most rapid, and leads to both the pinacol and the hydrol. The decrease in pinacol to ~0 at high pH would then depend on decomposition of pinacol, or possibly, on disproportionation of two radical ions.

The σ value of p-SO_3^- is +0.09[35] and this substituent leads to results similar to p-CO_2^-, Figure 2, 50% conversion of ketyl to hydrol at pH ~9 and slow decomposition of pinacol at pH 10, too slow to account for the observed yield of hydrol.

The p-$(CH_3)_3N^+$ group has a σ value of 0.82.[35] It led to further decrease in stability of the pinacol to alkali, and to 68% conversion of ketyl to pinacol at pH 8.0. The pinacol was stable under these conditions and the hydrol was formed directly, presumably by disproportionation of ketyl radical anion with ketyl radical. If ρ for dissociation of ketyl radicals is ~1, pK_a for the quaternary ammonium substituted ketyl is ~8.4 and it is ~80% dissociated at pH 8. Combination and disproportionation of radical anion, zwitterion in this case, with ketyl radical appear to occur in a ratio of about 2:1.

Neither charged substituents nor alkali are required for photoreduction to hydrols. Decafluorobenzophenone is photoreduced in 2-propanol to the hydrol,[36] and largely to the pinacol by 2-propanol in perfluorocyclohexane.[37] The pinacol does decompose to ketone and hydrol in 2-propanol[37] and it is not clear whether hydrol is formed in the photoreduction directly or *via* the pinacol. Disproportionation of the ketyl moieties might occur as the electronegative fluorine substituents increase the acidity of the ketyl radical and may lead to reactions of the radical anion in 2-propanol. The substituents may also make the dimeric product less stable and less readily formed.[34] Di(4-pyridyl) ketone also leads to the hydrol on photolysis in 2-propanol.[38] Presence of the pyridyl groups may lead to reactions of the radical anions and disproportionation, or they may weaken the central bond of the pinacol and facilitate its decomposition.

Acknowledgment. This work was supported by the U. S. Atomic Energy Commission Grants AT(30-1) 2448 and AT(11-1) 3118.

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Competitive Ar_1-5 and Ar_2-6 Participation in the Formolysis of 4-Aryl-*n*-butyl *p*-Bromobenzenesulfonates[1]

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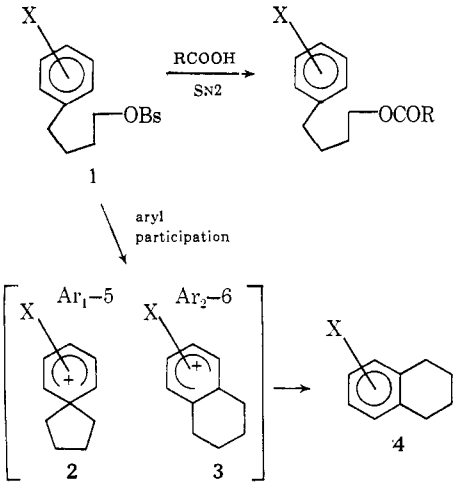
Abstract: The mechanism of aryl participation in the formolysis of 4-aryl-*n*-butyl *p*-bromobenzenesulfonates has been elucidated by the study of suitably deuterated substrates. The formolysis of 4-(*p*-methoxyphenyl)-*n*-butyl-2,2-d_2 *p*-bromobenzenesulfonate proceeded 74.2% by Ar_1-5 and 25.8% by Ar_2-6, in contrast to earlier assumptions of an exclusive Ar_1-5 pathway. The formolysis of the bromobenzenesulfonate of 4-(*p*-tolyl)-*n*-butyl-3,3,4,4-d_4 alcohol was also investigated, and in this system the Ar_2-6 pathway was shown to be preferred (69.4%). It is concluded that Ar_2-6 is inherently preferred over Ar_1-5, but not to so large an extent as to explain the complete specificity of cycloacylation reactions. The hydrogen–deuterium kinetic isotope effects for chromic acid oxidation of 6-methyltetralin to 6- and 7-methyl-α-tetralones were determined to be 3.4 and 3.8, respectively.

The first systematic study of aryl participation across five or six bonds was undertaken in 1956–1957 by Winstein and coworkers, who investigated the solvolysis reactions of 4-aryl-*n*-butyl *p*-bromobenzenesulfonates, **1**.[3–5] Acetolysis or formolysis of **1**, X = H, led largely to the corresponding open-chain ester, formed by a simple SN2 reaction. The rate for this anchimerically unassisted solvolysis was designated k_s. However, with a suitably activated substrate (*e.g.*, **1**, X = *p*-OCH_3) a rate enhancement in the removal of the leaving group was observed, the increase in rate being



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(4) (a) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3105 (1957); (b) *ibid.*, **79**, 3114 (1957).
(5) In an independent study, Corey and Sauers investigated the solvolysis of 4-aryl-*n*-butyl and 5-aryl-*n*-pentyl arylsulfonates.[6a] The assisted pathways were viewed as models for the transition state for electrophilic aromatic substitution and were assumed to be Ar_1-5 and Ar_1-6, respectively.

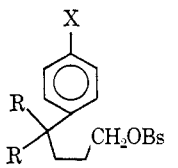
solely attributed to aryl participation. The rate constant for the assisted solvolysis was designated k_Δ, and thus the total rate constant for any given solvolysis could be expressed as $k_s + k_\Delta$, provided k_s was independent of the nature of the substitution on the phenyl ring.

Aryl participation was further evident from the composition of the reaction products, where cyclic compounds of the type **4** were formed in amounts directly related to k_Δ. Thus, the percentage of tetralin formed for a series of substrates **1** was found to agree well with the percentage of assisted solvolysis, $100k_\Delta/(k_s + k_\Delta)$, indicating that the dissection of total rates into assisted and unassisted pathways, and the equating of these pathways to the type of products formed, was a valid procedure.[4]

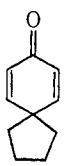
In discussing the actual mechanism of aryl assistance in these reactions, Winstein proposed two possible modes of participation, **2** and **3**. In **2**, the C-1 atom of the aromatic ring is implicated directly in the anchimeric assistance, leading to a transient 5-carbon ring; accordingly, such a process is symbolized Ar_1-5. A similar Ar_1-5 intermediate was postulated by Letsinger and Lansbury in 1956 to explain the isomerization of 8-benzhydryl-1-naphthoic acid under Friedel–Crafts conditions, *via* a 1,5 phenyl migration, to a cyclic hemiketal.[6b] The alternative mechanism, involving the aromatic C-2 with formation of a six-membered ring, **3**, is designated Ar_2-6.

There is no further direct evidence for intermediates of type **2** and **3**, and recent attempts to observe them in SbF_5–SO_2 at $-70°$ have failed.[7] Thus, 4-(*p*-methoxyphenyl)-*n*-butyl chloride did not yield **2** (X = *p*-OCH_3), but rather the observed nmr spectrum was compatible with the 1-(*p*-methoxyphenyl)-*n*-butyl cation. Nevertheless, such results in a medium known to stabilize free carbonium ions are perhaps less than relevant to the solvolysis reactions, particularly in the absence of a study of the products from quenching experiments.

With regard to which of the two modes of participation (Ar_1-5 and Ar_2-6) would be preferred, the assumption was made that when X is a para-activating group (*e.g.*, *p*-OCH_3, 2,4-$(OCH_3)_2$) the Ar_1-5 route would operate,[4a] whereas Ar_2-6 would be the pathway when the C-2 is activated (*e.g.*, X = *m*-OCH_3, 3,5-$(OCH_3)_2$).[4b] Indeed, because of the necessary rearrangement of **2** in the formation of products, it is clear that provided **2** has a plane of symmetry passing through the spiro carbon atom and the para position, it must rearrange *via* **3** and thus no distinction between the two mechanisms is possible. A distinction was possible, however, in the formolysis of 4-(*p*-methoxyphenyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate (**5a**), which was reported[3] to yield a cyclic product consisting "almost entirely" of 1,1-dimethyl-7-methoxytetralin, thereby implicating Ar_1-5 as the sole mechanism of participation (and the $(CH_3)_2C$- end of the chain as the exclusive migrating group). Subsequently, further evidence for the Ar_1-5 pathway was found in very favorably activated cases, namely in the formation of the spirodienone **6**[8] from the phenoxide ion **5b**,[9] and in related systems.[10,11]



5a, R = CH_3; X = OCH_3
b, R = H; X = O^-



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In contrast to these findings, there is absolutely no evidence for the involvement of the Ar_1-5 pathway in the cycloacylation of 4-phenyl-*n*-butyric acids and their derivatives, even in suitably activated systems.[13] For example, 7-methoxy-α-tetralone is the sole product of cycloacylation of 4-(*p*-methoxyphenyl)-*n*-butyric acid, with no trace of the product arising from the Ar_1-5 intermediate being discernible. It is therefore possible that the mechanism Ar_1-5 is inherently less favorable than Ar_2-6 and only occurs in reactions which are highly dependent on activation by substituents, or in which special conformational effects, such as might prevail in **5a**, play a dominant role. We now present evidence that the Ar_2-6 transition state is more favorable but not to an extent sufficient to account for the complete specificity of cycloacylation. Our findings are in agreement with the recently reported work of Winstein and Heck,[14] which appeared subsequent to the preliminary publication of our results.[1] Furthermore, their reinvestigation of the formolysis of **5a** disclosed that the cyclization did not proceed entirely by the Ar_1-5 route (see Discussion).

