EXPERIMENTAL

Materials. Trans-azobenzene, m.p. 68°, was obtained free from traces of the *cis* isomer by chromatography on alumina and recrystallization from ethanol in darkness. *Cis*-azobenzene, m.p. 71°, was prepared by irradiation of the *trans* compound[2] and chromatographic purification on alumina. Immediately before each occasion of use it was recrystallized from pentane in order to remove any spontaneously formed *trans*-azobenzene. The benzo[c]cinnoline used in these experiments was prepared according to Badger, Seidler, and Thompson.[9] After recrystallization from aqueous ethanol it melted at 154°. Isolation of benzo[c]cinnoline from irradiated acidic solutions of azobenzene has been described already.[1]

Absorption spectra. Solutions for spectroscopy were prepared by diluting stock solutions in absolute ethanol with aqueous sulfuric acid of appropriate normality. All spectra were measured in an Optica CF₄ Double Beam Recording Spectrophotometer at a wave-length drive of 0.4 mμ sec.⁻¹ Spectral changes in the absence and presence of light were studied through the entire range, 220–500 mμ, at every stage.

Ionization constants. The pKa values were evaluated by a standard procedure[10] following measurement of the spectra in various normalities (0.1–22N) of 10% (v.:v.) ethanolic sulfuric acid and neutral solution. Thermostatic control was not employed. All data therefore refer to room temperature (19–23°). Calculations for benzo[c]cinnoline were based on pH determinations with a glass electrode. The extended pH scale of Michaelis and Granick[7] was used for solutions of the azobenzenes. Although this scale is strictly applicable to purely aqueous sulfuric acid systems constant pKa values were obtained in 10% (v.:v.) ethanolic sulfuric acid over reasonably wide ranges of normalities. The values found, however, must be considered suitable for qualitative comparisons only.

ADELAIDE, SOUTH AUSTRALIA

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Kinetics of the Acetolysis of Some Alkyl-Substituted Neopentyl p-Bromobenzenesulfonates[1]

E. N. McELRATH, R. M. FRITZ, C. BROWN, C. Y. LeGALL, AND R. B. DUKE

Kinetics of the acetolysis of a series of alkyl-substituted neopentyl p-bromobenzenesulfonates, $R-C_\beta(CH_3)_2-C_\alpha H_2-OBs$, has been investigated. First-order rate constants have been determined at three temperatures and values for ΔH^* and ΔS^* derived for nine esters. Relative rates (CH_3 member = 1.0) show that (1) lengthening of the chain in R without branching beyond C_γ (C_2H_5, n-C_3H_7 and n-C_4H_9 members) gives a constant relative value of 2.4; (2) the effect of substitution of one, two, and three alkyl groups on C_γ (C_2H_5, i-C_3H_7 and sec-C_4H_9, t-C_4H_9 members) results in relative rates of 2.4, 7–8, and 34, respectively; (3) branching of R at C_δ (i-C_4H_9 member) gives a relative rate of 4.1. The overall variation of rate with structure corresponds closely to that observed in the structurally-related tertiary chlorides and appears to be explained best by a combination of carbon participation and a release of B-strain.

The behavior of alcohols of the type R_3C_β-$C_\alpha H_2OH$ (I) when subjected to conditions favorable to dehydration and rearrangement was first considered by Haller and Bauer[2] and later by Favorsky, who studied 2,2-dimethyl-1-butanol and 2-methyl-2-ethyl-1-butanol.[3] The extensive investigations of Whitmore on neopentyl alcohol (I, R = CH₃) and its derivatives[4] and of Meerwein and van Emster on camphene hydrochloride[5] led to formulation of an ionization mechanism for the rearrangements. Whitmore also investigated the relative migratory powers of the CH₃ and *n*-

C₄H₉ groups during dehydration of 2,2-dimethyl-1-hexanol.[4c] This early work was later verified and extended by Dostrovsky, Hughes, and Ingold[6] and by Winstein[7] using kinetic methods. Numerous other investigators employed a stereo-chemical approach[8] and the labelling technique[9] in an effort to arrive at a better understanding of 1,2-saturated nucleophilic rearrangements. In most of the cases investigated, relative reactivities and rearranged

(1) Abstracted from the Ph.D. thesis of R. M. F. and M. S. theses of C. B., C. Y. L., and R. B. D.

