Cyclohexyl *p*-toluenesulfonate, m.p. 43.6–44.2°, was obtained from Holness.[20]

1-*p*-Anisyl-1-phenyl-2-propyl *p*-bromobenzenesulfonate, m.p. 71–72°, was the material studied by R. Heck[6] and prepared by him from the diastereoisomeric "B" alcohol kindly provided by Professor D. Curtin of the University of Illinois and Mr. A. Bradley of Columbia University.

threo-3-Phenyl-2-butyl *p*-toluenesulfonate, m.p. 47.6–48.2°, was prepared in the usual manner from alcohol kindly supplied as the acid phthalate by Professor D. J. Cram of this Department.

Solvents.—The preparation of acetic acid, 0.01 *M* in acetic anhydride, with and without added salts, has previously been described.[2,21]

Kinetic Measurements.—The usual sealed ampoule technique was employed. Formation of arylsulfonic acid was followed by titration with sodium acetate in acetic acid, as previously described.[2,22]

The new data in Table I were based on an average of 6 points per run followed past 70–90% reaction. The observed kinetics were clearly first order within experimental error only for the 1-phenyl-1-*p*-anisyl-2-propyl ester. Upward drifts during the run were the rule for the other compounds. These drifts are summarized in Table III, which lists the per cent. increase in the integrated rate constant over the extrapolated initial value per 0.01 *M* reaction. In these cases, the initial rate constants were obtained by linear extrapolation to zero reaction of plots of integrated rate constant *vs.* per cent. reaction. These are listed in Table I.

TABLE III

UPWARD DRIFTS IN RATE CONSTANTS DURING ACETOLYSIS

$(LiClO_4)$, *M*	Temp., °C.	—% Increase in k_t per 0.01 *M* reaction— Pinacolyl OTs	Pinacolyl OBs	Cyclohexyl OTs	3-Phenyl-2-butyl OTs
0	50	0	2.7	1.5	0
	75	2.6	1.4	1	0
0.01	50			11	6.4
	75			9	10
.03	50	7	9	12	11
	75	10	9	11	8.5
.06	50	8.5		11	11
	75	6		7	11
.10	50			8	6
	75			9	8
.30	50			8	
	75			7	

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

(21) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(22) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Salt Effects and Ion Pairs in Solvolysis and Related Reactions. VIII. Special Salt Effects in Acetolysis of Cholesteryl and 2-(2,4-Dimethoxyphenyl)-ethyl Arylsulfonates

BY S. WINSTEIN AND E. CLIPPINGER[1]

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Special salt effects are especially striking in acetolysis of cholesteryl toluenesulfonate and bromobenzenesulfonate and 2-(2,4-dimethoxyphenyl)-ethyl bromobenzenesulfonate. As lithium perchlorate concentration is increased, the special stage of the salt effect appears to end at *ca.* 10^{-3} *M*. At higher concentrations, the normal linear salt effect pattern is observed. The magnitude of the special salt effects, measured by $k_{ext.}^0/k_t^0$, are similar to those observed in several other cases. However, the values of $(LiClO_4)_{1/2}$, the concentration of lithium perchlorate which produces half of the special salt effect, are of the order of 4–8 × 10^{-5} *M*. Thus, the cholesteryl and dimethoxyphenylethyl esters show the sharpest separation between special and normal salt effects. With cholesteryl toluenesulfonate, it has been shown that the normal salt effects are specific with regard to the nature of the salts. The observed salt order is $LiClO_4 \cong HClO_4 > DPGHClO_4 > DPGHOAc > LiOAc$. Also, there is specificity in the value of $(salt)_{1/2}$ in the special salt effects, the salt order for increasing values of $(salt)_{1/2}$ being the same as the one for decreasing normal salt effects. On the other hand, there is no specificity in the magnitude of the special salt effects; all the salts lead to the same $k_{ext.}^{\circ}$, the rate constant inclusive of special and exclusive of normal salt effects. The present results support the view that the special salt effects are concerned with reduction of ion pair return. The lack of specificity in the magnitude of the special salt effect shows that the same fraction of ion pair return is eliminated in the special salt effect by all the salts.