Results

Syntheses and Solvolyses. We chose to study the formolyses of the *p*-bromobenzenesulfonates **7** and **8**. The approach to **7** proceeded *via* Clemmensen reduction of 3-(*p*-toluoyl)propionic acid, using a D_2O–DCl medium. Mass spectrometry clearly showed that the resultant 4-(*p*-tolyl)-*n*-butyric acid contained four deuterium atoms, and nmr indicated that the deuteriums were incorporated into the 3 and 4 positions. Thus, the rate of enolization of the ketone group is competitive with its reduction, and 4-(*p*-tolyl)-*n*-butyric-*3,3,4,4-d*$_4$ acid results. Reduction of the methyl ester of this compound with lithium aluminum hydride led to 4-(*p*-tolyl)-*n*-butyl-*3,3,4,4-d*$_4$ alcohol. By mass spectral analysis the "d_4" alcohol was shown to have an overall deuteration of 3.77 ± 0.01 D/molecule, the composition being 12% d_5, 61% d_4, 19% d_3, and 8% d_2 species. The d_5 species reflects the fact that under the acidic reaction conditions used to introduce the deuterium, some exchange had also occurred in the aromatic region, and nmr integration confirmed the fact

(6) (a) E. J. Corey and C. K. Sauers, *J. Amer. Chem. Soc.*, **79**, 248 (1957); (b) R. L. Letsinger and P. T. Lansbury, *ibid.*, **78**, 2648 (1956).
(7) B. G. Ramsey and J. Cook, *Tetrahedron Lett.*, 535 (1969).
(8) An example of an Ar_1-6 process leading to spiro[5.5]undeca-1,4-dien-3-one, a homolog of **6**, has also been reported; A. S. Dreiding, *Helv. Chim. Acta*, **40**, 1812 (1957).
(9) (a) S. Winstein and R. Baird, *J. Amer. Chem. Soc.*, **79**, 756 (1957); (b) R. Baird and S. Winstein, *ibid.*, **84**, 788 (1962).
(10) (a) S. Dorling and J. Harley-Mason, *Chem. Ind. (London)*, 1551 (1959); (b) S. Masamune, *J. Amer. Chem. Soc.*, **83**, 1009 (1961).
(11) R. Barner, A. S. Dreiding, and H. Schmid, *Chem. Ind. (London)*, 1437 (1958). Described therein is an example of Ar_1-5 participation across a (boat) cyclohexane. Consequently, Ar_1-5 as well as Ar_2-6 must be considered as possible mechanisms for the acid-catalyzed conversion of 1-chloro-4-phenylcyclohexene to 1-chloro-1,4-ethano-1,2,3,4-tetrahydronaphthalene.[12]
(12) V. R. Haddon and L. M. Jackman, unpublished results.
(13) (a) S. Sethna in "Friedel-Crafts and Related Reactions," Vol. 3, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, p 911; (b) W. S. Johnson, *Org. React.*, **2**, 114 (1944).
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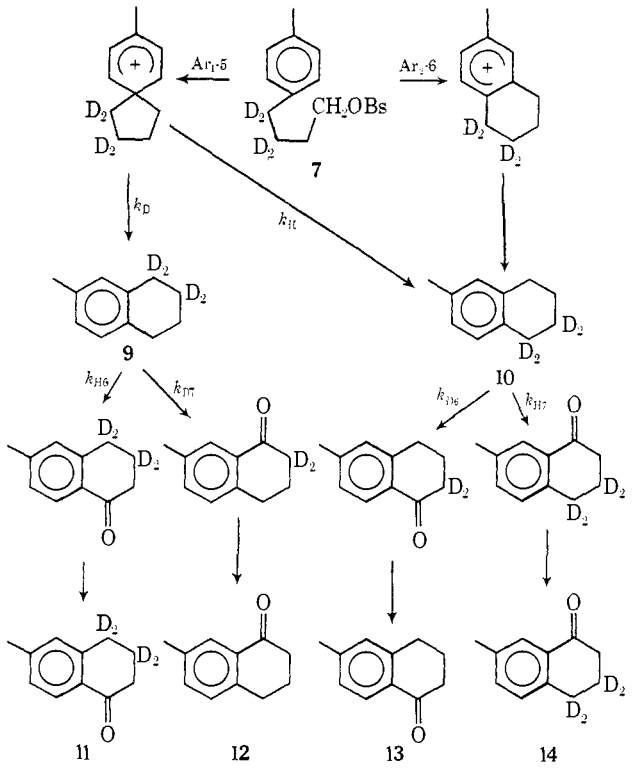


Figure 1. The route from 4-(*p*-tolyl)-*n*-butyl-*3,3,4,4-d*$_4$ *p*-bromobenzenesulfonate to deuterated 6- and 7-methyl-α-tetralones.

that approximately 0.3 D/molecule had been incorporated into the aromatic ring. Although the presence of deuterated species ranging from d_5 to d_2 in this molecule rendered the mass spectral patterns more complicated, a full analysis was still possible. The alcohol was converted to its *p*-bromobenzenesulfonate **7**, which was shown to have a deuterium content identical with that of the alcohol.

The synthesis of 4-(*p*-methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ alcohol began with the commercially available 3-(*p*-methoxybenzoyl)propionic acid, which was subjected to Clemmensen reduction and esterification with diazomethane to yield methyl 4-(*p*-methoxyphenyl)-*n*-butyrate. Base-catalyzed exchange of the protons in the 2 position of the ester was affected in methanol-d_1 solution at 60°. The 4-(*p*-methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ alcohol resulting from lithium aluminum hydride reduction of the deuterated ester was shown to contain 1.94 ± 0.01 D/molecule, present as approximately 95% d_2, 4% d_1, and 1% d_0 species. The *p*-bromobenzenesulfonate, **8**, was found to have a deuterium content identical with that of the parent alcohol. The solvolyses of **7** and **8** were carried out under Winstein's conditions and the mixtures of 6-substituted tetralins and formate esters so obtained were converted by lithium aluminum hydride reduction to mixtures of the tetralins and the corresponding 4-aryl-*n*-butyl alcohols.

The ratio of tetralin to alcohol in each mixture was determined by vapor phase chromatography (glc). The mixture derived from 4-(*p*-methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ *p*-bromobenzenesulfonate contained 54% 6-methoxytetralin and 46% alcohol, which agrees with the reported[4] product distribution in the undeuterated case. The 4-(*p*-tolyl)-*n*-butyl-*d* *p*-bromobenzenesulfonate yielded a mixture containing 33% 6-methyltetralin. The diminished amount of cyclized product reflects the decreased activation of the aromatic ring to stabilization of a positive charge, and can be compared to the 4-phenyl analog, which affords only 19% cyclized product.[4] The percentage of tetralin formed can be equated to $100k_\Delta/(k_s + k_\Delta)$. Accepting the literature value[4] of k_s as 2.78×10^{-5} at 75° in formic acid, it follows that the k_Δ for assisted formolysis of 4-(*p*-tolyl)-*n*-butyl *p*-bromobenzenesulfonate is 1.36×10^{-5} at 75°. This can be compared with the 4-(*p*-methoxyphenyl) analog, for which k_Δ equals 3.30×10^{-5}.[4]

In each case, separation of the tetralin and alcohol could be affected. The alcohols were analyzed by mass spectrometry and in each case were seen to contain precisely the same *amount* of deuterium as the starting alcohols. Furthermore, the *position* of the deuterium was unchanged, as shown unequivocally by nmr. If Ar_1-5 participation is involved, this lack of deuterium scrambling establishes the irreversibility of the formation of the Ar_1-5 intermediate, as ring opening of such as intermediate would have led to scrambling between the 1 and 4 (and the 2 and 3) positions. This result is in accord with the conclusions of Friedrich and Winstein[15] drawn from a study of the solvolysis of certain spirodienyl *p*-nitrobenzoates, which indicated that the ring expansion of the Ar_1-5 intermediate was very much faster than ring opening or solvolysis.

