to the ORD in the near-ultraviolet region. In this case it is therefore possible to use the ORD data to determine the proper scattering correction for the VUCD data, by scaling the correction to give the relative band areas extracted from the Drude analysis ($|k_1/k_2| = 10.2/29.2$). At 164 nm the scattering correction is twice the noise level, and the signal-to-noise ratio is 10:1.

Assuming that the CD bands are Gaussian, we can calculate from k_1 and k_2 mean residue rotational strengths[9] of approximately -9×10^{-40} and 32×10^{-40} erg cm^3 rad, respectively (or mean residue ellipticities of $[\theta]_{180} \simeq -23000$ and $[\theta]_{164} \simeq 48000°$ cm^2 dmol^{-1}, respectively), for curve 1 in Figure 1. These are rough estimates since (a) the conformation in solution under our experimental conditions is not completely helical, and (b) we used a CD correction factor derived from the partially ordered conformation although the film is almost completely in the helical form (P. Lillford, private communication). Nevertheless we can conclude that the ORD changes observed during the helix-coil transition[2-4] must be determined by changes in the magnitudes, and also possibly in the positions, of the two CD bands we observe.

These two CD bands must reflect two separate monomeric transitions, since they are too far apart to be accounted for in terms of an exciton splitting mechanism. Nelson and Johnson[10] observed, in an equilibrium mixture of D-galactose anomers, a negative band near 177 nm, and increasing negative dichroism to 164 nm, the wavelength limit of that study. Tetrahydropyran in the vapor phase has two vacuum ultraviolet absorption bands, at approximately 189 and 173 nm, attributed to excitation of the unshared electrons of the oxygen atom.[11] The CD bands we see here may well have a similar origin, and the 9-nm blue shift in each of the transitions may reflect the difference between the ether and the acetal chromophores.

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References and Notes

(1) N. S. Anderson, J. W. Campbell, M. M. Harding, D. A. Rees, and J. W. B. Samuel, *J. Mol. Biol.*, **45**, 85 (1969).
(2) D. A. Rees, I. W. Steele, and F. B. Williamson, *J. Polym. Sci., Polym. Symp.*, **28**, 261 (1969).
(3) A. A. McKinnon, D. A. Rees, and F. B. Williamson, *Chem. Commun.*, 701 (1969).
(4) D. A. Rees, W. E. Scott, and F. B. Williamson, *Nature (London)*, **227**, 390 (1970).
(5) A. Arnott, W. E. Scott, D. A. Rees, and C. G. A. McNab, *J. Mol. Biol.*, **90**, 253 (1974).
(6) T. M. Lowry, "Optical Rotatory Power", Dover Publications, New York, N.Y., 1964.
(7) E. Iizuka and J. T. Yang, *Biochemistry*, **3**, 1519 (1964).
(8) M. A. Young and E. S. Pysh, *Macromolecules*, **6**, 790 (1973).
(9) J. T. Yang in "A Laboratory Manual of Analytical Methods of Protein Chemistry", P. Alexander and H. P. Lundgren, Ed., Pergamon Press, New York, N.Y., 1969, Chapter 2.
(10) R. G. Nelson and W. C. Johnson, Jr., *J. Am. Chem. Soc.*, **94**, 3343 (1972).
(11) L. W. Pickett, N. J. Hoeflich and T.-C. Liu, *J. Am. Chem. Soc.*, **73**, 4865 (1951).

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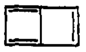
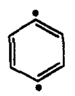
The Generation and Trapping of Butalene

Sir:

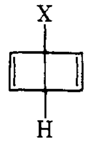
Among conjugated fused-ring systems those with two $4n$ π electron rings, which thus have overall $4n + 2$ π electrons, are particularly interesting. The question of whether they reflect the instability of their component antiaromatic rings or the stability of their overall $4n + 2$ π electrons has been the subject of several experimental and theoretical studies.[1] A fundamental structure in this regard is that of butalene (**1**), a 1,4-dehydrobenzene. In 1965 Berry reported[2] the detection of a relatively long-lived species C_6H_4 of undetermined structure from the flash thermolysis of benzenediazonium-4-carboxylate. More recently, Bergman[3] has described the trapping of 1,4-benzenediyl (**2**) from the thermolysis of diethynylethylene at 200°. He also reported[4] our preliminary observation that a different 1,4-dehydrobenzene, butalene (**1**), can apparently be trapped at low temperature. Dewar has calculated[5] using MINDO 3 that both **1** and **2** should be energy minima, with **1** being 19 kcal/mol less stable than **2**; only a 4.6 kcal/mol barrier was predicted for the isomerization of **1** to **2**. We now wish to describe our evidence[6] that butalene (**1**) can indeed be generated and trapped somewhat below room temperature.