(2) A. Haller and E. Bauer, *Compt. rend.*, **155**, 1581 (1912).

(3) Al. Favorsky and J. Zalessky-Kibardine, *Bull. soc. chim. France*, (4) **37**, 1227 (1925).

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(5) H. Meerwein and K. van Emster, *Ber.*, **55**, 2500 (1922).

(6) I. Dostrovsky, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 173, 192 (1956).

(7) S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948).

(8) (a) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949). (b) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3875 (1949). (c) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2129 (1952). (d) D. J. Cram and J. D. Knight, *J. Am. Chem. Soc.*, **74**, 5839 (1952). (e) D. J. Cram and J. Allinger, *J. Am. Chem. Soc.*, **79**, 2858 (1957). (f) D. J. Cram and J. Tadanier, *J. Am. Chem. Soc.*, **81**, 2737 (1959).

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TABLE I

ACETOLYSIS OF $RC(CH_3)_2CH_2OBs$

R	Concn., M	Temp.[a]	k_1 (sec.$^{-1}$)	ΔH^*, Kcal./ Mole	ΔS^*, E.U.
CH_3	0.0347	59.7	$(3.96 \pm 0.11) \times 10^{-8}$	31.2	$+1.1$
	0.0403	74.6	$(3.27 \pm 0.13) \times 10^{-7}$		
	0.0325	90.9	$(2.38 \pm 0.06) \times 10^{-6}$		
C_2H_5	0.0434	59.7	$(9.42 \pm 0.32) \times 10^{-8}$	30.3	-0.28
	0.0398	74.6	$(6.16 \pm 0.03) \times 10^{-7}$		
	0.0352	90.9	$(4.39 \pm 0.08) \times 10^{-6}$		
n-C_3H_7	0.0298	59.7	$(9.12 \pm 0.13) \times 10^{-8}$	30.0	-0.77
	0.0374	74.6	$(6.87 \pm 0.19) \times 10^{-7}$		
	0.0256	90.9	$(4.77 \pm 0.20) \times 10^{-6}$		
n-C_4H_9	0.0336	59.7	$(9.40 \pm 0.06) \times 10^{-8}$	29.9	-0.84
	0.0437	74.6	$(6.99 \pm 0.07) \times 10^{-7}$		
	0.0319	90.9	$(4.85 \pm 0.11) \times 10^{-6}$		
H	0.0421	59.7	$(1.27 \pm 0.02) \times 10^{-7}$	28.1	-5.8
	0.0318	75.0	$(8.35 \pm 0.12) \times 10^{-7}$		
	0.0293	90.8	$(5.08 \pm 0.05) \times 10^{-6}$		
i-C_4H_9	0.0336	59.7	$(1.61 \pm 0.04) \times 10^{-7}$	27.9	-6.0
	0.0348	74.6	$(1.01 \pm 0.01) \times 10^{-6}$		
	0.0334	90.9	$(6.44 \pm 0.04) \times 10^{-6}$		
i-C_3H_7	0.0343	59.7	$(2.83 \pm 0.03) \times 10^{-7}$	27.9	-4.8
	0.0337	74.6	$(1.66 \pm 0.04) \times 10^{-6}$		
	0.0287	90.9	$(1.13 \pm 0.02) \times 10^{-5}$		
sec-C_4H_9	0.0228	59.7	$(3.15 \pm 0.03) \times 10^{-7}$	29.3	-0.31
	0.0276	75.0	$(2.33 \pm 0.03) \times 10^{-6}$		
	0.0274	90.8	$(1.47 \pm 0.01) \times 10^{-5}$		
t-C_4H_9	0.0353	59.7	$(1.35 \pm 0.01) \times 10^{-6}$	27.5	-3.0
	0.0199	75.0	$(8.42 \pm 0.17) \times 10^{-6}$		
	0.0334	90.8	$(4.99 \pm 0.16) \times 10^{-5}$		