Attention was next directed to the tetralin products. The total tetralin component from the solvolysis of 4-(*p*-methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ *p*-bromobenzenesulfonate (**8**) was shown by mass spectral analysis to contain the same deuterium content as its precursors (1.94 ± 0.01 D/molecule). The tetralin component from solvolysis of **7**, however, contained 3.74 ± 0.01 D/molecule, present as 8% d_5, 66% d_4, 19% d_3, 6% d_2, and 1% d_1 species (*cf.* **7**, 3.77 D/molecule, present as 12% d_5, 61% d_4, 19% d_3, and 8% d_2). The difference, small but significant, reflects some loss of the aromatic deuterium upon ring closure. If all d_5 species are assumed to contain only one aromatic deuteron, distributed statistically over the four available aromatic positions, formation of tetralin would result in loss of a quarter of these d_5 species to yield additional d_4 species. The resulting composition, 9% d_5, 64% d_4, 19% d_3, and 8% d_2, 3.74 D/molecule, is very similar to that observed for the "d_4" tetralin, the difference being within the experimental error. This partial loss of the (spurious) aromatic deuterium does not affect the subsequent analysis, provided the tetralin deuterium content of 3.74 ± 0.01 D/molecule (and not starting alcohol content of 3.77) is taken as the standard to be compared with the ultimate tetralone deuterium content (see below).

Mechanistic Analysis. (a) The *p*-Methyl System (7). The fraction of Ar_1-5 participation in the *p*-methyl system is directly related to the relative amounts of the deuterated tetralins **9** and **10** formed (see Figure 1). Nnr was not suitable to distinguish between **9** and **10** as the absorptions of the 1 and 4 protons of 6-methyltetralin overlap. The method chosen for this purpose was the known[16] oxidation of 6-substituted tetralins to the corresponding 6- and 7-substituted α-tetralones.

(15) E. C. Friedrich and S. Winstein, *Tetrahedron Lett.*, 475 (1962).
(16) L. M. Jackman and D. T. Thompson, *J. Chem. Soc.*, 4794 (1961).

The relative amounts of the four possible ketones formed (**11**, **12**, **13**, and **14**, see Figure 1) depend on the relative amounts of **9** and **10**, and on k_{H6} and k_{H7}, the rate constants for formation of the 6- and 7-methyltetralones, respectively, and on k_{D6} and k_{D7}, the rate constants for oxidation *at the position of deuteration* to yield the 6- and 7-methyltetralones, respectively. The quantities k_{H6}/k_{D6} and k_{H7}/k_{D7} correspond to the primary isotope effect for oxidation at the 1 and 4 positions of 6-methyltetralin, respectively; a further discussion of these quantities is given below.

The relationship between product ratios and the fraction of Ar_i-5 participation is shown in eq 1, where k_H and k_D give a measure of the relative migratory aptitudes of the CH_2CH_2 and CD_2CD_2 portion of the alkyl chain in the Ar_i-5 intermediate.

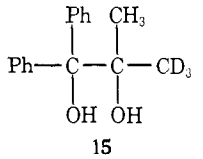
$$\frac{\mathbf{10}}{\mathbf{9}} = \frac{\mathbf{13}+\mathbf{14}}{\mathbf{11}+\mathbf{12}} = \frac{1-\left(\frac{k_D}{k_H+k_D}\right)Ar_i\text{-}5}{\left(\frac{k_D}{k_H+k_D}\right)Ar_i\text{-}5} \quad (1)$$

The chromium trioxide–acetic acid oxidation on the mixture of **9** and **10** was carried out under carefully controlled conditions designed to avoid oxidation of the ketonic products. The ratio of the 6 to 7 isomers was determined by planimeter integration of their respective glc peaks to be 1.4:1. The resulting mixture of four tetralones was subjected to acid-catalyzed exchange to convert any d_2 species to d_0. The subsequent mass spectral analysis was thereby simplified as the resulting tetralones, **11**, **12**, **13**, and **14**, had either the full compliment of deuterium or none at all. Separation of the 6- and 7-methyl-α-tetralone products was accomplished using preparative glc, whereby large amounts of both isomers were obtained completely pure.

The 6-methyl-α-tetralone component was shown by mass spectral analysis to contain 0.91 ± 0.01 D/molecule. Such a deuterium content results from a mixture of 6-methyl-α-tetralone-d_0 (**13**; 75.7%) and 6-methyl-α-tetralone-*3,3,4,4*-d_4 (**11**, containing 3.74 ± 0.01 D/molecule as in the tetralin precursor; 24.3%).

Mass spectral analysis of the 7-tetralone component indicated that it contained 3.64 ± 0.01 D/molecule, corresponding to 97.4% of **14** (having the same deuterium content as the tetralin precursor, *i.e.*, 3.74 D/molecule) and 2.6% of the d_0 species, **12**.

Combining these results with the product ratio result, the following product analysis was possible: **11**, 14.2%; **12**, 1.1%; **13**, 44.1%; **14**, 40.6%. Thus eq 1 could be solved, provided a reasonable estimate of the isotope effect for rearrangement of the Ar_i-5 intermediate could be made. Such an estimate is provided by the work of Schubert and LeFevre[17] who studied the conversion of the diol **15** to the ketone **16** and found the



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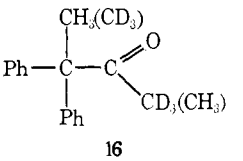

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ratio of rate constants for CH_3 *vs.* CD_3 migration in this system to be 1.2. In our case the comparison is between the more similar CH_2R and CD_2R groups where R is an alkyl group, and it is expected that a value of 1.2 should represent an upper limit. Using values of 1.0, 1.1, and 1.2 for k_H/k_D, the amount of Ar_i-5 participation was calculated according to eq 1 and the results as summarized in Table I indicate that Ar_i-5 is the minor pathway of aryl participation in this system.[18]

Table I. The Percentage of Ar_i-5 Participation in the Formolysis of 4-(*p*-Tolyl)-*n*-butyl-*3,3,4,4*-d_4 *p*-Bromobenzesulfonate with Varying k_H/k_D[a]

k_H/k_D	Ar_i-5 (%)
1.0	30.6
1.1	32.1
1.2	33.6

[a] k_H/k_D is the (secondary) isotope effect for the rearrangement of the Ar_i-5 intermediate from **7**.

In view of the importance of the chromic acid oxidation of 6-methyltetralin to our analysis, an investigation of the kinetic isotope effects for formation of the 6- and 7-methyl-α-tetralones was undertaken. The ratios of 6 to 7 isomers formed from oxidation of pure 6-methyltetralin-d_0 was determined by glc to be 3.7:1 ($= k_{H6}/k_{H7}$). Similar product ratio studies on the oxidation of 6-methyltetralin-*3,3,4,4*-d_4 (see Experimental Section) yielded a value for k_{H6}/k_{D7} of 14. Thus the isotope effect for oxidation in the 4 position to yield 7-methyl-α-tetralone was determined according to eq 2 to be 3.8.

$$k_{H7}/k_{D7} = (k_{H7}/k_{H6})(k_{H6}/k_{D7}) \quad (2)$$

The isotope effect for oxidation in the 1 position to yield 6-methyl-α-tetralone (k_{H6}/k_{D6}) was available from product ratio studies and from the relative amounts of tetralones **13** and **14** formed in the course of the solvolysis experiment (see Figure 1). Substituting the value 0.93 for k_{H7}/k_{D6} in eq 3, the value 3.4 for this isotope

$$k_{H6}/k_{D6} = (k_{H6}/k_{H7})(k_{H7}/k_{D6}) \quad (3)$$

effect results. The magnitude of these two isotope effects indicates that cleavage of the carbon–hydrogen bond is rate determining, which is consistent with observations on similar oxidations of arylalkanes.[19] It should be noted that the value of k_{H6}/k_{D7} derived from product ratios on direct oxidation agrees exactly with the product distribution (**11**/**12**) from the solvolysis experiment, thereby providing a check on the soundness of the mechanistic analysis.

(b) The *p*-Methoxy System (8). 4-(*p*-Methoxyphenyl)-*n*-butyl-*2,2*-d_2 *p*-bromobenzenesulfonate could yield two possible participation products, 6-methoxytetralin-*2,2*-d_2 (**17**) and 6-methoxytetralin-*3,3*-d_2 (**18**). Nmr was inadequate to distinguish between **17** and **18** as the resonances of the 2 and 3 protons appeared as one complex band. The oxidation of these tetralins by

(17) W. M. Schubert and P. H. LeFevre, *J. Amer. Chem. Soc.*, **91**, 7746 (1969).

(18) This result differs somewhat from that reported in the preliminary communication of this work,[1] where the analysis was based on solvolysis experiments on 7 and on 4-(*p*-tolyl)-*n*-butyl-*1,1*-d_2 *p*-bromobenzenesulfonate. At the suggestion of a referee, it was deemed preferable to base the analysis entirely on the more reliable results of the d_4 system.

