procedure.[1] Reaction of **1** with 1.5 equiv of CH_3Li in ether at 0° for 1 hr followed by treatment with CH_3OH and H_2O gave **2** (33%), the structure of which is established from the nmr spectrum in $CDCl_3$. The methyl group appears as a triplet (J = 1.0 Hz) at 1.15 ppm[6,7] and collapses to a singlet when decoupled from deuterium.[8] The multiplet in the spectrum of the undeuterated compound at 2.28 ppm (MeC*H*) is absent in the spectrum of **2**. The rest of the spectrum is also consistent with structure **2**.

Although the enzymatic hydration of oxepin–benzene oxide occurs by trans-1,2 addition, the enzyme-catalyzed trans-1,6 hydration of 8,9-indane oxide has been observed.[9] Further examples of addition reactions to **1** will be reported at a later date.

(6) Chemical-shift data are in parts per million downfield from tetramethylsilane.

(7) The methyl absorption in the unlabeled compound appears as a sharp doublet (J = 7.0 Hz).

(8) Spectrum recorded on a Perkin-Elmer R-20B spectrometer—broad band decoupling (9.213400 MHz). We thank Dr. D. D. Traficante for the spectrum.

(9) J. D. Daly, *et al.*, *J. Amer. Chem. Soc.*, **92**, 702 (1970).

Charles H. Foster, Glenn A. Berchtold*

Department of Chemistry, Massachusetts Institute of Technology Cambridge, Massachusetts 02139

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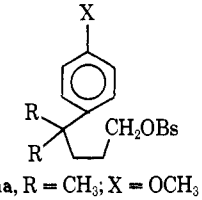
Competitive Ar_1-5 and Ar_2-6 Participation

Sir:

Phenyl participation in the solvolyses of 4-aryl-*n*-butyl *p*-bromobenzenesulfonates has been investigated by Winstein and his coworkers[1] who have presented kinetic evidence for mechanisms involving five- (Ar_1-5) and six- (Ar_2-6) membered rings. In their initial communication[1a] they cite the example of the formolysis of 4-(*p*-methoxyphenyl)-4-methyl-1-pentyl bromobenzenesulfonate (**1a**) which yields **a** cyclic product which is "almost entirely" 1,1-dimethyl-7-methoxytetralin, as evidence for exclusive Ar_1-5 participation. Subsequently, further evidence for the Ar_1-5 pathway was found in very favorably activated cases, namely in the formation of the spirodienone (**2**) from the phenoxide ion (**1b**),[2] and in related systems.[3,4]



1a, R = CH_3; X = OCH_3
b, R = H; X = O^-

2

(1) (a) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956); (b) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3105, 3114 (1957).

(2) (a) S. Winstein and R. Baird, *ibid.*, **79**, 756 (1957); (b) R. Baird and S. Winstein, *ibid.*, **84**, 788 (1962).

(3) (a) S. Dorling and J. Harley-Mason, *Chem. Ind. (London)*, 1551 (1959); (b) S. Masamune, *J. Amer. Chem. Soc.*, **83**, 1009 (1961).

(4) 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,[5] which we are currently studying.

(5) V. R. Haddon and L. M. Jackman, unpublished results.

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.[6] 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 **1a**, 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.

4-(*p*-Methoxyphenyl)-*n*-butyl alcohol-*2,2*-d_2 (1.94 ± 0.02 D/mol)[7] was prepared by base-catalyzed exchange of methyl 4-(*p*-methoxyphenyl)-*n*-butyrate followed by reduction with $LiAlH_4$. Formolysis of the corresponding *p*-bromobenzenesulfonate under Winstein's conditions[1b] yielded, after $LiAlH_4$ reduction, 6-methoxytetralin-d_2 (36%; 1.94 ± 0.02 D/mol) and 4-(*p*-methoxyphenyl)-*n*-butyl alcohol-*2,2*-d_2 (42%; 1.93 ± 0.02 D/mol).[8] The tetralin was oxidized with chromium trioxide in acetic acid to yield 6-methoxy-1-tetralone (79%),[10] mp 77–79°. The deuterium content of the tetralone, after removal by base-catalyzed exchange of any deuterium in the 2 position, corresponded to 63.1 ± 0.7% of 6-methoxy-1-tetralone-*3,3*-d_2. The unlabeled remainder (36.9%), corresponding to 6-methoxy-1-tetralone-*2,2*-d_2 prior to exchange, can only be formed by Ar_1-5 participation. Assuming a negligible β-isotope effect for the rearrangement of the Ar_1-5 intermediate, it follows that 73.8 ± 1.4% of tetralin formed arose *via* the Ar_1-5 pathway and that a surprisingly high proportion (26.2%) involved participation of the positions meta to the methoxyl substituent.