[a] Correct to $\pm 0.1°$.

products have been studied in structures derived by varying the degree of alkyl and aryl substitution in (I) and its derivatives at C_α and of aryl substitution at C_β.[10]

There appears to have been no study of relative rates of solvolysis and rearranged products in a series of compounds such as that represented by $RC(CH_3)_2CH_2$—OBs (II, R = alkyl or H, OBs = p-bromobenzenesulfonate) where the parent structure (R = CH_3) is believed to undergo certain solvolysis reactions by an ionization mechanism[5,6] and where the products of the solvolysis are known to be completely rearranged.[6] By keeping all structural features constant except the nature of the R group attached to C_β such a study might be expected to give information on (1) the relative migratory aptitudes of R and CH_3, (2) participation of R and CH_3 in the rate-controlling ionization, and (3) the possible appearance of steric acceleration resulting from the relief of B-strain associated with increased branching at R.[11]

The present investigation is concerned with a study of the acetolysis of a series of p-bromobenzenesulfonates (II) where R is H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9, sec-C_4H_9 and t-C_4H_9. The kinetic phase of the work is reported in the present paper, while results of a study of the rearranged products will appear in a forthcoming publication.

Rates of acetolysis for each of the indicated nine brosylates (II) were determined at three temperatures and first order rate constants, k_1, and values for the enthalpy and energy of activation, ΔH^* and ΔS^*, were derived for each ester. Experimental results of these kinetic studies are given in Table I. Table II shows the rate enhancements observed in the series relative to the CH_3 member.

The data presented in Table II shows certain trends which should be noted: (1) lengthening of the chain in R without branching beyond C_γ (C_2H_5, n-C_3H_7, and n-C_4H_9 members) gave a

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(11) (a) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, J. Am. Chem. Soc., 66, 435 (1944). (b) H. C. Brown, Science, 103, 385 (1946). (c) H. C. Brown and R. S. Fletcher, J. Am. Chem. Soc., 71, 1845 (1949). (d) P. D. Bartlett, Bull. soc. chim. France, (5) 18, C100 (1951). (e) H. C. Brown and H. L. Berneis, J. Am. Chem. Soc., 75, 10 (1953).

R	Relative Rate	R	Relative Rate
CH_3	1.0	i-C_4H_9	4.1
C_2H_5	2.4	i-C_3H_7	7.1
n-C_3H_7	2.3	sec-C_4H_9	7.9
n-C_4H_9	2.4	t-C_4H_9	34.0
H	3.2		

constant relative rate of 2.4; (2) the effect of substitution of one, two and three alkyl groups on C_γ (C_2H_5, i-C_3H_7 and sec-C_4H_9, t-C_4H_9 members) resulted in relative rates of 2.4, 7–8, and 34, respectively; (3) branching of the R chain at C_δ (i-C_4H_9 member) gave a relative rate of 4.1.

The most closely related series of compounds which have been studied in a similar manner is composed of a group of tertiary chlorides, RC-$(CH_3)_2Cl$(III), investigated by Brown and co-workers.[11c,e] First-order rate constants for solvolysis of (III) in 80% aqueous acetone in the series R = C_2H_5, n-C_3H_7 and n-C_4H_9 gave essentially constant relative values of 1.7, 1.6, and 1.4, respectively (CH_3 = 1.0), where the structural change involved amounted to a lengthening of the straight chain attached to C_β.[11c] Relative rates in the present series (II) showed even more constant values for corresponding structural changes, being in the order 2.4, 2.3, and 2.4 for R = C_2H_5, n-C_3H_7 and n-C_4H_9. Again, in the tertiary chlorides (III) with R = neopentyl, a structure which has a triple branching on C_γ, the relative rate increased to 22.[11e] This member corresponds to the t-Bu compound in the present series where a relative rate of 34 was observed.