(19) (a) K. B. Wiberg in "Organic Chemistry," Vol. 5-A, A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1965, p 69; (b) K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960).

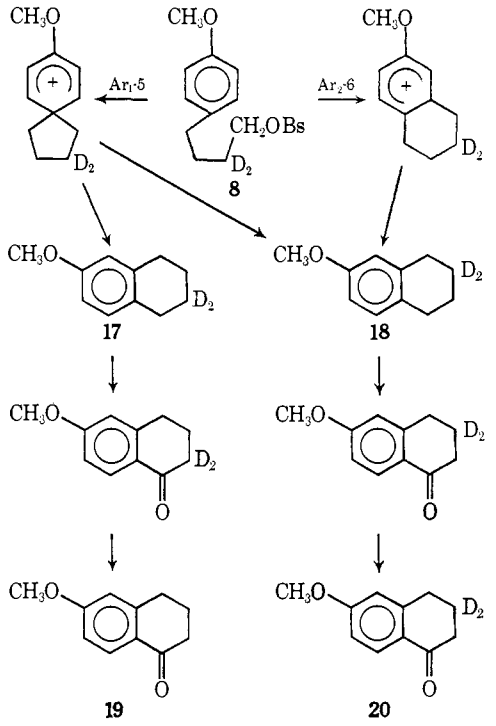


Figure 2. The route from 4-(*p*-methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ *p*-bromobenzenesulfonate to deuterated 6-methoxy-α-tetralone.

chromium trioxide in acetic acid was again the method of choice (see Figure 2). The presence of the strongly para-directing methoxy group resulted in 6-methoxy-α-tetralone being almost the exclusive product (<0.5% of 7-methoxy-α-tetralone was formed), and the analysis was consequently greatly simplified. Furthermore, as a more remote position of deuteration had been chosen in this system, both **17** and **18** were expected to proceed to product at the same rate and no allowance for kinetic isotope effects in the oxidation was necessary. Care was taken to avoid oxidation of the ketonic products, and the resultant mixture of 6-methoxy-α-tetralone-*2,2-d*$_2$ and -*3,3-d*$_2$ was subjected to base-catalyzed exchange to yield 6-methoxy-α-tetralone-*d*$_0$ (**19**) and -*3,3-d*$_2$ (**20**). The deuterium content of the 6-tetralone could then be directly related to the fraction of Ar_1-5 participation according to eq 4. After one recrystallization to remove

$$\frac{\mathbf{20}}{\mathbf{19}} = \frac{1 - (Ar_1\text{-}5)/2}{(Ar_1\text{-}5)/2} \qquad (4)$$

traces of the 7-tetralone, the product was found to contain 1.22 ± 0.01 D/molecule, present as 62.9% 6-methoxy-α-tetralone-*3,3-d*$_2$ (**20** containing 1.94 D/molecule as in the arylsulfonate precursor) and 37.1% of the undeuterated tetralone **19**. Substitution of these values in eq 4 yields a value for the percentage of Ar_1-5 participation of 74.2%.

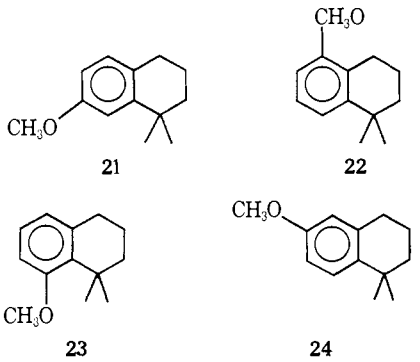
Discussion

By the approach outlined above, the relative importance of the Ar_1-5 and Ar_2-6 mechanisms in aryl participation during solvolyses of certain 4-aryl-*n*-butyl *p*-bromobenzenesulfonates has been determined. When the aryl group is *p*-tolyl, the Ar_2-6 pathway is favored, accounting for 69.4% of the participation. The Ar_2-6 mechanism has a twofold statistical advantage, but even with consideration of this factor, the ratio $k_{Ar_1\text{-}5}/k_{Ar_2\text{-}6}$ remains less than 1. In this system the Ar_1-5 and Ar_2-6 reactions are formally electrophilic attack at the positions para and meta to the methyl group, and as such can be compared with partial rate factors for electrophilic aromatic substitution in toluene. Stock and Brown[20] have compiled data on a series of 47 such reactions of toluene, and the ratio p_f/m_f (where p_f and m_f are the partial rate factors for para and meta substitution, respectively) range from 2.8 to 1000. The present ratio of 0.88 indicates that $RCH_2OSO_2C_6H_4Br$, although a poor electrophile, does not display a high selectivity for para substitution.

When the aryl group is *p*-methoxyphenyl, Ar_1-5 becomes the major pathway (74.2%), indicating that changes in substitution on the aromatic ring affect not only the extent of participation, but also its mechanism. The ratio of the rates, $k_{Ar_1\text{-}5}/k_{Ar_2\text{-}6}$ (again corrected for the statistical factor), is 5.75. This ratio reflects an extreme lack of substituent sensitivity in comparison with electrophilic aromatic substitution reactions of anisole. For a series of nine such reactions,[21] the ratio p_f/m_f varies between approximately 10^3 and 10^{10}.

Our findings indicate that the early assumption[4a] that participation in the 4-(*p*-methoxyphenyl)-*n*-butyl *p*-bromobenzenesulfonate formolysis proceeded entirely by Ar_1-5 is clearly incorrect. In view of our results for the *p*-tolyl system, where Ar_1-5 is a minor contributor, it would seem that the small amount of participation which occurs in the unactivated 4-phenyl series would be predominantly Ar_2-6. Furthermore, in those cases where substitution favors Ar_2-6, such as the 4-(*m*-methoxyphenyl)-*n*-butyl system, an exclusive Ar_2-6 mechanism is predicted.

These findings[1] and predictions have been supported in a recent paper by Winstein and Heck.[14] The formolysis of 4-(*m*-methoxyphenyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate yielded a tetralin mixture comprising 65% 1,1-dimethyl-7-methoxytetralin (**21**) and 35% 1,1-



dimethyl-5-methoxytetralin (**22**), both of which could arise from Ar_2-6 participation involving the aromatic carbons para and ortho to the methoxy group, respectively. From the infrared spectra, the authors judged that not more than 1% of the possible Ar_1-5 product, **23**, was present. It was concluded that the participation proceeded entirely by the Ar_2-6 pathway, although no mention was made of the other possible Ar_1-5 product, **24**, nor was it remarked that **21** and **22** could both arise from the Ar_1-5 pathway by rearrange-

(20) L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, 81, 3323 (1959).
(21) L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, 82, 1942 (1960).

ment involving the (less favorable) migration of the primary alkyl group.

The authors also reinvestigated the formolysis of 4-(*p*-methoxyphenyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate (**5a**) which earlier had been reported[3] to yield a tetralin product consisting "almost entirely" of the rearranged tetralin **21**. Upon reexamination,[14] the tetralin product was found to consist of a mixture of **24** (32%) and **21** (68%). A mechanistic interpretation of this result was complicated by the fact that 65% of the Ar_1-5 intermediate from **5a** opens to the tertiary carbonium ion. Suh an opening only becomes competitive with rearrangement when the carbonium ion so formed is tertiary (as in the proposed opening of certain Ar_1-4 and Ar_1-5 intermediates in the dehydration of primary phenyl alkanols to indans[22]). However, because control experiments indicated[14] that under the formolysis conditions the tertiary ion cyclizes exclusively to **21**, the **21** formed in formolysis of **5a** can only arise *via* an Ar_1-5 mechanism. Thus, neglecting the possibility of the Ar_1-5 intermediate rearranging by migration of the primary end of the chain to give **24** it can be inferred that the participation proceeds 32% by Ar_2-6 and 68% by Ar_1-5. Comparing these values with the solvolysis of the 4-(*p*-methoxyphenyl)-*n*-butyl case (26% Ar_2-6, 74% Ar_1-5), it appears that the mechanism is not altered dramatically by the presence of a *gem*-dimethyl group on the alkyl chain, although introduction of such a group does somewhat increase the extent of participation (54 to ~71%).[4a,14]

The question arises as to why Ar_2-6 is favored over Ar_1-5 as the mechanism of aryl participation in the systems studied. The participation of the aryl group involves the p-π orbital of the aromatic carbon concerned, and requires that the approach of the developing carbonium ion be in a direction perpendicular to the plane of the aromatic ring. Examination of molecular models suggests that a very close approach, without angle strain and with reasonable staggering of the methylene protons is possible for the Ar_2-6 intermediate. Ar_1-5 appears strainless when the aromatic and alkyl carbons are some distance apart, but closer approach is clearly associated with considerable Pitzer strain. The Ar_2-6 intermediate also enjoys increased stabilization of the positive charge by increased alkylation. An additional factor, which may well be the dominant one, is that Ar_1-5 formation requires attack at an aromatic position *which is already alkylated.* Although no study has been made of such an attack during electrophilic aromatic substitutions, it is expected to be unfavorable.