In an earlier study[2] of the acetolysis of cholesteryl toluenesulfonate, it was observed that the first order acetolysis rate constant was increased substantially and approximately identically by 0.01 *M* and 0.02 *M* sodium acetate, 0.01 *M* potassium acetate and 0.01 *M* lithium perchlorate. At the time,[2] these results made it clear that the accelerations in rate were not due to bimolecular substitution by acetate ion but to salt effects. In the light of more recent observations[3] on salt effects, the pattern of these salt effects appeared special[4] rather than normal.[5] Similar indications of special salt effects in acetolysis of 2,4-dimethoxyphenylethyl *p*-bromobenzenesulfonate were observed by R. Heck.[6] Further study has disclosed that special salt effects on acetolysis rates of both cholesteryl and 2,4-dimethoxyphenylethyl arylsulfonates are very marked at especially low salt concentrations. This paper reports the results of the investigation of the pattern of such salt effects in acetolysis of both systems.

Results

Cholesteryl *p*-Toluenesulfonate and *p*-Bromobenzenesulfonate.—From the pertinent rate constants collected in Table I it can be seen that the rate constant of 130 × 10^{-6} sec.$^{-1}$, which is steady[2,7] for cholesteryl *p*-toluenesulfonate at the 0.005 *M* concentration level employed, is increased

(1) U. S. Rubber Predoctoral Fellow, 1953–1954.

(2) S. Winstein and R. Adams, THIS JOURNAL, **70**, 838 (1948).

(3) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson: (a) *ibid.*, **76**, 2597 (1954); (b) *Chemistry and Industry*, 664 (1954).

(4) A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2767 (1956).

(5) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956).

(6) R. Heck, Thesis, UCLA, 1954.

(7) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, THIS JOURNAL, **78**, 328 (1956).

TABLE I

SUMMARY OF RATE CONSTANTS FOR ACETOLYSIS AT 50.0°

Compound	Other solute	10^6k (sec.$^{-1}$)
2-(2,4-Dimethoxyphenyl)-ethyl OBs		1.99 ± 0.01[a,b]
		48.9 ± 0.2[b,c]
	0.0311 *M* $LiClO_4$	2.32 ± 0.01[a,b]
	.0311 *M* $LiClO_4$	56.5 ± 0.3[b,d]
	.0100 *M* LiOAc	94 − 59[e]
	.0100 *M* LiOAc	89 − 32.3[f]
	.0100 *M* DPGHOAc	109 ± 2
	.0600 *M* DPGHOAc	118 ± 6
	1.00×10^{-5} *M* $LiClO_4$	53.4 − 40.1[g]
	1.00×10^{-4} *M* $LiClO_4$	75.7 − 58.4[h]
	1.00×10^{-3} *M* $LiClO_4$	99 ± 2
	5.00×10^{-3} *M* $LiClO_4$	107 ± 1
	0.0100 *M* $LiClO_4$	116 ± 3
	.0300 *M* $LiClO_4$	140 ± 3
	.060 *M* $LiClO_4$	178 ± 5
	.100 *M* $LiClO_4$	227 ± 4
	.300 *M* $LiClO_4$	535 ± 27
Cholesteryl OTs		130 ± 2
	0.0100 *M* LiOAc	325 ± 27
	.0300 *M* LiOAc	317 ± 20
	.0600 *M* LiOAc	342 ± 10
	.100 *M* LiOAc	357 ± 18
	.0100 *M* DPGHOAc	327 ± 10
	.0300 *M* DPGHOAc	366 ± 24
	.0600 *M* DPGHOAc	403 ± 56
	.100 *M* DPGHOAc	488 ± 27
	1.00×10^{-6} *M* $HClO_4$	131 ± 2
	1.00×10^{-5} *M* $HClO_4$	170 ± 5
	1.00×10^{-4} *M* $HClO_4$	237 ± 12
	1.00×10^{-3} *M* $HClO_4$	282 ± 12
	0.0100 *M* $HClO_4$	417 ± 11
	.0300 *M* $HClO_4$	610 ± 50
	.0600 *M* $HClO_4$	810 ± 130
	.100 *M* $HClO_4$	960 ± 120
	1.00×10^{-6} *M* $DPGHClO_4$	131 ± 3
	1.00×10^{-5} *M* $DPGHClO_4$	156 ± 2
	1.00×10^{-4} *M* $DPGHClO_4$	200 ± 4
	1.00×10^{-3} *M* $DPGHClO_4$	238 ± 5
	0.0100 *M* $DPGHClO_4$	341 ± 6
	.0300 *M* $DPGHClO_4$	434 ± 7
	.0600 *M* $DPGHClO_4$	531 ± 6
	.100 *M* $DPGHClO_4$	670 ± 40
	1.00×10^{-6} *M* $LiClO_4$	133 ± 9
	1.00×10^{-5} *M* $LiClO_4$	153 ± 5
	3.00×10^{-5} *M* $LiClO_4$	198 ± 4
	6.00×10^{-5} *M* $LiClO_4$	233 ± 8
	1.00×10^{-4} *M* $LiClO_4$	266 ± 8
	1.00×10^{-4} *M* $LiClO_4$	255 ± 7
	3.00×10^{-4} *M* $LiClO_4$	286 ± 11
	6.00×10^{-4} *M* $LiClO_4$	300 ± 9
	1.00×10^{-3} *M* $LiClO_4$	309 ± 6
	5.00×10^{-3} *M* $LiClO_4$	343 ± 12
	0.0100 *M* $LiClO_4$	389 ± 8
	.0300 *M* $LiClO_4$	548 ± 5
	.0600 *M* $LiClO_4$	814 ± 30
	.100 *M* $LiClO_4$	1150 ± 30
	.300 *M* $LiClO_4$	2780 ± 120
Cholesteryl OBs		451 ± 10
	1.00×10^{-5} *M* $LiClO_4$	511 ± 17
	1.00×10^{-4} *M* $LiClO_4$	775 − 618
	1.00×10^{-3} *M* $LiClO_4$	940 ± 20
	0.0100 *M* $LiClO_4$	1200 ± 30
	.0300 *M* $LiClO_4$	1770 ± 60