These rate increases in the tertiary chlorides (III), along with those observed on more highly branched members, were interpreted by the authors to point to an acceleration resulting from a release of steric strain.[11c,e] A steric factor was held responsible, as the structural variations employed were believed to be too far removed (C_β and C_γ) from the reaction center to produce a significant polar effect. Brown and Bonner[12] estimated the steric strain in hydrocarbons having the same degree of branching as was present in the tertiary chlorides and were able to parallel rate enhancements with the estimated increase in nonbonding interaction in the series.[13]

Alternative explanations for the above series (III) involve a possible electronic effect arising from inductive release and from C—H and C—C hyperconjugation,[14] the latter factor being of

particular importance where R is neopentyl.[15] The further suggestion has been made that participation of neighboring carbon may be an important influence, as solvolysis of highly-branched chlorides is often accompanied by extensive rearrangement.[11d] Even in the absence of actual rearrangement rate enhancement resulting from a neighboring group effect is possible.[16a]

In the present series (II) with the reaction center one position farther removed from the point of structural change than in the series of tertiary chlorides (III), certain of the electronic effects which have been advanced to account for the increased rates in that series have been eliminated or minimized in importance. Kinetic polar effects arising from C—H hyperconjugation are not possible, while the slight increase in inductive release and possibly in C—C hyperconjugation with increased branching of R should be of even less importance in (II). In both series, (II) and (III), assistance of the ionization by backside solvent approach is severely hindered[17] by the three alkyl groups attached to C_α in (III) and by hydrogens belonging to β-CH_3 groups in neopentyl derivatives (II, R = CH_3). This steric hindrance to solvation should be even greater in (II) than in (III), as hydrogens on β-CH_3 groups are better able to interfere with such an attack than are those attached to α-CH_3 groups.[16b] Furthermore, increased branching produced by successive replacement of H by alkyl groups on β-CH_3 (C_γ branching) should further decrease the possibility of interaction of solvent with the leaving group and the reaction center.

In spite of the minimization of certain common modes of electronic interaction which facilitate carbonium ion formation, the reaction rate increased with each successive substitution on C_γ many times faster than would be predicted on the basis of a simple additivity effect (1.0, 2.4, 4.8, 7.2) as compared with that actually observed (1.0, 2.4, 7–8, 34).

It appears that the observed sequence of rates is explained best by a combination of two effects, *i.e.*, the release of steric strain through participation of neighboring carbon. Unlike the series of chlorides (III), all of the brosylates (II) gave completely rearranged products, a fact which suggests that some degree of carbon participation be present in all cases.[11d]

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(13) H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson, and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 1 (1953).

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

(16) (a) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 521. (b) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, pp. 404–406.

(17) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

Furthermore, rearrangement studies, which are complete with all members of the series except t-C_4H_9, show CH_3 migration to be greater than that of R and exceeding the ratio predicted on a strictly statistical basis.[18] This suggests participation of the migrating group in ion-pair formation to give a transition state with some degree of non-classical ion character (IV),[11d] as CH_3 would be better able than R to not only stabilize (IV) by hyperconjugation but also to fulfill the steric

IV
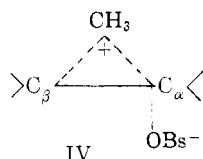
requirement for coplanarity with C_α and C_β as well. This explanation was advanced by Cram and Knight[8d] to account for the ability of CH_3 to compete with phenyl and to exceed C_2H_5 in migratory aptitude during acetolysis of the 3,4-dimethyl-4-phenyl-3-hexyl system.