The combined factors which favor the Ar_2-6 pathway are not so compelling that they cannot be partly overcome by suitable substitution in the aromatic ring. Thus, the complete specificity of the cycloacylation reaction of 4-aryl-*n*-butyric acids and their derivatives requires further explanation. Although only Ar_2-6-type products are observed for these reactions, it is possible that the Ar_1-5 intermediate may be formed but that opening to the acylium ion (*cf.* the opening of the Ar_1-5 intermediate from **5a** to the tertiary carbonium ion) is preferred to rearrangement. Rearrangement would require either the unlikely migration of the carbonyl group, or migration of the alkyl group leaving a positive charge adjacent to the carbonyl group.

(22) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **36**, 1040 (1971).

Experimental Section

All melting points reported were obtained on a Hoover melting point instrument, and are uncorrected.

The mass spectral data were obtained using an AEI-MS 9 mass spectrometer at 70 eV.

All solvents used in the described experiments were distilled. The "light petroleum" used was that fraction boiling between 40 and 60°.

The analytical vapor phase chromatography (glc) data were obtained using a Perkin-Elmer 881 gas chromatograph, and preparative glc experiments were conducted using a Varian Autoprep 705.

The nuclear magnetic resonance (nmr) spectra, unless otherwise stated, were obtained on a Varian A-60 spectrometer, using CCl_4 as solvent and TMS as internal standard. The chemical shifts are quoted in ppm downfield from TMS.

4-(*p*-Tolyl)-*n*-butyric-*3,3,4,4-d*$_4$ Acid. A mixture of mossy zinc (3.4 g), mercuric chloride (0.5 g), concentrated deuterium chloride (0.2 ml; 99% isotopic purity, 38% in D_2O), and D_2O (3.2 ml, 99.5%+) was shaken for 5 min. The aqueous solution was decanted and the amalgamated zinc covered with D_2O (3.2 ml) and concentrated DCl (4.8 ml).

3-(*p*-Toluoyl)propionic acid (1.6 g)[23] was added to the freshly prepared zinc amalgam, and the mixture was refluxed vigorously for 10 hr in an apparatus equipped with a drying tube ($CaCl_2$). Additional concentrated DCl (0.5 ml) was added after 5 hr.

The resulting mixture was subjected to standard ether work-up to yield 4-(*p*-tolyl)-*n*-butyric-*3,3,4,4-d*$_4$ acid (1.3 g, 87%, mp 51–57°), the exact deuterium content of which follows from the mass spectrum of the corresponding alcohol; nmr δ 6.99 (s, 4 H, Ar) and 2.28 (bs, 5 H, CH_3, H_3).

4-(*p*-Tolyl)-*n*-butyl Alcohol. 4-(*p*-Tolyl)-*n*-butyric acid (1.3 g) was added portionwise to a solution of diazomethane (*ca.* 0.6 g, as prepared from 3.6 g of commercial Diazald) in ether (100 ml). The solution was allowed to stand for 0.5 hr and was then poured onto dilute HCl (200 ml). After separation, the ether layer was washed with dilute HCl (1 × 100 ml), water (1 × 100 ml), and a saturated solution of $NaHCO_3$ (1 × 100 ml). The solution was dried ($CaCl_2$), concentrated to *ca.* 50 ml, and then added directly to a stirred, refluxing solution of lithium aluminum hydride (0.3 g) in dry ether (25 ml). After refluxing for 5 hr, the mixture was subjected to standard ether work-up to yield 4-(*p*-tolyl)-*n*-butyl alcohol (1 g, 84%), which after distillation was shown to be pure by glc (SE-30, 225°): bp 130° (0.4 mm); $n^{21}D$ 1.5178 (*cf.* lit.[24] $n^{20}D$ 1.5200); nmr δ 6.98 (s, Ar), 4.17 (s, OH), 3.48 (m, CH_2OH), 2.52 (m, $ArCH_2$), 2.24 (s, CH_3), 1.8–1.3 (m, 4 H, $CH_2CH_2CH_2CH_2$).

4-(*p*-Tolyl)-*n*-butyl-*3,3,4,4-d*$_4$ Alcohol. 4-(*p*-Tolyl)-*n*-butyric-*3,3,4,4-d*$_4$ acid (2.5 g) was added portionwise to a solution of diazomethane (*ca.* 1.2 g, as prepared from 7.2 g of commercial Diazald) in ether (200 ml). The solution was allowed to stand for 0.5 hr, and then treated as described above. The resulting ether solution (100 ml) was added under nitrogen to a stirred, refluxing solution of lithium aluminum hydride (0.6 g) in dry ether (100 ml). After refluxing for 24 hr, the mixture was worked up in the standard fashion to yield 4-(*p*-tolyl)-*n*-butyl-*3,3,4,4-d*$_4$ alcohol (2 g, 87%), which was pure by glc (SE-30, 225°): nmr δ 6.98 (s, *ca.* 3.7 H, Ar), 3.67 (s, OH), 3.48 (t, CH_2OH), 2.26 (s, CH_3), 1.7–1.2 (m, *ca.* 2.3 H, $CD_2CD_2CH_2CH_2$). Integration of the spectrum in the vicinity of δ 2.52 indicated that there was not more than 0.2 H/molecule in position $ArCD_2$. It also followed from integration that not more than 0.3 H/molecule remained in position $ArCD_2CD_2$, and further that approximately 0.3 D/molecule was incorporated into the aromatic ring. (Overall deuteration was not <3.7 D/molecule.) Mass spectra: parent peak 168; base peak 107. By comparison with the mass spectra of the undeuterated alcohol the deuterium content of this product was seen to be 3.77 ± 0.01 D/molecule, present as approximately 12% d_3, 61% d_4, 19% d_3, and 8% d_2.

4-(*p*-Tolyl)-*n*-butyl *p*-Bromobenzenesulfonate. A solution of 4-(*p*-tolyl)-*n*-butyl alcohol (1 g) in anhydrous pyridine (20 ml) was cooled to *ca.* 10°. *p*-Bromobenzenesulfonyl chloride (2.5 g) in pyridine (7 ml) was added with stirring, and the solution was kept overnight at *ca.* 5°.

The reaction mixture was poured into 5% HCl (200 ml), and the product was extracted with ether (2 × 50 ml). The combined ether extracts were washed with dilute HCl (3 × 50 ml), water

(23) (a) S. Dev, *J. Indian Chem. Soc.*, **25**, 315 (1948); (b) E. de B. Barnett, and F. G. Sanders, *J. Chem. Soc.*, 434 (1933).

(24) P. Tsukervanik and C. S. Kadyrov, *Uzb. Khim. Zh.*, 45 (1960).

Table II. Summary of Oxidation Conditions for Various 6-Methyltetralins

d content of tetralin	[Tetralin], mol	[CrO_3], mol	H_2O, ml	Total acetic acid, ml	Time of reaction	Tetralin remaining, %	Product ratio[e]	Yield, %
3.74	0.0030	0.0080	0.3	10	11 days	0	1.4	46[a]
0[b]	0.0048	0.016	0.25	25	4 hrs	3	3.7 ± 0.2[c]	100[d]
					1 day	0	4.0 ± 0.2[c]	83[d]
					10 days	0	4.5 ± 0.2[c]	70[d]
4.39[b] (*3,3,4,4-d*$_4$)	0.0013	0.0026	0.13	13	1 hr	15	13.9 ± 1[c]	100[d]
					7 hrs	0	21.5 ± 2[c]	82[d]
					5 days	0	25 ± 2[c]	79[d]

[a] Isolated yield. [b] In the presence of a marker substance, *m*-dinitrobenzene. [c] Areas of glc peaks measured by planimeter. [d] Calculated with reference to marker substance. [e] Ratio of 6- to 7-methyl-α-tetralone formed.

(1 × 50 ml), and saturated $NaHCO_3$ solution (2 × 50 ml), and then dried ($MgSO_4$). Removal of the ether yielded an oily solid which crystallized on trituration with light petroleum. The solid was separated by filtration to yield the crude ester (2.3 g, 98%) which was recrystallized twice from ethyl acetate to afford pure 4-(*p*-tolyl)-*n*-butyl *p*-bromobenzenesulfonate as colorless crystals: mp 45.5–46.5°; exact mass spectrum (mass measurement by high-resolution mass spectrometer), 384.0218 and 382.0214 (calcd for $C_{17}H_{19}BrO_3S$, 384.0217 and 382.0236); nmr δ 7.65 (m, 4 H, Br-Ar), 6.94 (m, 4 H, Ar), 3.99 (m, CH_2O), 2.49 (m, $ArCH_2$), 2.28 (s, CH_3), 1.9–1.3 (m, 4 H, $CH_2CH_2CH_2CH_2$).

