[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. III. The Effect of the Steric Requirements of Alkyl Substituents upon the Extent and Direction of Unimolecular Elimination in the Solvolysis of Secondary Alkyl Brosylates

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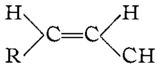
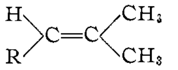
The solvolysis of the group of secondary alkyl brosylates, RCH$_2$CH(OBs)CH$_3$, with R = Me, Et, *i*-Pr, *t*-Bu, was studied in order to obtain data to compare the effect of the steric requirements of the group R in the secondary series with data previously obtained for the related tertiary series, RCH$_2$CBr(CH$_3$)$_2$. On the basis of the steric strain interpretation, it would be anticipated that the increasing steric requirements of the group R should be much less in the secondary series than in the related tertiary in increasing (1) the rate of acetolysis of the brosylate and (2) the ratio of 1- to 2-olefin in the product. The observed rate constants for the acetolysis at 70° do indeed exhibit a relatively minor dependence upon the steric requirements of R: Me, 1.29×10^{-4} sec.$^{-1}$; Et, 1.23×10^{-4}; *i*-Pr, 1.13×10^{-4}; *t*-Bu, 2.64×10^{-4}. Moreover, the ratios of 1- to 2-olefin in the products also exhibit only a relatively minor dependence upon the steric requirements of R: Me, 0.11; Et, 0.19; *i*-Pr, 0.25; *t*-Bu, 0.32. These results are quite different from those observed in the related tertiary bromides and are in accord with the predicted magnitudes of steric strains in the two series. The yield of olefin does vary with the steric requirements of R: Et, 31.5%; *i*-Pr, 46.5%; *t*-Bu, 68%. This is in accord with the previous proposal that the yield of olefin is primarily dependent upon the degree of steric hindrance to the substitution reaction of the carbonium ion and is not directly related to the degree of steric strain in the tetrahedral substitution product. Isolation and examination of the acetates formed in the solvolysis reveals that within the accuracy of the infrared analytical procedure, a maximum of 1–2% of rearrangement occurs in the solvolysis of 2-pentyl, 4-methyl-2-pentyl and 4,4-dimethyl-2-pentyl brosylates.

The marked changes observed in the rates of hydrolysis of the tertiary bromides, RCH$_2$CBr(CH$_3$)$_2$, with increasing steric requirements of R, were attributed to increasing steric strains in the parent compound.[2] Likewise, the marked shift in the ratio of 1- to 2-olefin in the product, resulting in Hofmann-type elimination in the case of R = *t*-Bu, was also attributed to steric strains.[2,3] These strains arise from the steric interaction of *cis* R and methyl groups in the 2-olefin, leading to an increased relative stability of the 1-olefin.

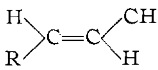
The study of the corresponding series of secondary derivatives, RCH$_2$CHXCH$_3$, offers a test of the proposed interpretation. If this interpretation is valid, the much lower steric crowding in the secondary derivative should result in much smaller steric assistance by R. Consequently, the rate of solvolysis should show a much smaller dependence upon the steric requirements of R than in the case of the related tertiary derivatives.

In the *cis*-2-olefins the steric effect of R should be the same as in the corresponding olefins from the tertiary bromides.





However, the formation of the *trans*-2-olefin provides a mechanism for avoiding the strain while retaining the greater hyperconjugative stabilization of the 2-olefin.



Consequently, on the basis of the steric strain theory, there should be observed with increasing steric requirements of R only a relatively slight shift in the ratio of 1- to 2-olefin, with a much more important shift in the ratio of *cis* to *trans* in the 2-olefin.

Since the acetolysis of arylsulfonic acid esters has been studied thoroughly as a means of producing secondary carbonium ions,[4,5] it was decided to utilize this reaction for the secondary series. Originally it was planned to work with the toluenesulfonates. However, the observation that 2-butyl and 2-pentyl tosylates were liquids which could not be crystallized led us to shift to the *p*-bromobenzenesulfonates (brosylates). Here the 2-butyl and 4,4-dimethyl-2-pentyl brosylates were solids which could be purified by crystallization, but the 2-pentyl and 4-methyl-2-pentyl brosylates proved to be liquids and were therefore utilized as such.

Results

The rates of solvolysis of the four brosylates, RCH$_2$CH(OBs)CH$_3$ with R = Me, Et, *i*-Pr and *t*-Bu, were run at 70° in anhydrous acetic acid by the procedure previously described by Winstein and his co-workers.[4] The results are summarized in Table I.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE SOLVOLYSIS OF ALKYLMETHYLCARBINYL BROSYLATES IN ANHYDROUS ACETIC ACID AT 70.0°

Secondary brosylate, RCH$_2$CH(OBs)CH$_3$	R	$k_1 \times 10^{-4}$ (sec.$^{-1}$)
2-Butyl	Me	1.29[a]
2-Pentyl	Et	1.23
4-Methyl-2-pentyl	*i*-Pr	1.13
4,4-Dimethyl-2-pentyl	*t*-Bu	2.64

[a] S. Winstein, B. K. Morse, K. C. Schreiber and J. Course, THIS JOURNAL, **74**, 1113 (1952), report 1.23×10^{-4} sec.$^{-1}$.