[a] Temperature 25.0°. [b] Absolute ethanol as solvent; data of A. Fainberg. [c] $\Delta H^{\ddagger}$ = 23.85 kcal./mole; $\Delta S^{\ddagger}$ = −4.6 e.u. at 50°. [d] $\Delta H^{\ddagger}$ = 23.81 kcal./mole; $\Delta S^{\ddagger}$ = −4.4 e.u. at 50°. [e] 9–76% Reaction range; extrapolated initial $k = 95 \times 10^{-6}$ sec.$^{-1}$. [f] 7–95% Reaction range; extrapolated initial $k = 93 \times 10^{-6}$ sec.$^{-1}$. [g] 4–83% Reaction range; extrapolated initial $k = 51 \times 10^{-6}$ sec.$^{-1}$. [h] 6–84% Reaction range; extrapolated initial $k = 80 \times 10^{-6}$ sec.$^{-1}$.

substantially by addition of even 10^{-5} *M* lithium perchlorate. As lithium perchlorate concentration is increased, the special stage of the salt effect appears to end at *ca.* 10^{-3} *M* salt. Further increases in concentration of lithium perchlorate give only the much more shallow linear salt effect which we have been designating as normal.[4,5]

The behavior of cholesteryl toluenesulfonate toward lithium perchlorate is best visualized with the aid of Figs. 1 and 2. From these it is seen that in the range of normal salt effects, a good linear relation obtains between titrimetric rate constant, k_t, and lithium perchlorate concentration from 10^{-3} to 10^{-1} *M*. Actually, the point at 0.3 *M* lithium perchlorate is also on the line.

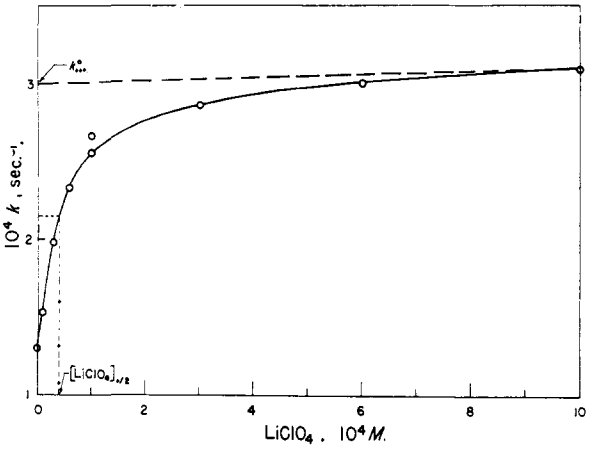

Fig. 1.—Special salt effect of lithium perchlorate on acetolysis rate of cholesteryl OTs at 50.0°.

