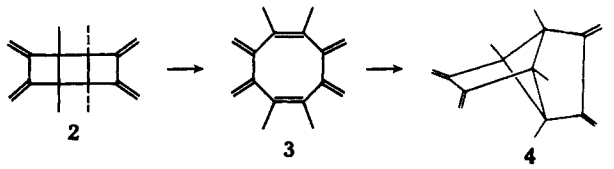
On pyrolysis in a flow system at 240°, **2** underwent smooth conversion to **3**:[9] nmr ($CDCl_3$) δ 1.80 (s), 4.80 (d, J = 1.5 Hz), and 5.10 (d, J = 1.5 Hz); ratio 3:1:1. At higher temperatures, however, another compound was observed, which was the only identifiable product at 380°. At this temperature **3** was also converted to the new isomer, whose nmr was very much like that of **2**, δ 0.70, 4.83, and 5.48, ratio 3:1:1, except for the shift of the methyl signal to higher field. Two structures are consistent with the spectral and analytical data for this compound—the syn isomer of **2** and **4**. The former structure seemed highly unlikely because of the demonstrated greater thermodynamic stability of **3** compared to **2**, whereas chemical analogy[1-5] supported the latter. Moreover, the upfield shift of the methyl resonance is readily explicable in terms of structure **4**, since such shielding of equatorial methyl groups on puckered cyclobutane rings is well documented.[14]

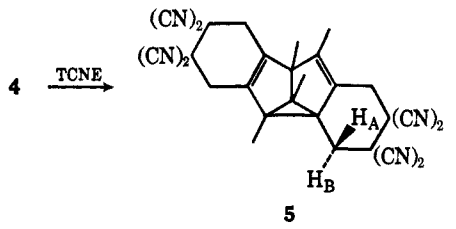


2 **3** **4**

In order to confirm the structure of **4**, it was subjected to Li reduction in NH_3–THF–*tert*-BuOH.[15] Instead of octamethylsemibullvalene, formed by rearrangement[8] of the octamethyltricyclo[3.3.0.0^{2,6}]octa-3,7-diene, which might be expected to be the initial reduction product, the material isolated was a complex mixture of isomeric octamethylbicyclo[3.3.0]octadienes.[9] However, when octamethylsemibullvalene[1] was itself subjected to the reduction conditions, the nmr and glc traces obtained from the product were superimposable on those from the product of the reduction of **4**.

The structure of **4** was further established by its reaction with 2 mol of tetracyanoethylene to give a crystalline adduct. Consistent with its formulation as **5**,[9] the adduct had a uv spectrum very similar to that of authentic octamethylsemibullvalene[1] and an nmr spectrum in which the effective C_2 symmetry of the molecule, caused by its fluxional character, was evident. The two types of methyl groups appeared at (acetone-d_6) δ 1.20 and 1.80 and four methylene protons at δ 3.28 as a somewhat broadened singlet. The remaining two sets of methylene protons appeared at δ 2.76 and 3.88 as an AB quartet with a geminal coupling constant of $|J|$ = 17 Hz. These resonances presumably come from H_A and H_B, the difference in chemical shift being ascribed to the anisotropy of the adjacent carbon.

We are currently studying other cycloaddition reactions of **3** and **4** as well as their photochemistry.



5

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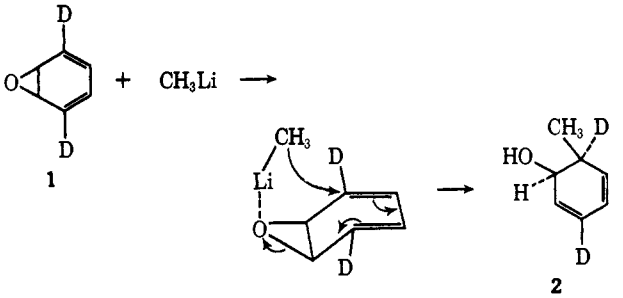
Cis-1,6 Addition of Methyllithium to Oxepin–Benzene Oxide

Sir:

Vogel[1] has reported that oxepin–benzene oxide reacts with methyllithium to give a mixture of *cis*- and *trans*-6-methylcyclohexa-2,4-dien-1-ols in which the cis–trans ratio is higher than 90:10. In our hands the reaction gave only the cis dienol. The absence of any trans isomer in our study may be due to the absence of any halide ion in the CH_3Li solution. The stereochemistry of the cis dienol product was established by reduction (H_2, Pd/C in ethyl acetate) to the known *cis*-2-methylcyclohexanol.[2] Epimerization is not expected during the reduction since it does not occur during the reduction of chorismic acid under similar conditions.[3] We have established that formation of the cis product occurs by a 1,6 addition of methyllithium to **1**. Cyclohexa-1,4-diene-*3,3,6,6-d*$_4$ was prepared from butadiene-*1,1,4,4-d*$_4$[4] as previously described,[5] and the diene was converted to **1** by Vogel's



1 **2**

(1) E. Vogel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).
(2) E. L. Eliel and C. A. Lukach, *J. Amer. Chem. Soc.*, **79**, 5986 (1957).
(3) J. M. Edwards and L. M. Jackman, *Aust. J. Chem.*, **18**, 1227 (1965).
(4) A. C. Cope, G. A. Berchtold, and D. L. Ross, *J. Amer. Chem. Soc.*, **83**, 3859 (1961). The butadiene consisted of 96.2% d_4 and 3.8% d_3 species. The retention of labeling throughout the experimental sequence was established by spectral data.
(5) W. P. Norris, *J. Org. Chem.*, **33**, 4540 (1968).

(13) R. Criegee, G. Schroder, G. Maier, and H. G. Fischer, *Chem. Ber.*, **93**, 1553 (1960).
(14) A. Suzuki and M. Itoh, *Tetrahedron Lett.*, 1003 (1967).
(15) Catalytic hydrogenation gave 1,2 rather than 1,4 reduction of the diene. This provides some chemical evidence that the diene moiety is not contained in a cyclobutane ring.[11]

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).

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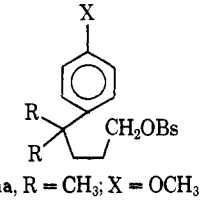
Competitive Ar_1-5 and Ar_2-6 Participation

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.