The acetolysis experiments for the examination of the olefin products were carried out at 118° in the presence of a slight excess of potassium acetate to neutralize the *p*-bromobenzenesulfonic acid and to prevent isomerization of the olefin. The yield of olefin was measured carefully and the product was

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[1] Post-doctorate assistant at Purdue University, 1953–1954, in part on a contract supported by the Office of Naval Research and in part on a research grant supported by the National Science Foundation.

[2] H. C. Brown and M. Nakagawa, THIS JOURNAL, **77**, 3610 (1955).

[3] H. C. Brown and I. Moritani, *ibid.*, **77**, 3607 (1955).

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

[5] J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, Jr., *ibid.*, **74**, 4283 (1952).

analyzed by infrared. The results are summarized in Table II.

TABLE II

YIELD AND COMPOSITION OF OLEFINS FORMED IN THE SOLVOLYSIS OF ALKYLMETHYLCARBINYL BROSYLATE IN ANHYDROUS ACETIC ACID AT 70°

Secondary brosylate, $RCH_2CH(OBs)CH_3$	R	Yield, %	Composition 1-	*cis*-2-	*trans*-2-	Ratio 1-/2-
2-Butyl tosylate[a]	Me		10.3	43.2	46.5	0.11
2-Pentyl tosylate[a]	Et	25	16	35	49	.19
2-Pentyl brosylate	Et	31.5	15.7	35.5	48.8	.19
4-Methyl-2-pentyl brosylate	*i*-Pr	46.5	19.7	27.3	53.0	.25
4,4-Dimethyl-2-pentyl brosylate	*t*-Bu	68	24.3	0.9	74.8	.32

[a] Ref. 3.

2-Butyl brosylate was not run. However, data are available for 2-butyl tosylate.[3] The similarity in the results for the 2-pentyl brosylate and tosylate lends confidence in the use of the data for 2-butyl tosylate for the comparison of the effects of the structural changes on the extent and direction of olefin formation.

It has been reported recently that the solvolysis of radiocarbon tagged 2-butyl tosylate proceeds with 8% rearrangement.[5] It therefore appeared of interest to isolate the acetates formed in the solvolysis of the brosylates of the present investigation in order to ascertain the extent of rearrangement accompanying the acetolysis. The results are summarized in Table III. From the physical properties and the infrared examination of the products (Figs. 1 and 2) it appears that the acetolyses of the three secondary brosylates proceed without significant rearrangement.

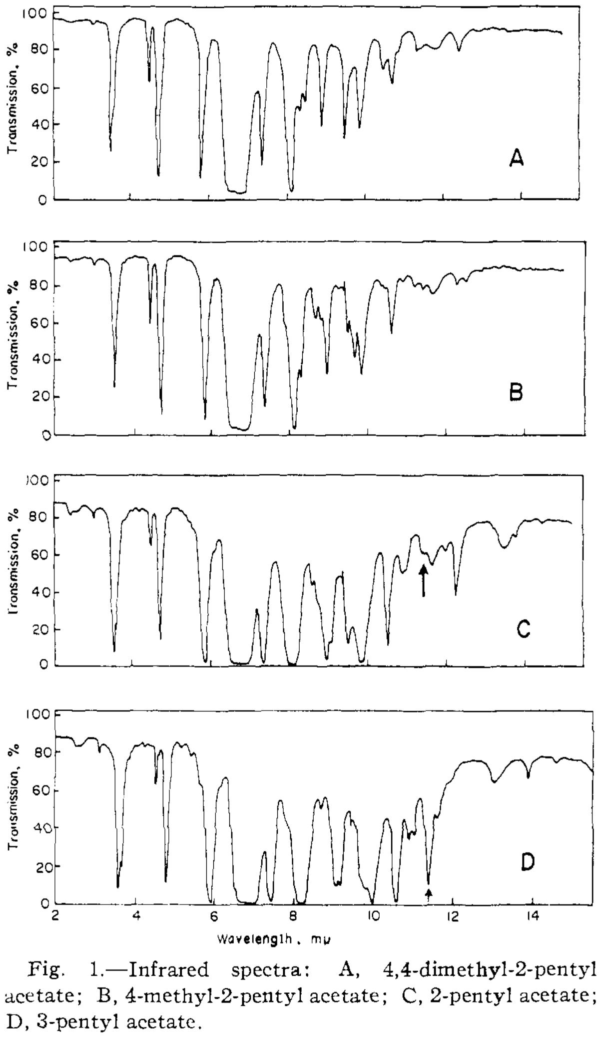

Fig. 1.—Infrared spectra: A, 4,4-dimethyl-2-pentyl acetate; B, 4-methyl-2-pentyl acetate; C, 2-pentyl acetate; D, 3-pentyl acetate.

