rate coefficients, obtained from the integrated rate laws, are given in Tables I–V, together with the average deviations from the mean.

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Stoichiometric concentration of n-Bu_4NCl was used, without allowance for incomplete dissociation.

Product Analysis. Reaction mixtures were extracted with pentane, and the pentane layer was washed with water (in the case of III also with dilute acid and sodium bicarbonate) and dried over $MgSO_4$; most of the solvent was evaporated and the remaining solution was analyzed by glc. Conditions were: for olefins IV–VII, 25% Carbowax 4000 on Chromosorb W at 160–175°; for VIII and IX, 6% SE-30 on Chromosorb W at 30°; for X, 5% Carbowax 4000 on Chromosorb W at 67°.

Samples of 1- and 3-phenylcyclopentene,[21] of norbornene and nortricyclene,[22] and of *exo*- and *endo*-2-norbornyl chloride,[23] used for comparison, were available from earlier work. In some cases, absolute analysis of compounds VIII–IX and X was performed, using cyclohexane and decane, respectively, as internal standards, In all other cases relative amounts were determined. Relative areas were taken as the ratio of isomers in the case of olefins IV and V. as well as of VI and VII.

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Allylic Oxidation of Olefins by Mercuric Acetate[1]

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Abstract: Both the oxidation of allylbenzene by $Hg(OAc)_2$ and the solvolysis of cinnamylmercuric acetate give 40% α-phenylallyl acetate and 60% cinnamyl acetate. The solvolysis of crotylmercuric acetate and the oxidations of 1-and 2-olefins C_nH_{2n} by $Hg(OAc)_2$ give under kinetic control exclusively the secondary allylic esters. The oxidation rate is apparently first order in the olefin–$Hg(OAc)_2$ adduct. Rate-determining formation of the allylic HgOAc by an S_E' reaction and consecutive product-determining solvolysis of the mercurial are suggested to be involved in the allylic oxidation. The allylic isomerizations of allylic mercurials and allylic acetates are discussed.

Reaction of olefins with metal acetates $M(OAc)_n$ ($M = Hg^{II}$,[4] Pd^{II},[5] Tl^{III},[6] Pb^{IV})[7] gives a variety of products including π complexes, adducts, diacetates, rearranged products, and allylic esters.[8] The allylic product has been visualized to arise by elimination of $HM(OAc)_{n-1}$ from the olefin–metal acetate adduct.[9] However, in the allylic oxidation by mercuric acetate[4,10] the allylic mercuric acetates are usually the suggested oxidation intermediates. Their formation by allylic proton abstraction, followed by a radical decomposition, was initially suggested[10a] but the radical route was later discarded.[10b] They may also be formed from the adduct by the loss of HOAc.[11] Initial formation of an olefin–metal salt complex,[12] which then gives rapidly the allylic mercurial, or electrophilic attack by $HgOAc^+$ with simultaneous rearrangement of the double bond,[13] both followed by C–Hg bond heterolysis, were also suggested.

Most systems oxidized (1- and 1,4-substituted cyclohexenes and cyclopentenes, other cycloolefins, 1- and 3-menthene)[14] were symmetrical and only one allylic product exists. Evidence that the cleavage of the C–Hg bond leads in these cases to a symmetrical intermediate, presumably a carbonium ion, was given by oxidation of ^{13}C-[15] or ^{2}H-[16] labeled cyclohexene or by oxidizing (+)-carvomenthene.[10a,11] The equilibration of the label or the loss of optical activity corresponds to an intermediate in which C-α and C-γ

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