The most stable conformation for (II) would appear to be (V), especially for those members where R is relatively highly branched. This disposition of groups is favorable for R migration while the somewhat less stable conformation

V   VI
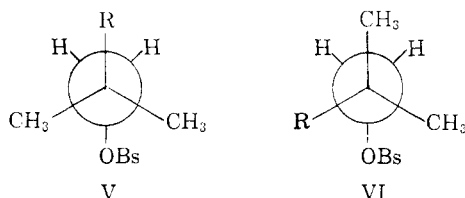
(VI) is favorable for CH_3 migration. The fact that CH_3 migration predominates over that of R[18] may result from rotation about the C_α — C_β axis as the C_α — OBs bond distance increases, the energy barrier for such a rotation being more than compensated by the increased stabilization of the transition state made possible (IV). That portion of the rearrangement involving migration of R rather than CH_3 would be expected on the above basis to involve a lesser degree of participation and might even proceed through an essentially open type of carbonium ion, as has been postulated for the rearrangement of neopentyl halides in wet formic acid.[10b]

The second effect which appears to contribute to the observed rate acceleration may be attributed to a relief of B-strain, made possible by participation in the transition state (IV). Spitzer and Pitzer,[19] as well as Brown and Bonner,[12] estimated steric strains in branched hydrocarbon structures (as compared to the n-isomer) from heats of formation. These values were reported to represent the

degree of destabilization of the hydrocarbon resulting from non-bonding interaction on adjacent carbon atoms and would be expected to be approximately the same for functional derivatives of the hydrocarbons. By application of these values (Table III) for steric strain to related brosylate structures in the present series (II), as did Brown for the tertiary chlorides,[12] the same increase in strain paralleling increases in reaction rate are noted.

TABLE III

STERIC STRAINS IN HYDROCARBONS CORRESPONDING TO $RC(CH_3)_2CH_2OBs$

R	Hydrocarbon	Steric Strain,[a] Kcal./Mole
CH_3	2,2-Dimethylpropane	−0.1
C_2H_5	2,2-Dimethylbutane	0.2
n-C_3H_7	2,2-Dimethylpentane	0.2[b]
n-C_4H_9	2,2-Dimethylhexane	0.7[b]
i-C_3H_7	2,2,3-Trimethylbutane	2.2
i-C_4H_9	2,2,4-Trimethylpentane	2.5[b]
t-C_4H_9	2,2,3,3-Tetramethylbutane	5.0

[a] Ref. 19. [b] Ref. 12.

The relative rate of acetolysis (4.1) for the i-C_4H_9 brosylate (two C_δ branches) appears to be explained adequately by the above combination of effects. The strain (2.5 kcal.) indicated in the corresponding hydrocarbon is approximately the same as that for the hydrocarbon which corresponds to the i-C_3H_7 member (two C_γ branches) and a sizable rate enhancement resulting from release of B-strain should be expected. The crowding and resulting strain arise chiefly from interaction of groups on C_α and C_β with the two CH_3 groups which correspond to C_ϵ and not so much from interactions associated with adjacent carbons. While these interactions appear to be steric in origin, an electronic consequence which could contribute to stabilization of the transition state and to rate enhancement would involve a bridging between C_α and C_ϵ by the six hydrogen atoms attached to ϵ-carbon atoms. Such a picture would be an example of the general principle stated recently by Pauling that "an electron-deficient atom causes adjacent atoms to increase their ligancy to a value greater than the orbital number."[20]

The rate effect obtained with the i-C_4H_9 brosylate suggests that a similar investigation of the neopentyl member of the series (II) would be of interest. That study is now in progress.

The differences in ΔH^* and ΔS^* values (Table I) for the series are not pronounced. The greatest difference in ΔH^* exists between the CH_3 and t-C_4H_9 members and amounts to 3.7 kcal./mole which corresponds exactly to the difference noted in the tertiary chloride series (III) between the

(18) S. B. Mainthia, private communication.