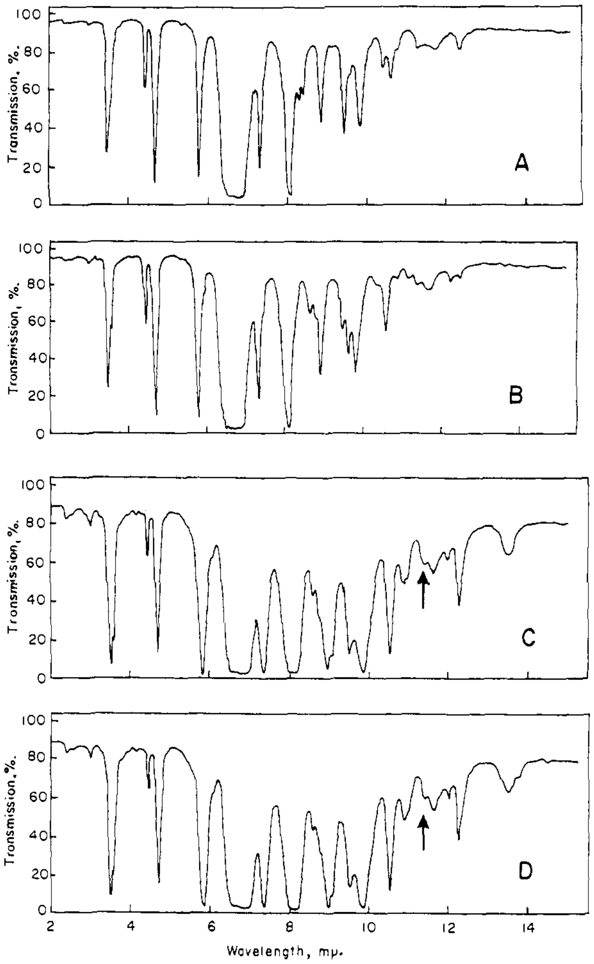

Fig. 2.—Infrared spectra: A, acetolysis product of 4,4-dimethyl-2-pentyl brosylate; B, acetolysis product of 4-methyl-2-pentyl brosylate; C, acetolysis product of 2-pentyl brosylate; D, synthetic mixture of 98.3% 2-pentyl and 1.7% 3-pentyl acetate.

The presence of 1–2% of 3-pentyl acetate in the 2-pentyl derivative can be detected readily by the characteristic absorption peak at 11.3 μ (Fig. 2, D). From the infrared spectra of the recovered acetate (Fig. 2, C) it appears that any rearrangement under the reaction conditions used for the acetolysis must be relatively small, certainly no greater than 1–2% as a maximum.

Discussion

The rate of solvolysis decreases slightly from R = Me to Et to *i*-Pr with an increase at *t*-Bu. The total increase in rate from 2-butyl brosylate to 4,4-dimethyl-2-pentyl brosylate (from R = Me to *t*-

TABLE III

DATA ON THE YIELD AND PHYSICAL PROPERTIES OF ACETATES FORMED IN THE SOLVOLYSIS OF THE SECONDARY ALKYL BROSYLATES

Secondary alkyl brosylate	$RCH_2CH(OBs)CH_3$ g.	$RCH_2CH(OBs)CH_3$ mole	Forerun g.	Forerun $n^{20}D$	Main fraction[a] g.	Main fraction[a] $n^{20}D$	Main fraction[a] B.p., °C. (mm.)	Yield, %	Purity,[b] %
2-Pentyl brosylate	92.1	0.3	0.7	1.3964	19.3	1.3963	131-131.5 (741)	50	98.7
4-Methyl-2-pentyl brosylate	96.2	.3	.3	1.4012	15.4	1.4005	141-144 (738)	36	100
4,4-Dimethyl-2-pentyl brosylate	61.0	.18	.3	1.4062	3.44	1.4064	76.5-77 (50)	12	103

[a] See Table IV for physical properties of synthetic samples. [b] Infrared analysis. See Table VII.

Bu) is only a factor of 2. This compares with the corresponding factor of 12 for the same structural change in the tertiary bromide series.[2]

The much greater effect of the steric requirements of the group R in the tertiary as compared to the secondary series is made evident in Fig. 3. The results are evidently in accord with the predicted effect of the increasing steric requirements of R on the relative steric strains in the secondary and tertiary systems and the postulated effect of these strains in facilitating ionization.[6]