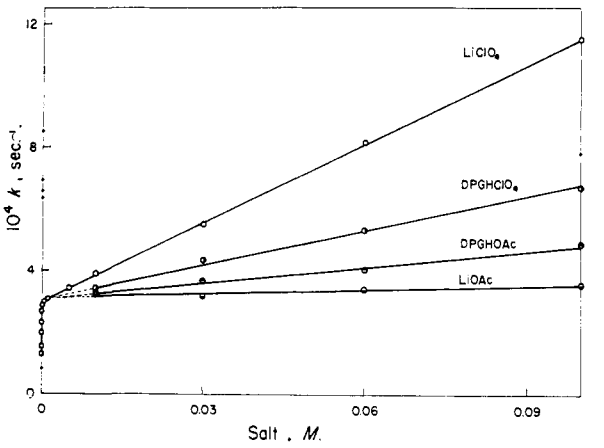

Fig. 2.—Salt effects of several salts on acetolysis rate of cholesteryl OTs at 50.0°.

Other series of acetolysis runs on cholesteryl toluenesulfonate with added perchloric acid or diphenylguanidinium perchlorate (DPGHClO$_4$) are also summarized in Table I. Except for greater experimental error in measurements at high perchloric acid concentrations, because of the relatively small increase in a large acid titer during a run, the pattern of salt effects for perchloric acid and diphenylguanidinium perchlorate was qualitatively similar to that for lithium perchlorate.

Salt effects of the bases, diphenylguanidinium acetate (DPGHOAc) and lithium acetate, were also explored. However, with these salts it was not possible to study low concentrations since the salts are neutralized by the acid produced in acetolysis.

At the concentrations of these bases employed, even as low as 0.01 M, good first-order behavior in acetolysis of cholesteryl toluenesulfonate was observed. As illustrated in Fig. 2, the variation of rate constant with salt concentration is nicely linear in the range of 0.01–0.1 M.

All of the data for cholesteryl toluenesulfonate are summarized in Table II on the basis of equation[3,4] 1. The table lists, for each salt, the values of b for the normal salt effects and also the intercepts, $k_{ext}°$, the rate constants inclusive of special and exclusive of normal salt effects.[4] Also listed

$$k_t = k_{ext}° [1 + b (salt)] \quad (1)$$

in Table II are the values of $(salt)_{1/2}$, the salt concentration at which half the special salt effect has been introduced.

TABLE II

SUMMARY OF SALT EFFECTS IN ACETOLYSIS OF CHOLESTERYL AND 2,4-DIMETHOXYPHENYLETHYL DERIVATIVES AT 50°

Salt	$10^6 k_{ext}°$ (sec.$^{-1}$)	$k_{ext}°/k_t°$	$(salt)_{1/2}$, M	b
Cholesteryl OTs				
$LiClO_4$	300[a]	2.3	4×10^{-5}	28
$HClO_4$	*ca.* 315	2.4	*ca.* 6×10^{-5}	*ca.* 28
$DPGHClO_4$	305	2.3	4×10^{-4}	12
DPGHOAc	306	2.3	b	6
LiOAc	305	2.3	b	2
Cholesteryl OBs				
$LiClO_4$	920	2.1	6×10^{-5}	30
2-(2,4-Dimethoxyphenyl)-ethyl OBs				
$LiClO_4$	103	2.19	8×10^{-5}	12[c]
DPGHOAc	107	2.26		2
LiOAc			*ca.* 3×10^{-3}	

[a] Average $k_{ext}°$ for all five salts is $(306 \pm 3) \times 10^{-6}$ sec.$^{-1}$. [b] Below 2×10^{-3} M. [c] Up to 0.1 M $LiClO_4$; extrapolated k at 0.3 M $LiClO_4$ is 11% below observed value.

Both the special and normal salt effects of lithium perchlorate on the rate of acetolysis of cholesteryl p-bromobenzenesulfonate were quite analogous to those on the toluenesulfonate. The pertinent data are summarized in Tables I and II.