(19) R. Spitzer and K. S. Pitzer, J. Am. Chem. Soc., 70, 1261 (1948).

(20) L. Pauling, The Nature of the Chemical Bond, third ed., Cornell University Press, Ithaca, N. Y., 1960, p. 363.

TABLE IV

PHYSICAL PROPERTIES OF R—C(CH$_3$)$_2$—CH$_2$—OH AND R—C(CH$_3$)$_2$—CH$_2$—OBs

R	R—C(CH$_3$)$_2$—CH$_2$—OH, Yield, %[a]	B.P. (Mm.) Obs.	B.P. (Mm.) Lit.	R—C(CH$_3$)$_2$—CH$_2$—OBs, M.P.
H	[b]	105–107	107[f]	28–29
Me	[b]	111–113	110–111[g]	69–70
Et	35	43–44 (10)	135–138[g]	35[n]
n-Pr	16	154	[h]	31[o]
i-Pr	10	156–157	157–158[i]	32
n-Bu	20	69–72 (10)	80–82 (14)[j]	63
sec-Bu	32[c]	71 (10)	[k]	22[p]
i-Bu	11	72–73 (15)	79–80 (23)[l]	47–48
t-Bu	[d]	149–151[e]	149–150[m]	83–84[q]

[a] Based on tertiary chloride. [b] Obtained commercially. [c] Based on isobutyronitrile. [d] Not determined because of volatility of alcohol. [e] M.p. [f] R. F. Brunel, *Ber.*, **44**, 1004 (1911). [g] J. B. Conant, C. N. Webb, and W. C. Mendum, *J. Am. Chem. Soc.*, **51**, 1249 (1929). [h] Not reported; however, Eastman Chemical Products, Inc. made available a product, b.p. 152–154°, after the synthesis had been carried out in the present work. [i] T. A. Ford, H. W. Jacobson, and F. N. McGrew, *J. Am. Chem. Soc.*, **70**, 3793 (1948). [j] Ref. (4) (c). [k] Unreported. [l] M. A. Davis and W. J. Hickinbottom, *J. Chem. Soc.*, 1998 (1957). [m] M.p., Ref. (30). [n] *Anal.* Calcd. for C$_{12}$H$_{17}$BrO$_3$S: C, 45.00; H, 5.31; Br, 24.65; S, 9.83. Found: C, 44.86; H, 5.29; Br, 24.92; S, 9.97. [o] *Anal.* Calcd. for C$_{13}$H$_{19}$BrO$_3$S: C, 46.55; H, 5.74; Br, 23.60; S, 9.53. Found: C, 46.57; H, 5.67; Br, 23.89; S, 9.55. [p] *Anal.* Calcd. for C$_{14}$H$_{21}$BrO$_3$S: C, 48.12; H, 6.06. Found: C, 48.30; H, 6.48. [q] *Anal.* Calcd. for C$_{14}$H$_{21}$BrO$_3$S: C, 48.12; H, 6.06. Found: C, 48.52; H, 6.47.

CH$_3$ and neopentyl members.[11e] In both series the structure of lower energy of activation was that having a completely branched C$_γ$. No rearrangement was noted with the neopentyl member of (III) which would suggest that carbon participation is of less importance here than in (II).

Although results obtained in the present study appear to correlate well with previous work on the tertiary chlorides, the relative contributions of B-strain and carbon participation to the rate increases noted cannot as yet be assessed.[21] The two effects may, in fact, merge in the reacting molecule and, according to Winstein,[10a] perhaps participation is a means of relief of steric strain.

EXPERIMENTAL[22]

Alkyl-substituted neopentyl alcohols. Neopentyl and isobutyl alcohols were obtained commercially. All other members of the series were synthesized with yields and boiling points listed in Table IV.