4-(*p*-Tolyl)-*n*-butyl-*3,3,4,4-d*$_4$ *p*-Bromobenzenesulfonate. 4-(*p*-Tolyl)-*n*-butyl-*3,3,4,4-d*$_4$ alcohol (2.0 g) was converted to its *p*-bromobenzenesulfonate (4.0 g, 87%) by the above method. The nmr and mass spectrum of the product reflected the same isotopic distribution as in the starting alcohol: nmr δ 7.66 (m, 4 H, Br-Ar), 6.97 (m, *ca.* 3.7 H, Ar), 4.00 (t, CH_2O), 2.28 (s, CH_3), 1.9–1.3 (m, *ca.* 2.3 H, $CD_2CD_2CH_2CH_2$).

Anhydrous Formic Acid. Commercial formic acid (97+%) was allowed to stand over boric anhydride for 2 weeks, distilled, and stored over molecular sieves (Linde type 4A). The water content of the acid so treated was determined by nmr integration.

Formolysis of 4-(*p*-Tolyl)-*n*-butyl *p*-Bromobenzenesulfonate. 4-(*p*-Tolyl)-*n*-butyl *p*-bromobenzenesulfonate (10 g) was added to a solution of dry sodium formate (2.1 g) in formic acid (400 ml, <0.4% H_2O by weight as determined by nmr) at 75°. The mixture was stirred at 75° for *ca.* 110 hr, by which time the *p*-bromobenzenesulfonate was shown to be absent (tlc, alumina–benzene). The cooled solution was poured into water (1 l.) and extracted with light petroleum (4 × 350 ml). The combined extracts were washed with water (2 × 300 ml) and aqueous $NaHCO_3$ (300 ml). After removal of the solvent by distillation, the crude mixture was dissolved in dry ether (50 ml) and added to a refluxing solution of lithium aluminum hydride (1 g) in dry ether (50 ml). The mixture was refluxed under nitrogen for 6 hr and then worked up in the usual manner. The product so obtained was shown by glc (SE-30, 235°) to consist of 6-methyltetralin (32%) and 4-(*p*-tolyl)-*n*-butyl alcohol (68%). The mixed product was chromatographed on alumina (250 g, Brockmann No. 1). Elution with pentane (*ca.* 700 ml) yielded 6-methyltetralin (0.8 g, 21%; pure by glc): nmr δ 6.78 (bs, Ar), 2.65 (m, H_1, H_4), 2.21 (s, CH_3), 1.72 (m, H_2, H_3).

Further elution with ether (*ca.* 800 ml) afforded 4-(*p*-tolyl)-*n*-butyl alcohol (2.35 g, 55%; pure by glc) whose nmr and mass spectral characteristics were identical with those described earlier for this compound.

Formolysis of 4-(*p*-Tolyl)-*n*-butyl-*3,3,4,4-d*$_4$ *p*-Bromobenzenesulfonate. The formolysis of 4-(*p*-tolyl)-*n*-butyl-*3,3,4,4-d*$_4$ *p*-bromobenzenesulfonate (4 g) was carried out in formic acid (150 ml, <0.3% H_2O) containing dry sodium formate (0.9 g), at 75°. The mixture was worked up and reduced with lithium aluminum hydride (0.4 g) to yield a crude mixture shown by glc (SE-30, 235°) to consist of 6-methyltetralin (33%) and 4-(*p*-tolyl)-*n*-butyl alcohol (67%). The mixture was chromatographed on alumina (250 g, Brockmann No. 1) and eluted with pentane (*ca.* 400 ml) yielding 6-methyltetralin-*d*$_4$ (0.5 g, 32%; pure by glc); mass spectrum parent peak 150; base peak 135. By comparison with the mass spectrum of the undeuterated tetralin, the isotopic composition was seen to be very similar to that of the starting alcohol (8% d_5, 66% d_4, 19% d_3, 6% d_2, and 1% d_1; 3.74 ± 0.01 D/molecule).

Further elution with methanol (*ca.* 400 ml) afforded 4-(*p*-tolyl)-*n*-butyl-*3,3,4,4-d*$_4$ alcohol (0.9 g, 52%; pure by glc), whose nmr and mass spectral characteristics were identical with those described earlier for this compound.

Oxidation of 6-methyltetralin-*d*$_0$ and -*d*$_4$ was accomplished by the general method described below for 6-methyltetralin-*d*$_4$. The amounts of reactants and time of reaction for each oxidation are summarized in Table II, together with product ratios and yields.

Chromium trioxide (0.8 g) in water (0.3 ml) and acetic acid (5 ml) was added dropwise with stirring to a solution of 6-methyltetralin-*d*$_4$ (0.450 g) in acetic acid (5 ml) at 5–10°. The solution was stirred at 5° for 1 hr, and then at room temperature for 11 days. The mixture was poured into water (100 ml) and extracted with pentane (4 × 50 ml). The combined pentane extracts were washed with aqueous Na_2CO_3 (2 × 50 ml) and dried ($CaCl_2$). Removal of solvent yielded a crude mixture of 6- and 7-methyl-α-tetralones (0.226 g, 46%) shown by glc (Carbowax, 235°) to be present in the ratio 1.4:1.

Nmr of 6-methyl-α-tetralone (from oxidation of 6-methyltetralin and purified by preparative glc) (CCl_4, extrapolated to infinite dilution): δ 7.82 (d, H_8, $J_{7,8}$ = 8.0 Hz), 7.07–6.96 (cm, H_7, H_5), 2.90 (t, H_4, $J_{3,4}$ = 6.0 Hz), *ca.* 2.53 (cm, H_2), 2.35 (s, CH_3), *ca.* 2.13 (cm, H_3).

Exchange and Separation of Tetralones from the Oxidation of 6-Methyltetralin-*d*$_4$. The crude mixture of tetralones (200 mg) from the oxidation of 6-methyltetralin-*d*$_4$ was refluxed overnight with water (60 ml) and HCl (5 ml). The mixture was cooled and extracted with ether (3 × 30 ml), and the ether extracts were washed with water (2 × 50 ml) and dried ($CaCl_2$). The solution was concentrated and then subjected to separation on a Carbowax column (20 ft × 3/8 in.) at 216–218° (helium flow rate *ca.* 200 ml/min). The retention times of the 7- and 6-methyl-α-tetralones under these conditions were 54 and 60 min, respectively. Two fractions were collected, and were seen by analytical glc (Carbowax, 230°) to consist of pure 6-methyl-α-tetralone (17 mg, 9%) and pure 7-methyl-α-tetralone (13 mg, 6%).

6-Methyl-α-tetralone from Oxidation of 6-Methyltetralin-*d*$_4$. The appearance of the nmr spectrum was similar to that of 6-methyl-α-tetralone-*d*$_0$, but integration indicated that there was some deuteration at positions 3 and 4. From a comparison with the mass spectrum of 6-methyl-α-tetralone-*d*$_0$, the present sample was seen to contain 0.91 ± 0.01 D/molecule.

7-Methyl-α-tetralone from Oxidation of 6-Methyltetralin-*d*$_4$. Absorption in the regions δ 2.89 and 2.12 (H_4 and H_3) of the nmr were almost negligible, and integration suggested that overall deuteration was greater than 92%. This is compatible with the more accurate mass spectral results (see below). The absorption due to H_2 was considerably simplified and approached a broadened singlet (*ca.* δ 2.54). From a comparison with the mass spectrum of 7-methyl-α-tetralone-*d*$_0$, the present sample was seen to contain 3.64 ± 0.01 D/molecule.

7-Methyl-α-tetralone. 4-(*p*-Tolyl)-*n*-butyric acid (8.7 g) was placed in a polyethylene bottle equipped with a polyethylene stirrer, and hydrogen fluoride (*ca.* 200 ml) was allowed to condense into the reaction bottle. The resulting purple solution was stirred until all the hydrogen fluoride had evaporated (*ca.* 24 hr) and then aqueous Na_2CO_3 (200 ml) was poured cautiously into the reaction vessel. The mixture was extracted with ether (3 × 200 ml) and the combined extracts were washed with water (2 × 200 ml) and dried ($MgSO_4$). Removal of the solvent yielded the crude tetralone as a dark oil (7.5 g, 96%), which was readily purified by chromatography on Brockmann No. 1 alumina. Elution with chloroform (*ca.* 500 ml) and removal of the solvent yielded 7-methyl-α-tetralone (7.2 g) as very pale yellow crystals: mp 32–33° (lit.[25] 31–33°), pure

(25) M. S. Newman, *J. Amer. Chem. Soc.*, **62**, 1683 (1940).

by glc (Carbowax, 227°); nmr (CCl_4, extrapolated to infinite dilution) δ 7.74 (s, H_8), 7.16, 7.04 (*ca.* AB quartet, H_5, H_6, $J_{5,6} \approx$ 7.8 Hz), 2.89 (t, H_4, $J_{3,4}$ = 6.0 Hz), *ca.* 2.54 (cm, H_2), 2.36 (s, CH_3), *ca.* 2.12 (cm, H_3).