2-(2,4-Dimethoxyphenyl)-ethyl Bromobenzenesulfonate.—Except for differences connected with common ion rate depression[6,7] during a kinetic run, the effects of salts on acetolysis rate of 2,4-dimethoxyphenylethyl bromobenzenesulfonate summarized in Table I were similar to those observed with the cholesteryl system. The drift in acetolysis rate constant of the 2,4-dimethoxyphenylethyl ester observed previously[6,7] was still evident at low lithium perchlorate concentrations, and initial rate constants were derived by extrapolation. At higher lithium perchlorate concentrations, good first-order kinetics were observed. Similarly, no drift in first-order acetolysis rate constant was observed with added 0.01 or 0.06 M diphenylguanidinium acetate. The treatment of the data graphically and with the aid of equation 1 is shown in Fig. 3 and Table II.

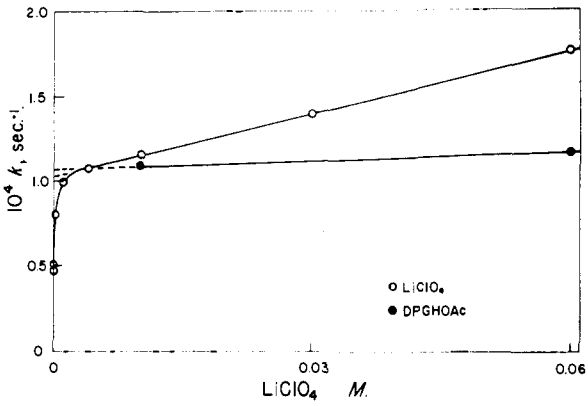

Fig. 3.—Salt effects on acetolysis rate of 2,4-dimethoxyphenylethyl OBs at 50.0°.

The inclusion of lithium acetate obviously gives rise to a special salt effect, but lithium acetate does not diminish the drift in rate constant during a run as efficiently as does diphenylguanidinium acetate. In order to estimate the value of $(LiOAc)_{1/2}$, the acetolysis of 0.02 M alkyl bromobenzenesulfonate was studied with only 0.50 equivalent of base present. As expected, the instantaneous rate constant in this kind of a run starts high, drops slowly at first and then very rapidly as the concentration of lithium acetate approaches and passes through the value of $(LiOAc)_{1/2}$. From a plot of $\ln(a - x)$ *vs.* time, the initial rate constant was 94×10^{-6} sec.$^{-1}$, some 9% lower than the $k_{ext}°$ observed with lithium perchlorate. The rate constant after depletion of the base was steady at 32×10^{-6} sec.$^{-1}$, a value identical with that observed previously[7] in acetolysis with 0.01 M added lithium bromobenzenesulfonate. The instantaneous rate constant was half way between 94×10^{-6} and 32×10^{-6} sec.$^{-1}$ at an estimated lithium acetate concentration equal to 3.2×10^{-3} M.

As summarized in Table I, the effect of lithium perchlorate on ethanolysis rate of 2,4-dimethoxyphenylethyl bromobenzenesulfonate was briefly probed. The small effect of 0.03 M lithium perchlorate shows that no appreciable special salt effect is in operation, paralleling the behavior of the p-anisylethyl system.[4]

Discussion

To assist in the consideration of the normal and special salt effects of lithium perchlorate in acetolysis of cholesteryl toluenesulfonate and dimethoxyphenylethyl bromobenzenesulfonate, the present results are summarized in Table III along with related information on some representative members of a spectrum of compounds previously investigated.