The C$_2$H$_5$, n-C$_3$H$_7$, n-C$_4$H$_9$, i-C$_3$H$_7$, and i-C$_4$H$_9$ members of the series were prepared by carbonation of the corresponding tertiary chloride, R—C(CH$_3$)$_2$Cl, in a Grignard reaction[23] and reduction of the carboxylic acid product with lithium aluminum hydride.[24] The sec-C$_4$H$_9$ and t-C$_4$H$_9$ members could not be prepared by this procedure because of isomerization at the tertiary chloride stage[11c] in the former and complete failure of the carbonation step in the latter.

2,2,3-Trimethyl-1-pentanol. The alkylation of 90 g. (1.3 moles) of isobutyronitrile by 137 g. (1.0 mole) of 2-bromobutane in liquid ammonia containing 35 g. (1.5 moles) of

sodium and 1.0 g. of ferric nitrate nonahydrate, was essentially that of Tieford, van Campen, and Shelton.[25] The nitrile fraction boiling at 170–175° amounted to 58 g. (46%). Refractionation gave dimethyl-sec-butylacetonitrile, b.p. 172.8° (765), n_D^{25} 1.41727.

Hydrolysis was carried out by heating 37.2 g. (0.29 mole) of the alkylated nitrile for 1 hr. in 68 g. of 75% sulfuric acid, followed by the addition of 42.8 g. of sodium nitrite.[26] The 2,2,3-trimethylpentanoic acid product, b.p. 145.0–145.5° (50 mm.), n_D^{25} 1.43298, amounted to 36.8 g. (89%). Reduction of the acid with lithium aluminum hydride[24] gave 78% conversion to 2,2,3-trimethyl-1-pentanol, b.p. 175° (768 mm.), n_D^{25} 1.43828.

Anal. Calcd. for C$_8$H$_{18}$O: C, 73.79; H, 13.9. Found: C, 73.20; H, 14.1.

2,2,3,3-Tetramethyl-1-butanol. Attempts were made to prepare 2,2,3,3-tetramethylbutanoic acid by carbonation of the corresponding tertiary Grignard reagent,[23] by oxidation of 5-(dimethyl-t-butylcarbinyl)-2-furoic acid,[27] and by oxidation of methyl triptyl ketone.[28] The yields in every case were too low to allow for production of the necessary quantity of the corresponding alcohol.

Methylation of t-butylacetonitrile as suggested by Newman[29] was successful. A suspension of 13.6 g. (0.35 mole) of sodamide in 300 ml. of liquid ammonia was cooled to −45° to −50° and 17 g. (0.17 mole) of t-butylacetonitrile dissolved in 20 ml. of anhydrous ether added. To this mixture was added 54.8 g. (0.38 mole) of methyl iodide during 20 min. After stirring for 15 hr. an additional quantity (0.38 mole) of the iodide was added. The mixture was stirred for 20 hr. and the ammonia evaporated on the steam bath. Sublimation of white crystals onto the walls of the vessel was observed during the evaporation. The residue was dissolved in an ether-benzene (3:2) mixture and in water. The organic layer was washed successively with 10% sodium thiosulfate solution, 2N hydrochloric acid, 5% sodium hydroxide solution, and saturated sodium chloride solution.

(21) E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Henry Holt and Company, New York, 1959, p. 586.

(22) Microanalyses by Huffman Microanalytical Laboratories, Wheatridge, Colo. Melting points were determined on a Fisher-Johns block and are uncorrected.

(23) M. S. Karasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, 1954, p. 913.

(24) W. G. Brown, *Org. Reactions*, **6**, 488 (1951).

(25) C. H. Tieford, M. C. van Campen, Jr., and R. S. Shelton, *J. Am. Chem. Soc.*, **69**, 2902 (1947).

(26) L. Tsai, T. Miwa, and M. S. Newman, *J. Am. Chem. Soc.*, **79**, 2530 (1957).

(27) T. Reichstein, H. R. Rosenberg, and R. Eberhard, *Helv. Chim. Acta*, **18**, 721 (1935).