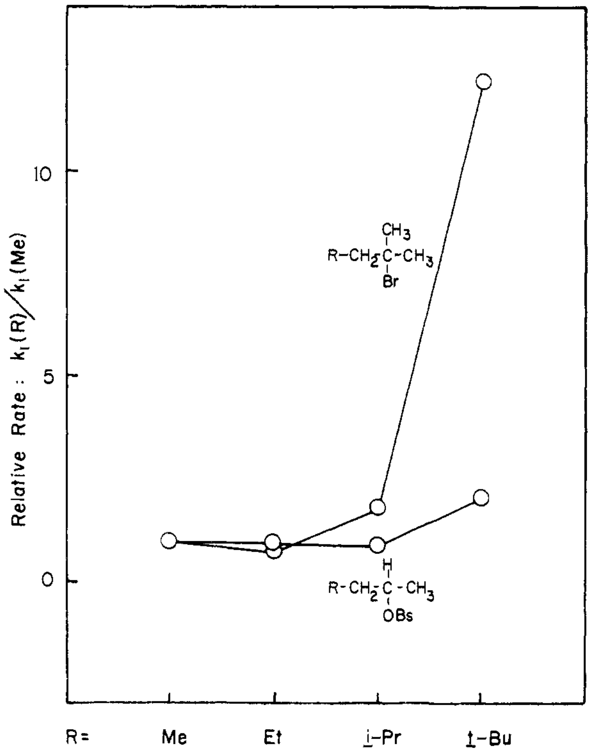

Fig. 3.—A comparison of the effect of R on the relative solvolysis rates in the secondary and tertiary alkyl series, $RCH_2CH(OBs)CH_3$ and $RCH_2CBr(CH_3)_2$.

In the tertiary series there was observed an increase in the ratio of 1- to 2-olefin with increasing steric requirements of R. The ratio changed from 0.27 for R = Me to 4.26 for R = *t*-Bu. This corresponds to Hofmann elimination for R = *t*-Bu. In the secondary system the shift in the ratio of 1- to 2-olefin is much smaller, from 0.11 for R = Me to 0.32 for R = *t*-Bu (Fig. 4). Thus all eliminations in the secondary series proceed in accordance with the Saytzeff rule.

It is significant that the ratios of *cis*- to *trans*-2-olefin in the secondary series exhibit a regular decrease with the increasing steric requirements of R. Indeed, in the case of 4,4-dimethyl-2-pentyl brosylate (R = *t*-Bu) the analysis indicates the presence of but 0.9% of *cis*-2-olefin, with 75% of the *trans* 2-derivative present. The *cis*-2-olefin, as has been pointed out, would have a *t*-butyl and methyl group in a highly crowded steric relationship of the same type previously postulated to account for the existence of Hofmann-type elimination in dimethylneopentylcarbinyl bromide.

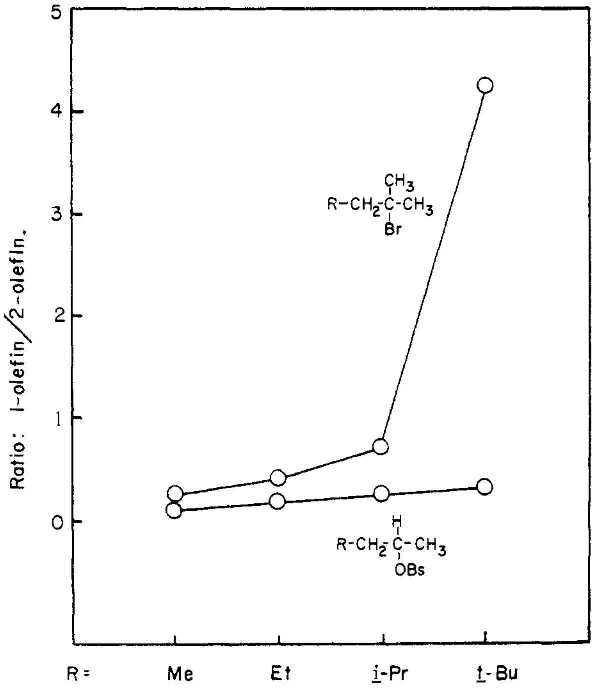

Fig. 4.—A comparison of the effect of R on the ratio of 1- to 2-olefin in the solvolysis of the secondary and tertiary alkyl series, $RCH_2CH(OBs)CH_3$ and $RCH_2CBr(CH_3)_2$.

Again these results are in complete agreement with the predicted effect of the steric requirements of the group R on the relative stabilities of the 1- and 2-olefins, as well as upon the effect of the group on the stabilities of the *cis*- and *trans*-2-olefins. Thus both the rate of solvolysis data and the results on the direction of elimination are entirely consistent with the theory of steric strain.

In the tertiary series the rate of hydrolysis data show a very small decrease from R = Me to R = Et, followed by an increase with R = *i*-Pr, and a very large increase with R = *t*-Bu. Ignoring for the present the small decrease observed with R =

(6) H. C. Brown, *Science*, **103**, 385 (1946).

Et, we can say that the changes are in accord with the predicted increases in steric strain in the tertiary alkyl bromide. Only small increases should result from the replacement of one methyl group by an ethyl or isopropyl. The geometries of these groups are such that they can minimize the steric strain by rotation to a position of minimum compression. The *t*-butyl group, however, possesses spherical symmetry and rotation cannot serve to alter the strain significantly. Hence, the *t*-butyl group causes a sudden large increase in the rate of solvolysis.

In the secondary series the same behavior is evident. There are small decreases in the rate of solvolysis in going from Me to Et and *i*-Pr, with an increase by a factor of 2 observed with R = *t*-Bu. Here also it is believed that the *t*-Bu group results in the presence of strain which facilitates the ionization. However, because of the less crowded condition of the secondary derivative, the effect of the *t*-butyl group should be considerably smaller than in the tertiary derivative, in agreement with observation.