Normal Salt Effects.—Considering first the normal salt effects of lithium perchlorate, it is obvious that the dimethoxyphenylethyl bromobenzenesulfonate displays a normal salt effect essentially identical in magnitude with those observed with p-anisylethyl[4] and p-methoxyneophyl[5] toluenesulfonates, analogous primary derivatives. Cholesteryl toluenesulfonate exhibits considerably larger normal salt effects than the dimethoxyphenylethyl bromobenzenesulfonate, as evidenced by a b value of 28 compared to one of 12. The larger b value for cholesteryl toluenesulfonate is analogous to the increased b values observed with other secondary derivatives. With both cholesteryl toluenesulfon-

TABLE III

SALT EFFECTS IN ACETOLYSIS OF VARIOUS ARYLSULFONATES

Compound	Temp., °C.	Common ion dep.	OBs–OTs exchange	Normal salt effct.[a,b]	Special salt effect[a] Presence	$(LiClO_4)_{1/2}$, M	$k_{ext}°/k_t°$
exo-Norbornyl OBs[7-9]	25	No	No	38	No		1.0
threo-3-Phenyl-2-butyl OTs[9]	50	No		37	No		1.0
1-*p*-Anisyl-2-propyl OTs[7,10]	50	No		27	Yes	3×10^{-3}	2.4
3-*p*-Anisyl-2-butyl OBs[7,10]	25	No[b]	Yes[b]	18	Yes[c]	4×10^{-3}	3.1
2-*p*-Anisylethyl OTs[4]	50	Yes		11	Yes	3.4×10^{-4}	3.3
Cholesteryl OTs[7]	50	Yes	Yes	28	Yes	4×10^{-5}	2.3
2-(2,4-Dimethoxyphenyl)-ethyl OBs[7]	50	Yes	Yes	12	Yes	8×10^{-5}	2.2

[a] $LiClO_4$ as salt. [b] *Threo* diastereomer. [c] *Erythro* diastereomer.

TABLE IV

SPECIFIC OR NON-SPECIFIC NATURE OF SALT EFFECTS IN ACETOLYSIS OF ARYLSULFONATES

Salt effect	Specific or non-specific	Salt order
Normal	Specific	$LiClO_4 \cong HClO_4 >$ DPGHClO$_4$ > DPGHOAc > LiOAc
Special $1/(Salt)_{1/2}$	Specific	$LClO_4 \cong HClO_4 >$ DPGHClO$_4$ > LiOAc
Special $k_{ext}°/k_t°$	Non-specific	$LiClO_4 = HClO_4 =$ DPGHClO$_4$ = DPGHOAc = LiOAc

ate and dimethoxyphenylethyl bromobenzenesulfonate, the normal salt effects are specific with regard to the nature of the salts. In order of decreasing magnitude of normal salt effects, the salts arrange themselves in the order: $LiClO_4 \cong HClO_4 >$ DPGHClO$_4$ > DPGHOAc > LiOAc. As far as the results overlap, this salt order agrees with the one observed in acetolysis of the neophyl arylsulfonates.[5]

Special Salt Effects.—Considering special salt effects, one notices in Table III that these occur only with the systems giving rise to the longer-lived carbonium ion species. Regarding any correlation between the incidence of special salt effects of lithium perchlorate and the incidence of common ion rate depression, it is clear that special salt effects are encountered earlier than common ion rate depression in descending the structural series in Table III. On the other hand, the indications are that the correlation will be better between the incidence of special salt effects and bromobenzenesulfonate–toluenesulfonate exchange[7] during acetolysis.

Regarding the magnitude of the lithium perchlorate special salt effect observed with cholesteryl toluenesulfonate and dimethoxyphenylethyl bromobenzenesulfonate, the $k_{ext}°/k_t°$ values of 2.3 and 2.2, respectively, are similar to those observed in several other cases. On the other hand, the values of $(LiClO_4)_{1/2}$ for cholesteryl and dimethoxyphenylethyl derivatives are of the order of 4–8 $\times 10^{-5}$ *M*, smaller by a factor of *ca.* 5 than the corresponding value for *p*-anisylethyl toluenesulfonate and by a factor of *ca.* 50 than the values for the 1-*p*-anisyl-2-propyl and 3-*p*-anisyl-2-butyl derivatives. Thus, the cholesteryl and dimethoxyphenylethyl esters show the sharpest separation between special and normal salt effects.

It is instructive to observe how the various salts employed in the present work compare in special salt effects. Just as there is specificity in normal salt effects, there is specificity in the value of $(salt)_{1/2}$ in the special salt effects. Furthermore, as is clear from Table IV, the salt order for increasing values of $(salt)_{1/2}$ is the same as the one for decreasing normal salt effects. Whereas the value of $(salt)_{1/2}$ for perchloric acid is approximately equal to the value for lithium perchlorate, this value is some ten times as large for diphenylguanidinium perchlorate and some forty times as large for lithium acetate.