In the para methyl system, the formolyses of the bromobenzenesulfonates of 4-(*p*-tolyl)-*n*-butyl alcohol-*1,1*-d_2 and -*3,3,4,4*-d_4 were studied.[11] This system is complicated by the fact that the oxidation of 6-methyltetralin yields comparable amounts of the 6- and 7-methyl-1-tetralones and the actual ratios of the two isomers formed are, by virtue of the primary isotope effect, also dependent on the deuterium contents at the 1 and 4 positions. The 6- and 7-methyl-1-tetralones were readily separated by glc. The deuterium content of the 6-methyltetralones from the solvolysis product of **3**, *i.e.*, **[4]**/**[5]** is dependent on the distribution of deuterium in the tetralin precursor and on a quantity γ which is a function of the various rate constants for the oxidation (see eq 1 and Scheme I). A similar relation exists for the 3,3,4,4-tetradeuterio series (eq 2)

(6) (a) S. Sethna in "Friedel–Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, p 911; (b) W. S. Johnson, *Org. React.*, **2**, 114 (1944).

(7) All deuterium contents were determined mass spectrometrically.

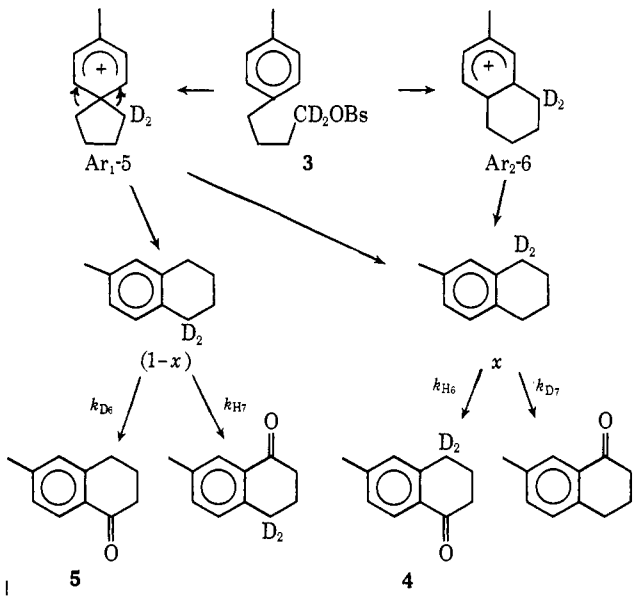
(8) The assignment of the deuterium to the 2 position follows from the identity of the nmr spectrum of this product with that of the original deuterated alcohol. In particular, absorption attributable to the outer components of the triplet (J = 6 Hz) at δ 3.50 arising from the 1-methylene group in the undeuterated alcohol was not observed. This result establishes the irreversibility of the formation of the Ar_1-5 intermediate in accord with the conclusion based on similar observations reported by Winstein and his collaborators.[1a,9]

(9) E. C. Friedrich and S. Winstein, *Tetrahedron Lett.*, 475 (1962).

(10) L. M. Jackman and D. T. Thompson, *J. Chem. Soc.*, 4794 (1961). This and similar oxidations referred to below were carried out under carefully controlled conditions and were monitored to avoid oxidation of the ketonic products.

(11) Nmr indicated the complete absence of deuterium scrambling in the recovered alcohol; *cf.* ref 8.

Scheme I[a]



[a] $x = (Ar_2\text{-}6) + (Ar_1\text{-}5)/2$; $1 - x = (Ar_1\text{-}5)/2$.

$$x\gamma/(1 - x) = [4]/[5] = d_2/d_0 \quad (1)$$

$$(1 - x)\gamma/x = d_4/d_0 \quad (2)$$

where $\gamma = (1 + k_{H7}/k_{D6})/(1 + k_{D7}/k_{H6})$.

Equations 1 and 2 were solved for x, the value of which shows that only 17 ± 1.5% of the cyclization to tetralin proceeded by the Ar_1-5 pathway.[12]

The relative rates (k_{Ar_1-5}/k_{Ar_2-6}), corrected for the statistical factor, are 5.6 and 0.41 for the para methoxy and para methyl systems, respectively. The former result, in particular, indicates a selectivity far less than that expected for an electrophilic aromatic substitution by such a poor electrophile as $RCH_2OSO_2C_6H_4Br$.[14] It is evident that either the Ar_2-6 transition state is sterically more favorable (as would appear from molecular models) or that attack at an alkylated aromatic carbon atom is more difficult than at an unsubstituted one. It is seen, however, that the difference between the two transition states is too small to explain the specificity of cycloacylation. We suggest that the Ar_1-5 intermediate may form during cycloacylation but that ring opening 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.