The *t*-butyl group does not result in a sudden large increase in the 1- to 2-olefin ratio in the secondary series. However, in these compounds there is available an alternative route for the relief of strain—the formation of the *trans* 2-olefin—and the carbonium ion elects this route for elimination.

The total yield of olefin in the solvolysis of the compounds $RCBr(CH_3)_2$ increases fairly regularly with the increasing bulk of the group R (R = Me < Et < *i*-Pr < *t*-Bu). The failure to observe any sudden large increase in yield with R = *t*-Bu suggests that an increase in the steric requirements of the group R is of much smaller consequence in the carbonium ion $RC^+(CH_3)_2$ than it is in the tertiary halide itself. The conclusion that the steric requirements of the group R exert a relatively small effect in the carbonium ion itself, suggests that the large effect of R on the olefin yield cannot be primarily an effect of R on the rate of the elimination reaction. Instead, it would appear that the increase in olefin yield in this series must be due primarily to a decreased rate of substitution, k_S, arising from resistance of the planar carbonium ion to the addition of a solvent molecule with the consequent formation of a strained tetrahedral arrangement.

This conclusion is supported by the data in the secondary series. Here also the *t*-butyl group fails to exhibit any large effect. Instead, just as in the tertiary series, the olefin yield increases fairly regularly in the series R = Me < Et < *i*-Pr < *t*-Bu.

In conclusion, the results of these studies are consistent with the interpretation that large bulky groups increase the rate of solvolysis through release of steric strain (steric assistance) and they favor a shift from Saytzeff to Hofmann elimination because of the steric strains in the 2-olefin. Large bulky groups also favor an increase in the k_E/k_S ratio, primarily through a decrease in k_S because of steric hindrance to the substitution reaction.

Our failure to observe more than 1-2% rearrangement in the acetolysis of the secondary alkyl brosylates is puzzling in view of the 8% rearrangement reported for the acetolysis of 2-butyl tosylate.[5] We are unable to account for the difference in results in the 2-butyl and 2-pentyl systems and are continuing our studies in an attempt to resolve the difference in results.[7]

Experimental Part

Materials.—2-Pentanol was prepared in 82% yield by the reaction of 4 moles of methylmagnesium iodide on 3.6 moles of *n*-butyraldehyde (b.p. 73–73.5° (735 mm.), $n^{20}D$ 1.3792).

3-Pentanol was prepared in 55% yield by the reaction of 1.5 moles of ethylmagnesium bromide with 0.75 mole of ethyl formate (b.p. 53–54° (746), $n^{20}D$ 1.3541).

4-Methyl-2-pentanol was synthesized in 84% yield by the sodium borohydride reduction in methanol of 3 moles of methyl isobutyl ketone (b.p. 114-115° (745 mm.), $n^{20}D$ 1.3954).

4,4-Dimethyl-2-pentanone (b.p. 123–125° (743 mm.), $n^{20}D$ 1.4038) was prepared in 41% yield by the oxidation of 3.0 moles of diisobutylene (b.p. 99.5–102° (745 mm.), $n^{20}D$ 1.4090) with potassium dichromate (4 moles) and sulfuric acid (16 moles).[8]

4,4-Dimethyl-2-pentanol was synthesized by the reduction of the ketone with sodium borohydride. A mixture of 100 ml. of ethanol and 4,4-dimethyl-2-pentanone, 144 g., 1.26 moles, was added dropwise to a stirred solution of 14.2 g. (0.375 mole) in 140 ml. of ethanol. After addition was complete, the reaction mixture was heated under reflux for 2 hr. A solution of 30 g. of sodium hydroxide in 100 ml. of water then was added to hydrolyze the intermediate and heating under reflux continued for one hour. The cold reaction mixture was poured into ice-water and the organic fractions were washed with cold water and dried over anhydrous potassium carbonate. The product was distilled through a modified Widmer column and material of constant refractive index collected. The yield was 123 g., 85%.

The physical properties of the alcohols are listed in Table IV.

The acetates of these carbinols were prepared to supply standards for the infrared analysis of the acetates formed in the solvolysis. The acetates were prepared by treating the alcohol with acetic anhydride in pyridine solution and the acetates were fractionated until b.p. and $n^{20}D$ exhibited satisfactory constancy.

The physical constants of the acetates are listed in Table IV.

Preparation of the *p*-Bromosulfonates.—Commercial *p*-bromobenzenesulfonyl chloride was dissolved in benzene, the solution washed with aqueous sodium carbonate, water and dried. The chloride, precipitated with ligroin at 0°, exhibited m.p. 77–78°. The equivalent amount of purified *p*-bromobenzenesulfonyl chloride was added in one portion to a solution of 0.1 mole of carbinol in 100 ml. of anhydrous purified pyridine cooled in an ice-salt-bath. After standing overnight in a refrigerator, the reaction mixture was added dropwise with stirring to 200 ml. of strongly cooled 6 *N* hydrochloric acid. The acidic aqueous layer was separated from the heavy oily layer or crystalline mass and was extracted with chloroform. The chloroform extract was combined with the crude brosylate and the solution washed successively with water, sodium bicarbonate solution and water. After drying, the solvent was removed at 15 mm. The liquid brosylates were evacuated to 0.01 mm. for 8 to 9 hr. at room temperature to remove volatile impurities. The solid brosylates were recrystallized from petroleum ether (b.p. 35–65°).