In contrast with the specificities in $(salt)_{1/2}$ is the constancy in $k_{ext}°$ shown by different salts. With cholesteryl toluenesulfonate, as is clear from Fig. 2 and Table II, all five salts investigated yielded the same intercept value of $k_{ext}°$ within experimental error, the average value of $k_{ext}°$ (306 ± 3) $\times 10^{-6}$ sec.$^{-1}$, corresponding to a $k_{ext}°/k_t°$ of 2.3. Although no measurements on sodium and potassium acetates were carried out in the present study, the earlier work of Winstein and Adams[2] indicates these salts have effects nearly equal in magnitude to those of lithium acetate. The rate constants recorded in the earlier study were 131 $\times 10^{-6}$ sec.$^{-1}$ without added salt and 402 $\times 10^{-6}$ sec.$^{-1}$ at 0.01 *M* lithium perchlorate, in good agreement with the present values of (130 ± 1) $\times 10^{-6}$ and (389 ± 8) $\times 10^{-6}$ sec.$^{-1}$, respectively. Winstein and Adams[2] reported rate constants of 330 $\times 10^{-6}$ sec.$^{-1}$ for 0.01 *M* potassium acetate and 333 $\times 10^{-6}$ sec.$^{-1}$ for both 0.01 and 0.02 *M* sodium acetate, comparable to the present values for analogous concentrations of lithium acetate. Thus, sodium, potassium and lithium acetate apparently have very small normal salt effects and essentially identical special salt effects. On this basis, we can say that the same $k_{ext.}°/k_t°$ ratio is observed for seven salts rather than five.

The same lack of specificity in the magnitude of the special salt effect observed with different salts is evident in the case of dimethoxyphenylethyl bromobenzenesulfonate. With both lithium perchlorate and diphenylguanidinium acetate, the same $k_{ext}°$ within experimental error is observed, as is clear from Table II. The specific or non-specific nature of normal salt effects and of the two aspects of special salt effects are summarized in Table IV.

The present results are consistent with the supposition that special salt effects in acetolysis are concerned with the reduction or elimination of ion

(8) E. Clippinger, unpublished work.

(9) A. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2780 (1956).

(10) A. Fainberg, G. C. Robinson and S. Winstein, *ibid.*, **78**, 2777 (1956).

pair return.[3,4,7] The lack of specificity in the magnitude of the special salt effect produced by different salts shows that the same fraction of ion pair return is eliminated in the special salt effects by all the salts. With all of the systems so far reported in detail, the question remains unanswered whether this fraction is equal to or less than one. The next two papers in this series are concerned with the answer to this question in two specific cases.

Experimental Part

The arylsulfonates employed in the present work were the same materials used previously.[7] The procedures for the rate measurements were those described previously.[4,5,7]

The concentrations of the 2,4-dimethoxyphenylethyl bromobenzenesulfonate in the solvolysis runs were *ca.* 0.01 *M* in acetolysis without lithium acetate, *ca.* 0.02 *M* in acetolysis with lithium acetate and *ca.* 0.025 *M* in ethanolysis. Cholesteryl arylsulfonates were acetolyzed at a concentration of *ca.* 5×10^{-3} *M*.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

Stereochemistry of the Lithium Aluminum Hydride Reduction of Ketones

BY JEAN BLANCHARD UMLAND AND MARGARET I. JEFRAIM

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Lithium aluminum hydride reduction of 2-methylcyclopentanone yields a mixture of *cis*- and *trans*-2-methylcyclopentanols containing 75% of the *trans* isomer. Preponderant formation of the more stable *trans* isomer is consistent with proposals that lithium aluminum hydride reduction of ketones which are not markedly hindered sterically affords the thermodynamically more stable isomer, but contrary to predictions based on considerations of steric hindrance. The material previously reported as *cis*-2-methylcyclopentanol is shown to be a mixture containing 58% *cis*- and 42% *trans*-2-methylcyclopentanol.