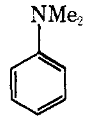
1



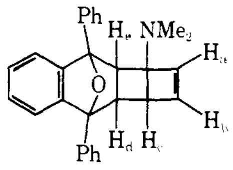
2



3, X = Cl
6, X = NMe$_2$



4



5

The starting material for the work was 3-chloro[2.2.0]bicyclohexadiene[7] (**3**). This compound is quite stable to most strong bases,[6] but with 0.1 *M* $LiNMe_2$ in $HNMe_2$–THF at 0° for 45 min, **3** is quantitatively converted to *N*,*N*-dimethylaniline (**4**). When $DNMe_2$ is used, the product **4** is 25% d_1, 38% d_2, 22% d_3, and only 6.3% d_0. The NMR spectrum, clarified with the use of $Eu(fod)_3$, showed that **4** is 76% para deuterated, 15% meta deuterated, and 48% (of 2 protons) ortho deuterated. When tetramethylethylenediamine is added to the above reaction mixture, the process can be carried out at −35° with quantitative conversion of **3** to **4** and 76, 5, and 25% deuteration of the para, meta, and ortho protons of **4** respectively. Under these same conditions, in the presence of a fivefold excess of diphenylisobenzofuran (DPIBF), the adduct **5** can be isolated in 10–15% yield. The structure of **5** follows from the mass spectrum (*m/e* 391) and NMR spectrum. Signals at δ 6.29, 6.21, 2.98, 2.60, and 2.45 are found for H's a–e, respectively; the assignments were confirmed by appropriate decoupling experiments ($J_{ab} = 1.5$ Hz, $J_{bc} = 1.0$ Hz, $J_{cd} = 1.6$ Hz, $J_{de} = 3.0$ Hz). When $DNMe_2$ is used rather than $HNMe_2$ the isolated adduct **5** contains 90% deuterium at H_c; within the 10% limits of experimental accuracy no deuterium is observed at any other position regardless of whether H_2O or D_2O work-up is employed.

Several controls help to establish that butalene is an intermediate in these reactions. Thus, **3** does not isomerize to chlorobenzene at these temperatures, and chlorobenzene is not converted to **4** under these conditions. Furthermore, **3** does not react with DPIBF under our reaction conditions in the absence of base, and dimethylaniline **4** is not deuterated by our reaction mixture. We therefore conclude that the conversion of **3** to **4** and **5** is initiated by base-promoted elimination of HCl to generate butalene. This could then undergo a 1,4 addition of dimethylamine to generate Dewar dimethylaniline **6**, which would isomerize to (*p*-deuterio)-**4**. However, this simple sequence does not explain all the data, in particular the observed deuteration of **4** in the ortho, as well as para, positions. The conversion of butalene to dimethylaniline may well involve more complex mechanisms, including for instance some initial 1,2 addition of dimethylamine.[8]

The conversion of butalene to adduct **5** also could result from at least two pathways. Thus, if 1,4 addition of dimethylamine generates **6**, this could then be trapped to form **5**. However, one would have to invoke spiroconjugative[9] activation of **6** by the dimethylamino group, since the analogous **3** does not react with DPIBF. An alternative pathway involves edge reaction of DPIBF with butalene to form an initial adduct which is then trapped by addition of dimethylamine. Either path could explain the clean deuteration results in **5**.

Although some ambiguity thus remains in the precise reaction pathway, it seems clear that butalene must be an intermediate in both these reactions. Furthermore, judging from the typical free radical reactions[3] of **2** in the gas phase, it is not an intermediate in either of our observed processes. Thus, the prediction[5] that **1** and **2** can have a separate existence, and different chemistry, is confirmed. The vigorous conditions required to generate butalene from **3** also support our previous conclusion[1a,b] that such fused-ring systems are not strongly stabilized by their overall content of $4n + 2$ π electrons.

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References and Notes

(1) (a) R. Breslow, *Acc. Chem. Res.*, **6**, 393 (1973); (b) R. Breslow, M. Oda, and T. Sugimoto, *J. Am. Chem. Soc.*, **96**, 1639 (1974); (c) R. G. Bergman, *Acc. Chem. Res.*, **6**, 25 (1973).
(2) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, 1003 (1965). Cf. also I. P. Fisher and F. P. Lossing, *J. Am. Chem. Soc.*, **85**, 1018 (1963).
(3) R. R. Jones and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 660 (1972).
(4) Our private communication, reported in footnote 9 of ref 3.
(5) M. J. S. Dewar and W-K. Li, *J. Am. Chem. Soc.*, **96**, 5569 (1974).
(6) Taken in part from the Ph.D. Thesis of J. Napierski, Columbia University, 1972.
(7) R. Breslow, J. Napierski, and A. H. Schmidt, *J. Am. Chem. Soc.*, **94**, 5906 (1972).
(8) The complexity of this transformation is also indicated by the spectroscopic detection (ref 6) of an unstable intermediate in the conversion of **3** to **4** which is apparently neither **1** nor **6**. The intermediate cannot be trapped by DPIBF, and thus is involved in the later stages of the formation of **4**.
(9) H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, **89**, 5208 (1967).