The yields were 85–89% except in the case of the 4,4-dimethyl-2-pentanol, where the yield was only 29%. This brosylate showed evidence of instability, especially in the

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(7) It should be mentioned that our experiments were carried out with anhydrous acetic acid which was 0.7 *M* in potassium acetate, whereas the solvolysis of the 2-butyl-1-C^{14} *p*-toluenesulfonate (ref. 5) was carried out in acetic acid which was 0.46 *M* in potassium acetate and 0.45 *M* in potassium *p*-toluenesulfonate. It is therefore possible that the difference in results may have its origin in either the difference in reaction conditions or in the use of the brosylate instead of the tosylate. We are currently examining the solvolysis of 2-pentyl tosylate under the identical conditions of Roberts and co-workers (ref. 5) in order to ascertain whether these factors are responsible for the extent of rearrangement.

(8) W. A. Mosher and J. C. Cox, Jr., THIS JOURNAL, **72**, 3702 (1950). These authors report b.p. 124–125° (760 mm.), $n^{20}D$ 1.4018.

TABLE IV

PHYSICAL PROPERTIES OF MATERIALS

Compound	Observed constants B.p., °C. (mm).	n^{20}D	Literature constants B.p., °C. (mm.)	n^{20}D	Ref.
2-Butanol	98–99 (747)	1.3967	99 (758)	1.3954	a
2-Pentanol	118–118.5 (749)	1.4060	120.1 (743)	1.4068	b
3-Pentanol	113.5–133.7 (738)	1.4097	116	(1.4057)	c
			115.4 (754)	(1.4077)	d
4-Methyl-2-pentanol	129–129.5 (737)	1.4110	131.4 (745)	1.4132	b
4,4-Dimethyl-2-pentanol	137–137.5 (736)	1.4180	135.4 (742)	1.4241	b
			137–137.5 (746)	1.4188	e
2-Pentyl acetate	131–131.5 (741)	1.3969	131.8–132 (746)	1.3960	f
3-Pentyl acetate	130–130.5 (743)	1.3980	132.5–133 (748)	1.4005	f
			131	1.3966	g
4-Methyl-2-pentyl acetate	143–143.5 (740)	1.4005	147–148		h
4,4-Dimethyl-2-pentyl acetate	76–76.5 (47)	1.4066			
2-Butyl brosylate	M.p. 30–32		M.p. 31–32		i
2-Pentyl brosylate		1.5313			
4-Methyl-2-pentyl brosylate		1.5260			
4,4-Dimethyl-2-pentyl brosylate	M.p. 52–53				

[a] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **103**, 1935 (1913). [b] R. C. Huston and H. E. Tiefenthal, *J. Org. Chem.*, 16, 673 (1951). [c] F. H. Norton and H. B. Hass, THIS JOURNAL, **58**, 2147 (1936); refractive index n^{25}D. [d] R. F. Brunnel, *ibid.*, **45**, 1334 (1923); refractive index n^{25}D. [e] F. C. Whitmore and A. H. Homeyer, *ibid.*, **55**, 4194 (1933). [f] H. E. French and G. G. Wrightsman, *ibid.*, **60**, 50 (1938). [g] J. Kenyon, *J. Chem. Soc.*, **105**, 2226 (1914). [h] M. Guerbet, *Compt. rend.*, **149**, 129 (1909). [i] S. Winstein, *et al.*, THIS JOURNAL, **74**, 1119 (1952).

TABLE V

RATE DATA FOR THE ACETOLYSIS[a] OF 4,4-DIMETHYL-2-PENTYL BROSYLATE[b] AT 70.0°

Time, sec.	Sodium acetate, ml.	x	$a - x$	$k_1 \times 10^4$, sec.$^{-1}$
0	0.590			
1200	1.240	0.650	1.760	2.62
2400	1.720	1.130	1.280	2.64
3600	2.080	1.490	0.960	2.67
4800	2.320	1.730	.680	2.64
6000	2.510	1.920	.490	2.66
7200	2.640	2.050	.360	2.64

[a] Anhydrous acetic acid, 0.02 *N* in acetic anhydride. [b] 0.5071 g. of brosylate in 50.0 ml. of solvent: 0.03027 *M*; calcd. infinity titer was 3.033 ml. as compared to 3.000 ml. obsd. (99%).

impure state. Moreover, it was difficult to purify. A pure product was obtained by repeated recrystallization from petroleum ether.

Anal. Calcd. for $C_{13}H_{19}SBrO_3$: C, 46.57; H, 5.67. Found: C, 46.81; H, 5.88.