(12) Two assumptions concerning isotope effects are made. The first is that the α-isotope effect for Ar_1-5 and Ar_2-6 can be neglected. The second is that the α-isotope effect for the rearrangement of the Ar_1-5 intermediate makes a negligible contribution to x. Calculations using a value of 1.2[13] for the latter quantity indicate that the second assumption is valid.

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

(14) Using $\sigma^+_{p\text{-MeO}}$ for Ar_1-5 and $\sigma^+_{m\text{-MeO}} + \sigma^+_{p\text{-CH}_3}$ ($\sigma^+_{p\text{-CH}_3}$ is an approximation to the effect of the ortho methylene group) for Ar_2-6, one obtains $\rho^+ \sim -1.5$, which is substantially lower than the most unselective electrophilic aromatic substitutions.[15]

(15) L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, **81**, 3323 (1959).

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Virginia R. Haddon, L. M. Jackman*
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802
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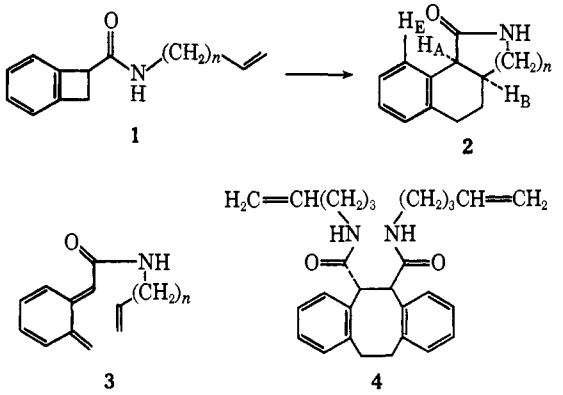
Intramolecular Cycloadditions of *o*-Quinodimethanes[1]

Sir:

As part of a general program directed toward stereoselective syntheses of annelated heterocyclic systems,[2] thermal rearrangements of benzocyclobutenes, typified by **1**,[3] have been examined. After heating a



5% solution in toluene of the propenylamide **1**, $n = 1$[4] (prepared from benzocyclobutene-1-carboxylic acid chloride[5] and allylamine), in an autoclave at 190° for 16 hr the *cis*-benz[*e*]isoindole **2**, $n = 1$[4] (mp 171–172°; nmr $J_{AB} = 8$ Hz), crystallized from the cooled solution in 85% yield. Thermolysis of the homologous butenylamide **1**, $n = 2$,[4] in boiling *o*-dichlorobenzene (8% solution) afforded the *cis*-benz[*h*]isoquinoline **2**, $n = 2$[4,6] (mp 112–113°; nmr $J_{AB} = 5$ Hz; 85%). When a 0.5% solution of the pentenylamide **1**, $n = 3$,[4] in *o*-dichlorobenzene was refluxed for 16 hr the expected naphth[1,2-*c*]azepine **2**, $n = 3$[4] (mp 195–197°; nmr ($CDCl_3$) $J_{AB} = 8$ Hz, $\delta_{HE} \leq 7.2$ ppm), was isolated together with the dimer **4**[4] (mp 159–161°) in yields of 20 and 6%, respectively. This supports the hypothesis that *o*-quinodimethanes of type **3** are intermediates in the reaction[7] and suggests that the activation entropy in the intramolecular cycloaddition **3** → **2** depends strongly

(1) Presented in part at the IUPAC Symposium Cycloaddition Reactions, Munich, Germany, Sept 7–10, 1970.

(2) W. Oppolzer and K. Keller, *Tetrahedron Lett.*, 1117, 4313 (1970); W. Oppolzer and H. P. Weber, *ibid.*, 1121, 3034 (1970); W. Oppolzer, *ibid.*, 3091 (1970).

(3) 1-Substituted benzocyclobutenes are readily available; for a recent review, see I. L. Klundt, *Chem. Rev.*, 70, 471 (1970).

(4) Elemental analytical data and ir and nmr spectra in excellent agreement with the assigned structure were obtained for this substance.

(5) J. A. Skorcz and J. E. Robertson *J. Med. Chem.*, **8**, 255 (1965).

(6) The product was correlated chemically with a reference compound, the structure of which has been established by X-ray crystallographic analysis; J. M. Bastian and H. P. Weber, private communication.

(7) (a) Direct evidence for the intermediacy of *o*-quinodimethanes in this type of reaction is reported in the subsequent communication. (b) For the occurrence of *o*-quinodimethane intermediates during the intermolecular reactions of 1,2-diphenylbenzocyclobutenes with typical dienophiles, see R. Huisgen and H. Seidl, *Tetrahedron Lett.*, 3381 (1964); G. Quinkert, K. Opitz, W. W. Wiersdorff, and M. Finke, *Justus Liebigs Ann. Chem.*, **693**, 44 (1966).