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Evidence for a Remote Secondary Deuterium Kinetic Isotope Effect Arising from a Sterically Congested Ground State

Sir:

We wish to report a substantial secondary deuterium kinetic isotope effect whose origin may be attributed principally to relief of nonbonded repulsions in passage from a sterically congested tetrahedral initial state to a less congested trigonal carbocationic transition state.

Table I. Comparison of γ-Deuterium Kinetic Isotope Effects

Compound	Solvent[a]	T, °C	k_H/k_D	Ref
1d	95% EtOH	25	1.11	*b*
$CH_3CH{=}C(CD_3)CHClCH_3$	95% EtOH	25	0.965	*c*
$(CH_3)_2CClCH_2CD_3$	80% EtOH	25	0.975	*d*
$(CD_3)_3CCH_2OMes$	H_2O	90	1.017	*e*
$(CD_3)_3CCH(OBs)CH_3$	97% TFE	25	1.011	*f*
	50% EtOH	25	1.003	*f*
	43% EtOH	40	0.979	*g*
	95% TFA	10	0.986	*g*

[a] TFE is 2,2,2-trifluoroethanol. TFA is trifluoroacetic acid. [b] This work. [c] R. H. Griffin and J. G. Jewett, *J. Am. Chem. Soc.*, 92, 1104 (1970). [d] Reference 10. [e] M. J. Blandamer and R. E. Robertson, *Can. J. Chem.*, 42, 2137 (1964). [f] V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *J. Am. Chem. Soc.*, 91, 7748 (1969). [g] W. M. Schubert and P. H. LeFevre, *ibid.*, 91, 7746 (1969).

The theoretical basis for understanding secondary deuterium kinetic isotope effects is well established within the context of transition state theory.[1] Briefly stated, a difference in the rates of reaction between the protium- and deuterium-substituted reactants is generally expected if bonds to the light and heavy isotopes experience changes in their vibrational force constants upon passage to the transition state. The rate difference is seen as resulting, in large part, from the inequality in zero point energy differences between the initial and transition states of the protium and deuterium compounds, but *not* to differences in the potential energy surface experienced along the reaction coordinate. The vexing problem of rationalizing kinetic isotope effects in terms relating to reaction mechanisms thus becomes one of ascribing an origin to the vibrational changes taking place as the reaction proceeds. With suitable precautions, the problem may be discussed in terms of the relative importance of inductive, hyperconjugative, and steric intramolecular interactions. The particular question of how adequately the steric origin hypothesis advanced by Bartell[2] explains observed kinetic isotope effects has been the topic of several investigations.[3] However, with few exceptions,[4] studies to date have involved systems in which either the severe steric constraints are incurred at the transition state rather than in the initial state (with $k_H/k_D < 1$)[5] or else the relative importance of inductive and hyperconjugative modes of interaction seems open to question.[6]

In an effort to gain practical information concerning the importance of initial state steric effects in a system in which other modes of intramolecular interaction might be expected to be minimal, we have studied the kinetic isotope effect associated with the solvolysis of 2-*tert*-butyl-2-adamantyl *p*-nitrobenzoate (**1**)[7] deuterated in the *tert*-butyl group. Compound **1h** is one of the most reactive tertiary alkyl substrates known, solvolyzing 459000 times faster than *tert*-butyl *p*-nitrobenzoate and 239000 times faster than 2-methyl-2-adamantyl *p*-nitrobenzoate do under the same conditions.[7] Its extreme reactivity has been ascribed to the serious nonbonded strain interactions in the tetrahedral initial state **1h** which are relieved in the trigonally arranged cation **2**. The source of this strain was seen as arising primarily from the nonbonded repulsions between methyl group R on the axially disposed *tert*-butyl group and the axial hydrogens on the same face of the inflexible chair-form cyclohexane ring. Strain calculations indicated that these repulsive interactions are largely diminished in carbocation **2**. Rate enhancement through methyl participation was deemed unlikely in view of the fact that 16% of the solvolysis products was unrearranged alcohol.[7]