When a ketone which already contains an asymmetric center is reduced, the alcohol which is formed has a new asymmetric atom and the problem arises as to which epimer will be formed in larger amounts. It has been suggested that reduction of a carbonyl group by lithium aluminum hydride is a bimolecular addition reaction so that steric factors should operate.[1] On the other hand, Barton[2] and Nace and O'Connor[3] have proposed that lithium aluminum hydride reduction of a keto group which is not markedly hindered sterically affords the thermodynamically more stable isomer.[4]

Probably the best evidence for the latter proposal is provided by the observation of Noyce and Denney[5] that the *trans*-alcohols predominate from the reduction of the 2- and 4-methylcyclohexanones, while the *cis*[6] isomer predominates from 3-methylcyclohexanone. However, because the most stable conformation of the methylcyclohexanones is one in which the methyl group is equatorial, the methyl group does not hinder either side of the carbonyl group and it is not clear whether the axial hydrogens on C_2 and C_6 or those on C_3 and C_5 would be more effective in preventing the approach of the hydrogen.

The purpose of the present investigation was to study the diastereoisomeric composition of the product obtained by the reduction of a simple model compound where considerations of steric hindrance would predict the formation of one diastereoisomer and considerations of thermodynamic stability the other. 2-Methylcyclopentanone is such a compound. Scale models show that in 2-methylcyclopentanone the methyl group hinders one side of the carbon–oxygen double bond.[7] If steric hindrance determines the stereochemistry of lithium aluminum hydride reduction of ketones, the hydrogen should approach the side opposite the methyl group yielding *cis*-2-methylcyclopentanol. On the other hand, *trans*-2-methylcyclopentanol is more stable than the *cis* isomer since the methyl and hydroxyl groups interfere in the latter.[8] Therefore considerations of stability would predict the formation of *trans*-2-methylcyclopentanol.

Reduction of 2-methylcyclopentanone with sodium in moist ether yielded 2-methylcyclopentanol. The pure *trans* isomer was obtained from the reduction product by recrystallization of the 3,5-dinitrobenzoate to constant melting point[9]; reduction of *trans*-2-methylcyclopentyl 3,5-dinitrobenzoate with lithium aluminum hydride, a method of regenerating the free alcohol from an ester which has been shown not to involve any cleavage of the alkyl–oxygen bond,[10] yielded *trans*-2-methylcyclopentanol. The melting points of derivatives agreed well with those recorded in the literature.[11] The configura-

(1) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 687 (1950).

(2) D. H. R. Barton, *ibid.*, 1027 (1953).

(3) H. R. Nace and G. L. O'Connor, THIS JOURNAL, **73**, 5824 (1951).

(4) Barton defines a keto group as subject to steric hindrance when it does not react readily with reagents like semicarbazide and the phenylhydrazines.

(5) D. S. Noyce and D. G. Denney, THIS JOURNAL, **72**, 5743 (1950).

(6) The isomer called "*trans*" by Noyce and Denney has recently been shown to be *cis* (H. L. Goering and C. Serres, Jr., *ibid.*, **74**, 5908 (1952); D. S. Noyce and D. B. Denney, *ibid.*, **74**, 5912 (1952); S. Siegel, *ibid.*, **75**, 1317 (1953)).

(7) The cyclopentane ring is probably slightly puckered (F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, **18**, 1519 (1950)) due to torsional forces about the carbon–carbon bonds arising from hydrogen–hydrogen repulsions. Small deviations from planarity would affect the argument only if C_2 puckered out of the plane of the ring making the methyl group pseudoequatorial. However lithium aluminum hydride probably coördinates with the carbonyl group as well as with ether making the oxygen effectively a bulky group and therefore it is unlikely that it should be opposed to the methyl group.

(8) Reduction of 2-methylcyclopentanone with sodium and alcohol, a procedure which gives a mixture of alcohols of the same composition as is obtained by direct equilibration (see ref. 2), gives predominantly *trans*-2-methylcyclopentanol.

(9) A good criterion of homogeneity in this case since the binary melting point diagram shows that the melting point of each isomer is depressed considerably by a small amount of the other diastereoisomer.

(10) W. v. E. Doering and H. H. Zeiss, THIS JOURNAL, **72**, 147 (1950).

(11) (a) W. Huckel and H. D. Sauerland, *Ber.*, **87**, 1003 (1954); (b) R. B. Turner, THIS JOURNAL, **72**, 878 (1950).