A lower melting crystalline material, m.p. 39–41°, was isolated from the mother liquid from which the pure brosylate had been isolated. This material in part solvolyzed at a rate corresponding to that of the pure brosylate, and in part at a much slower rate. The analytical data agreed roughly with that of a mixture of 1 mole of 4,4-dimethyl-2-pentyl brosylate and 0.5 mole of *p*-bromobenzenesulfonyl chloride.

Anal. Calcd. for $C_{13}H_{19}SBrO_3 + 0.5\ C_6H_4SBrClO_2$: C, 41.47; H, 4.96. Found: C, 42.54; H, 5.10.

A weighed sample of each of the brosylates was solvolyzed in acetic acid and the liberated sulfonic acid was titrated. 2-Butyl and 4,4-dimethyl-2-pentyl brosylates, both solids, yielded 99% of the calculated acid. The remaining two brosylates, liquids, yielded 95% of the calculated acid.

Physical properties for the brosylates are summarized in Table IV.

Rates of Acetolysis of the Brosylates.—The technique used was similar to that previously described.[9] Rate data for a representative kinetic run on 4,4-dimethyl-2-pentyl brosylate are reported in Table V. The mean value of k_1 is $(2.65 \pm 0.02) \times 10^{-4}$ sec.$^{-1}$. A duplicate run yielded $k_1 = (2.63 \pm 0.02) \times 10^{-4}$ sec.$^{-1}$. The data are representative of the precision realized in all of the determinations.

Elimination Experiments.—The following general procedure was utilized. One-tenth mole of the brosylate was placed in a round-bottomed flask with 0.11 mole of anhydrous potassium acetate and 150 ml. of anhydrous acetic acid (0.02 *N* in acetic anhydride). The mixture was attached to a Todd micro column and the olefin was distilled out of the reaction mixture into a cooled receiver. The distillate was washed with dilute sodium hydroxide and dried over potassium carbonate. Analysis was by infrared, using Bureau of Standards and A.P.I. Project 45 samples of the pure hydrocarbons as standards.

TABLE VI

SUMMARY OF EXPERIMENTAL CONDITIONS AND YIELD AND COMPOSITION DATA ON THE OLEFINS FORMED IN THE ACETOLYSIS OF THE SECONDARY ALKYL BROSYLATES

Secondary alkyl brosylate	$RCH_2CH(OBs)CH_3$ g.	Mole	Solvent, ml.	Potassium acetate g.	Mole	Olefin, g.	Yield, %	n^{20}D	Olefin composition 1-	*cis*-2-	*trans*-2-
2-Pentyl	61.4	0.2	300	20.6	0.21	4.25	30	1.3792[a]	15.7	35.5	48.8
	30.7	.1	150	10.8	.11	2.34	33	1.3792			
4-Methyl-2-pentyl	64.1	.2	300	20.6	.21	7.47	44	1.3878[b]	19.7	27.3	53.0
	32.05	.1	150	10.8	.11	4.17	49	1.3881			
4,4-Dimethyl-2-pentyl	61.0	.18	270	19.6	.20	11.9	68	1.3969[c]	24.3	0.9	74.8

[a] Calcd. n^{20}D from olefin composition, 1.3792. [b] Calcd. n^{20}D 1.3875. [c] Calcd. n^{20}D 1.3966.

The experimental data on these elimination experiments are summarized in Table VI.

Isolation of Acetates.—The residues of the acetolysis experiments for each of the brosylates were combined, mixed with water (50 ml. water per 100 ml. of acetic acid mixture), and neutralized with sodium bicarbonate under strong cooling and vigorous stirring. Precipitated sodium acetate was redissolved by adding the minimum amount of water. The homogeneous, weakly alkaline solution was extracted with ether. The washed ether solution was dried over potassium carbonate and the solvent distilled away through a column.

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(9) S. Winstein, *et al.*, THIS JOURNAL, **70**, 821 (1948).

The residual crude acetate was distilled through a short distillation head. The small amount of low boiling fraction was placed in a small flask, cooled to 0°, and evacuated to remove any residual ether.

The data on the yield, physical properties and composition of the acetates are summarized in Table III.

The identity of the acetates isolated from the acetolysis of the brosylates with those synthesized from the carbinols is evident from the infrared spectra (Figs. 1 and 2). Comparison of the spectra of the acetates isolated from the solvolysis of 4,4-dimethyl-2-pentyl brosylate (Fig. 2,A) and 4-methyl-2-pentyl brosylate (Fig. 2,B) with the spectra of synthetic samples of the acetates (Figs. 1,A and 1,B, respectively) indicated that the products were essentially pure, containing no more than very minor amounts of the rearranged acetate (Table VII).

The availability of both 2- and 3-pentyl acetate permitted a more detailed analysis for the rearranged product. Blank experiments revealed that it was possible to determine small amounts of the 3-pentyl acetate in the 2-derivative to within ±0.5%. Typical analyses of this kind are reported in Table VII. Application of this procedure to the acetate obtained in the solvolysis of 2-pentyl acetate indicated the presence of a maximum of 1–2% of 3-pentyl acetate in the product (Table VII).