7-Methyl-α-tetralone-*2,2-d*$_2$. 7-Methyl-α-tetralone (0.3 g) was refluxed overnight with D_2O (3 ml, 99.5%+) and deuterium chloride (0.5 ml, 99% isotopic purity, 38% in D_2O). The solution was cooled and extracted with ether (3 × 20 ml), and the ether solution was washed with water (2 × 20 ml) and dried ($CaCl_2$). The 7-methyl-α-tetralone recovered on removal of solvent was refluxed for an additional 12 hr with similar amounts of D_2O and deuterium chloride. The solution was worked up in the same manner to yield 7-methyl-α-tetralone-*2,2-d*$_2$ (yield quantitative). Absorptions in the region δ 2.5 (H_2) of the nmr were almost negligible. Integration over this region was compatible with the more precise estimation of deuterium content from the mass spectrum (parent peak 162; base peak 132). By a comparison with the mass spectrum of 7-methyl-α-tetralone-*d*$_0$, the present sample was seen to contain *ca.* 1.95 D/molecule, distributed as 94% d_2 and 6% d_1.

6-Methyltetralin-*3,3,4,4-d*$_4$. A mixture of mossy zinc (6.68 g), mercuric chloride (1 g), D_2O (6.7 ml), and deuterium chloride (0.3 ml) was shaken for 5 min. The amalgamated zinc under D_2O (9 ml) and deuterium chloride (7 ml) was refluxed overnight with 7-methyl-α-tetralone-*2-d*$_2$ (0.3 g), and then the mixture was worked up in the standard fashion. The 6-methyltetralin so obtained (0.2 g, 72%) was shown to be pure by glc (Carbowax, 220°); mass spectrum parent peak 150, base peak 135. By a comparison with the mass spectrum of 6-methyltetralin-*d*$_0$, it was apparent that the present sample contained approximately 4.39 D/molecule, distributed among d_4 (81%), d_3 (17%), and d_6 (5%) species. The d_5 and d_6 species arise from the exchange of protons in the aromatic ring under Clemmensen conditions. The complete absence of d_3 or less deuterated species assured full deuteration in the 4 position, and rendered the present sample suitable for an analysis of kinetic isotope effects from product ratios in the chromic acid oxidation of 6-methyltetralin-*d*$_0$ and 6-methyltetralin-*3,3,4,4-d*$_4$.

Methyl 4-(*p*-Methoxyphenyl)-*n*-butyrate. 4-(*p*-Methoxyphenyl)-*n*-butyric acid (42 g) was added portionwise to a solution of diazomethane (*ca.* 12.6 g, as prepared from 76.3 g of commercial Diazald) in ether (1 l.). The solution was allowed to stand for 0.5 hr, and then worked up in the usual manner. The crude ester so obtained (44.9 g, 99.6%) was distilled, and then carefully fractionated through a 10-in. spinning band column (reflux ratio of 30:1) to give methyl 4-(*p*-methoxyphenyl)-*n*-butyrate (>99.5% pure by glc; SE-30, 225°): bp 98° (1.9 mm); $n^{25.5}D$ 1.5052; exact mass spectrum (mass measurement by high-resolution mass spectrometer) 208.1086 (calcd for $C_{12}H_{16}O_3$, 208.1099); nmr (100 MHz) δ 7.02, 6.76 (AA′BB′,Ar), 3.66 (s, $ArOCH_3$), 3.56 (s, $COOCH_3$), 2.55 (t, H_4), 2.37–2.11 (cm, H_2), 2.07–1.67 (cm, H_3).

Exchange of Methyl 4-(*p*-Methoxyphenyl)-*n*-butyrate. Sodium (0.14 g) was added cautiously to methanol-*d*$_1$ (19.5 g, >99% isotopic purity, Diaprep Inc.) under an argon atmosphere. After reaction ceased, methyl 4-(*p*-methoxyphenyl)-*n*-butryate (7 g) was added, and the mixture was protected with a drying tube and warmed in an oil bath at 60° for 24 hr. An nmr spectrum of an aliquot of the methanolic solution indicated that approximately theoretical exchange had taken place (89% deuteration in the 2 position, as calculated by integration of the near-absent nmr absorptions in the region δ 2.37–2.11).

The methanol was removed with a rotary evaporator, and fresh methanol-*d*$_1$ (24.8 g) was added under argon. The mixture was left at 60° for 2 days, and again an nmr spectrum of an aliquot revealed approximately theoretical exchange (98% deuteration). Evaporation of methanol yielded a cloudy oil (7.5 g), a small portion (0.5 g) of which was added to cold 0.2 *M* acetic acid (15 ml), and extracted with carbon tetrachloride (1 × 20 ml). After washing the organic extract with water (1 × 20 ml) and drying ($MgSO_4$), the solution was concentrated sufficiently for nmr purposes: nmr δ 7.01, 6.77 (AA′BB′, Ar), 3.66 (s, $ArOCH_3$), 3.56 (s, $COOCH_3$), 2.75–2.32 (cm, H_4), 2.06–1.63 (cm, H_3). Integration of the region δ 2.32–2.06 indicated 0.06 H/molecule, *i.e.*, 97% deuteration in the 2 position; mass spectrum parent peak 210, base peak 121. By a comparison with the mass spectrum of the undeuterated ester the present ester was seen to contain 1.95 ± 0.01 D/molecule, as 95% d_2 species and 5% d_1 species.

4-(*p*-Methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ Alcohol. The oily product (6.6 g) from the exchange of methyl 4-(*p*-methoxyphenyl)-*n*-butyrate was immediately dissolved in anhydrous ether (50 ml), and added, under argon, to a solution of lithium aluminum hydride (1.5 g) in anhydrous ether (50 ml). The mixture was refluxed overnight and then worked up as usual to afford 4-(*p*-methoxyphenyl)-*n*-butyl *2,2-d*$_2$ alcohol (5.0 g, 87.5%; pure by glc; SE-30, 200°): nmr δ 7.01, 6.73 (AA′BB′, Ar), 3.96 (s, OH), 3.65 (s, OCH_3), 3.48 (s, CH_2OH), 2.52 (m, $ArCH_2$), 1.56 (*ca.* 2 H, m, $ArCH_2CH_2CD_2$). Integration indicated that the compound was approximately 98% deuterated in the 2 position; mass spectrum parent peak 182, base peak 121. Comparison with the mass spectrum of the undeuterated alcohol indicated that the compound contained 1.94 ± 0.01 D/molecule in the 2 position (97 ± 0.5% deuteration), the approximate distribution being 95% d_2, 4% d_1, and 1% d_0.

4-(*p*-Methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ *p*-Bromobenzenesulfonate. A solution of 4-(*p*-methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ alcohol (4.9 g) in anhydrous pyridine (40 ml) was mixed slowly with stirring with a solution of *p*-bromobenzenesulfonyl chloride (12.5 g) in pyridine (60 ml) at 0°. The mixture was left for 4 days at 5°, and then worked up in the usual manner to yield the product as a dark oil (7.0 g, 65%). Two recrystallizations from benzene–light petroleum yielded 4-(*p*-methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ *p*-bromobenzenesulfonate as a white solid (4.0 g), mp 41–44.5°. The nmr and mass spectrum of the product reflected the same deuterium content as the starting alcohol: nmr δ 7.64 (m, Br-Ar), 6.92, 6.72 (AA′BB′, Ar), 3.98 (s, CH_2), 3.70 (s, OCH_3), 2.47 (m, 2 H, H_4), 1.53 (m, ~2 H, H_3); mass spectrum parent peaks 402, 400; base peak 121.

Formolysis of 4-(*p*-Methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ *p*-Bromobenzenesulfonate. 4-(*p*-Methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ *p*-bromobenzenesulfonate (3.70 g) was treated in the manner described for the 4-(*p*-tolyl)-*n*-butyl *p*-bromobenzenesulfonate, to yield 6-methoxytetralin-*d*$_2$ (0.55 g, 36%) and 4-(*p*-methoxyphenyl)-*n*-butyl *2,2-d*$_2$ alcohol (0.713 g, 42%). Both products were shown to be pure by glc (SE-30, 230°). The mass spectrum of the tetralin showed it to contain the same overall deuterium content as that of the starting *p*-bromobenzenesulfonate. Similarly, the nmr and mass spectrum of the alcohol were identical with those described for the alcohol used in preparation of the starting *p*-bromobenzenesulfonate.