(28) M. Stiles and R. P. Mayers, *J. Am. Chem. Soc.*, **81**, 1502 (1959).

(29) M. S. Newman, private communication.

After drying over anhydrous magnesium sulfate, the solvent was removed and the solid residue was crystallized from 95% ethyl alcohol to give a white crystalline material, m.p. 135–136°, in a sealed capillary tube. The yield was 3.5 g. corresponding to a 12% conversion to dimethyl-t-butyacetonitrile. Newman and coworkers report a meeting point of 133.6–134.2°.[29]

Hydrolysis of 3.5 g. (0.28 mole) of the nitrile was carried out according to the procedure of Tsai, Miwa, and Newman.[26] The white crystalline material, m.p. 197–199°,[26] obtained by recrystallization from petroleum ether (b.p. 60–90°) amounted to 2.5 g. (62%) of 2,2,3,3-tetramethylbutanoic acid.

Reduction of this acid with lithium aluminum hydride[24] gave a white crystalline material when recrystallized from petroleum ether. This substance melted at 149–151° in a sealed capillary tube, had a pronounced camphor-like odor and was very volatile.[30] The entire quantity of 2,2,3,3-tetramethyl-1-butanol was not isolated from ether solution because of its volatility and no yield was determined. This solution was used for preparation of the p-bromobenzenesulfonate.

Preparation of p-bromobenzenesulfonates. The p-bromobenzenesulfonates of II were prepared by the method of Brown and Nakagawa.[31] Melting points and analytical data are given in Table IV.

Rate measurements. The glacial acetic used was Baker Reagent grade having a water concentration of 0.055M. The water content was determined by the Karl Fisher procedure according to the dead-stop titration method and utilized a Beckman Zeromatic pH meter fitted with a polarizing jumper and two platinum electrodes. In order to determine whether the concentration of water were a significant factor in determination of the magnitude of the rate constants, a run was made at 59.7° on the i-C$_4$H$_9$ member of the series (II) in acetic acid which had been refluxed for 9 hr. with excess acetic anhydride and distilled. This acid had a water concentration of 0.0025M and gave a rate constant of 1.20 × 10^{-7} as compared to a value of 1.61 × 10^{-7} determined in the untreated solvent. This slight change in rate for a relatively large change in water concentration indicates that the latter is not a significant factor, at least over this particular range in concentration.

Rate measurements were carried out by the ampoule technique previously described[32] and the liberated p-bromobenzenesulfonic acid determined by a potentiometric

titration[33] with standard solutions of sodium acetate in glacial acetic acid. The reaction was followed to from 12% (for C$_2$H$_5$ member) to 90% (for t-C$_4$H$_9$ member) completion at 59.7°, to more than 70% completion at 74.6° and to more than 80% completion at 90.9°. The values for k_1 (Table I) showed an average deviation of from 1–4%. Table V gives typical data obtained in the determination of k_1.

TABLE V

ACETOLYSIS OF 2,2,4-TRIMETHYL-1-p-BROMOBENZENESULFONATE (ROBs) AT 74.6°

Time, 10^5 Sec.	ROBs, M	10^6k_1, Sec.$^{-1}$
0	0.0348	
3.21	0.0251	1.02
5.72	0.0197	0.99
8.53	0.0145	1.03
9.19	0.0138	1.01
11.8	0.0109	0.98
15.3	0.0074	1.01
	Mean	1.01 ± 0.01

Plots of log k_1 vs. 1/T for each of the brosylates gave good straight lines from which the slopes were determined by the method of least squares.[34] ΔH* was derived in the usual way and ΔS* determined by use of the Eyring equation.[35]

(30) F. C. Whitmore, R. E. Marker, and L. Plambeck, *J. Am. Chem. Soc.*, **63**, 1626 (1941).

(31) H. C. Brown and M. Nakagawa, *J. Am. Chem. Soc.*, **77**, 3614 (1955).

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