TABLE VII

INFRARED ANALYSIS OF ACETATES PRODUCED IN THE ACETOLYSIS OF SECONDARY BROSYLATE

Acetate unknown	Solution Acetate, g.	Solution CS_2, g.	Wave length, μ	Analysis, %
4,4-Dimethyl-2-pentyl[a]	0.1051	1.4050	8.95	105
			10.63	101
4-Methyl-2-pentyl[a]	.1111	1.3152	8.90	101
			9.50	101
			10.67	98
2-Pentyl[a]	.5005	1.2423	12.27	101(2–)
			11.3	1.4(3–)
2-Pentyl[b]	.4942(2–)	1.2465	12.27	98.7(2–)
	.0088(3–)		11.3	1.2(3–)
2-Pentyl[c]	.2425(2–)	0.6469	12.27	98.2(2–)
	.0056(3–)		11.3	1.8(3–)

[a] Product from acetolysis of brosylate. [b] Synthetic mixture: 98.3% 2- and 1.7% 3-pentyl acetate. [c] Synthetic mixture: 97.7% 2- and 2.3% 3-pentyl acetate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. IV. The Question of Rearrangements as a Factor in the Extent and Direction of Unimolecular Elimination

BY HERBERT C. BROWN AND Y. OKAMOTO[1]

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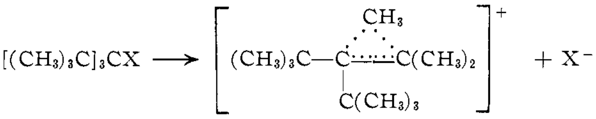
The solvolysis of 2-chloro-2,3,3-trimethylpentane in 80% aqueous ethanol forms pure 2,3,3-trimethyl-1-pentene in 58% yield. The mixture of alcohol and ethyl ether in the solvolysis is converted by hydrogen chloride into a tertiary chloride with identical properties with the original material. In 80% acetone the solvolysis proceeds to give the pure olefin (50% yield) and pure 2,3,3-trimethyl-2-pentanol (20% yield). The solvolysis of 3-chloro-2,2,3-trimethylpentane in 80% aqueous acetone results in the formation of pure 2,3,3-trimethyl-3-pentanol (18% yield) and olefin (58% yield). The olefin fraction contains none of the rearranged structure, 2,3,3-trimethyl-1-pentene. Treatment of the olefin fraction with hydrogen chloride converts it into 3-chloro-2,2,3-trimethylpentane. Careful examination of the products by infrared analysis reveals the absence of any measurable rearrangement within the limits of the analytical method, 1–2%. It appears, therefore, that the ionization, substitution and elimination reactions of these highly branched derivatives proceed without significant rearrangement. It is concluded that there is presently no evidence that bridging and rearrangements play any significant role in affecting either the rate of ionization or the extent and direction of elimination in these and related highly branched alkyl halides.

In earlier publications it has been proposed that the enhanced rate of ionization[2] and the increased tendency toward elimination[3] of highly branched tertiary halides resulted from the operation of steric strain. Evidence has been presented in the present group of papers in support of this interpretation.[4,5]

However, a number of alternative proposals have appeared recently, based upon the possible formation of relatively stable bridged carbonium ions.[6] Thus, it has been suggested that the enhanced rate of solvolysis of tri-*t*-butylcarbinyl derivatives may be due to the formation of a relatively stable bridged intermediate in the ionization stage.



$$[(CH_3)_3C]_3CX \longrightarrow \left[(CH_3)_3C—\overset{\overset{CH_3}{\cdot\,\cdot}}{\underset{\underset{C(CH_3)_3}{|}}{C}} \cdots\!\!— C(CH_3)_2 \right]^+ + X^-$$

Similarly Hughes, Ingold and Shiner[8] would prefer not to attribute the large quantities of olefins formed in the solvolysis of highly branched tertiary halides to the operation of steric strain. Instead, they propose that "synartetic" effects (*i.e.*, bridging) are responsible for the high proportion of olefin obtained in the solvolysis of the tertiary chloride, *t*-BuCClMe$_2$.

$$H\cdot CH_2\cdot CMe(Me)\cdot\overset{+}{C}Me_2 \longrightarrow H^+ + CH_2{:}CMe\cdot CMe_2(Me)$$

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[1] Research assistant at Purdue University, 1952–1955, on a contract supported by the Office of Naval Research for the study of "Steric Strains in Chemical Reactions."

(2) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

(3) H. C. Brown and R. S. Fletcher, *ibid.*, **72**, 1223 (1950).

(4) H. C. Brown and I. Moritani, *ibid.*, **77**, 3607 (1955).

(5) H. C. Brown and M. Nakagawa, *ibid.*, **77**, 3610, 3614 (1955).

(6) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 211–213.

(7) P. D. Bartlett, *J. Chem. Education*, **30**, 22 (1953); *Bull. soc. chim.*, **18**, 100 (1951).

(8) E. D. Hughes, C. K. Ingold and V. J. Shiner, *J. Chem. Soc.*, 3827 (1953).