Oxidation of 6-Methoxytetralin-*d*$_2$ and Exchange of the Product. The 6-methoxytetralin (0.514 g) formed on formolysis of 4-(*p*-methoxyphenyl)-*n*-butyl-*2,2-d*$_2$ *p*-bromobenzenesulfonate was dissolved in acetic acid (3.92 ml) and cooled to 10°. A solution of chromium trioxide (1.01 g) in water (0.18 ml) and acetic acid (1.46 ml) was added dropwise with stirring, and the mixture was stirred at 10° for 1 hr and then at room temperature for a further 16 hr. The reaction was worked up in the usual manner to yield a solid (0.441 g, 79%), shown by glc (SE-30, 260°) to consist of 6-methoxy-α-tetralone (*ca.* 99%) and 7-methoxy-α-tetralone (*ca.* 1%).

The mixture of ketones was refluxed overnight with water (5 ml), methanol (5 ml), and a trace of K_2CO_3 (0.03 g). The water and methanol were removed by rotary evaporator, fresh portions of water (5 ml) and methanol (5 ml) were added, and the mixture was refluxed for a further 12 hr. The reaction mixture was then worked up in the usual manner to yield the solid product (0.423 g, 96% recovery). One recrystallization from light petroleum gave 6-methoxy-α-tetralone, mp 76.5–79°, shown to be pure by glc. Integration of the absorptions in the region δ 2.28–1.83 (H_3) of the nmr relative to the areas corresponding to H_4 and H_2, indicated that *ca.* 0.79 H/molecule (1.21 D/molecule) remained in the 3 position. From a comparison with the mass spectrum of 6-methoxy-α-tetralone-*d*$_0$, the present sample was seen to contain 1.22 ± 0.01 D/molecule.

7-Methoxy-α-tetralone. 4-(*p*-Methoxyphenyl)-*n*-butyric acid (4 g) was placed in a polyethylene bottle equipped with a polyethylene coated magnetic stirrer, and a large amount of hydrogen fluoride (*ca.* 150 ml) was allowed to condense into the reaction bottle. The solution was stirred overnight, and when evaporation of hydrogen fluoride was complete, aqueous Na_2CO_3 solution (200 ml) was poured cautiously into the reaction vessel. The mixture was extracted with ether (2 × 100 ml), and the ether extracts were washed with water (2 × 100 ml) and dried ($MgSO_4$). Removal of the solvent yielded the 7-methoxy-α-tetralone (3.1 g, 86%) as a yellow solid, pure by glc (SE-30, 245°). Under the analysis conditions, 1% of 6-methoxy-α-tetralone would have been detectable. Recrystallization of the product from light petroleum afforded pale yellow needles: mp 58.5–60.5° (*cf.* lit.[26] 60–61°); nmr δ 7.39 (d, H_8), 7.07, 6.95 (*ca.* AB quartet, H_5, H_6, $J_{5,6} \approx$ 8.3 Hz), 3.80 (s, OCH_3), 2.85 (t, H_4), 2.69–2.31 (cm, H_2), 2.31–1.76 (cm, H_3).

6-Methoxytetralin. 6-Methoxy-α-tetralone (6.5 g) was subjected to Clemmensen reduction, to yield 6-methoxytetralin (5.6 g, 94%

(26) F. Krollpfeiffer and W. Schäfer, *Ber.*, **56**, 620 (1923).

which was pure by glc (SE-30, 230°): nmr δ 7.0–6.3 (cm, Ar), 3.60 (s, OCH_3), 2.9–2.3 (cm, H_1, H_4), 2.0–1.4 (cm, H_2, H_3).

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Formolysis of 4-(*p*-Methoxyphenyl)butyl *p*-Bromobenzenesulfonate

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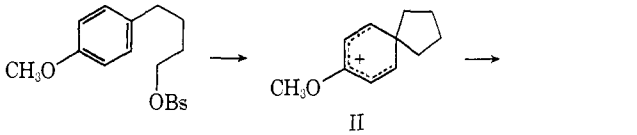
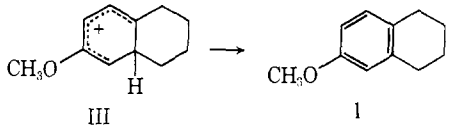
Abstract: That fraction of the formolysis of 4-(*p*-methoxyphenyl)butyl *p*-bromobenzenesulfonate leading to 6-methoxytetralin proceeds through a symmetrical intermediate to the extent of 69.5% and through an unsymmetrical intermediate to the extent of 30.5%. The secondary deuterium isotope effect for the partition of the symmetrical intermediate is about 10%.

Winstein and his collaborators[1] have studied the solvolysis of a number of ω-aryl alkyl *p*-bromobenzenesulfonates and in the case of the formolysis of the 4-(*p*-methoxyphenyl)butyl ester showed that somewhat more than half of the product was 6-methoxytetralin (I).[2] The formation of this substance was ascribed to aryl participation to form an Ar_1-5 intermediate II which proceeded, presumably through



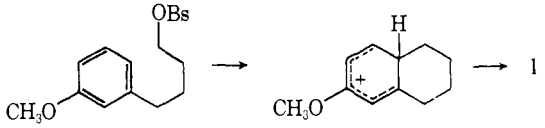
II



III I

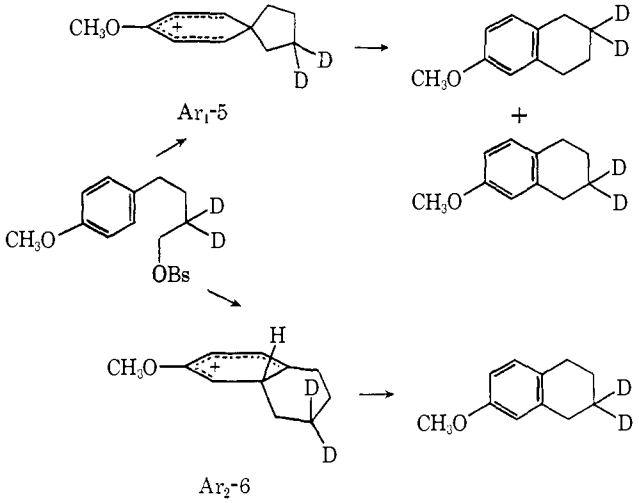
the intermediate III, to I. Aryl participation in the transition state leading to II was recognized as not large, however, on the basis of several criteria. (1) Rate enhancement over unassisted solvolysis was only a factor of 1.77 and is very much smaller than the rate enhancement produced by a *p*-methoxy group in, for example, bromination, where the rate enhancement is *ca.* 10^{10}.[3] (2) The low entropy of activation (−16.1 eu) is characteristic of unassisted rather than assisted solvolyses.[4]

It appears to have been tacitly assumed by Winstein that 4-(*p*-methoxyphenyl)butyl *p*-bromobenzenesulfonate proceeds to 6-methoxytetralin largely if not exclusively through intermediate II, whereas the corresponding *m*-methoxyphenyl compound yielded the same tetralin through intermediate IV, formed by Ar_2-6 participation.



IV

Haddon and Jackman,[5] however, have recently reported the formolysis of 4-(*p*-methoxyphenyl)butyl-*2,2-d_2* *p*-bromobenzenesulfonate (as well as that of the 4-(*p*-tolyl)-1-butyl-*1,1-d_2* and *-3,3,4,4-d_4* *p*-bromobenzenesulfonates). In the former case, the results were interpreted as indicating that 73.8% of that fraction of the solvolysis leading to 6-methoxytetralin (36%) went by the Ar_1-5 route and 26.2% went by the Ar_2-6 route.



Ar_1-5 + Ar_2-6

We had completed[6] a study of the formolysis of the very closely related 4-(*p*-methoxyphenyl)butyl-*1,1-d_2* *p*-bromobenzenesulfonate when the publication of Haddon and Jackman appeared, and have more recently studied the 4-(*p*-methoxyphenyl)butyl-*4,4-d_2* *p*-bromobenzenesulfonate, and present our results here.

(1) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, 12, 138 (1956); S. Winstein, *Chem. Ind. (London)*, 562 (1954); S. Winstein and R. Baird, *J. Amer. Chem. Soc.*, **79**, 756 (1957); and especially R. Heck and S. Winstein, *ibid.*, **79**, 3105, 3114 (1957).

(2) Referred to in Winstein's papers as 7-methoxytetralin.

(3) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1764 (1951).

(4) S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4801 (1956).

(5) V. R. Haddon and L. M. Jackman, *J. Amer. Chem. Soc.*, **93**, 3832 (1971).

(6) D. L. Frank, Ph.D. Dissertation, University of Rochester, 1970; *Diss. Abstr. Int. B*, **32**, 1446 (1971).