because it requires the formation of vinyl cation C or D as the precursor. Such a mode of generation of a vinyl cation by cleavage or loosening of a C–C bond has no precedence to the best of our knowledge. Work is now under progress to further elucidate the nature of the intermediate.

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Aromatic Halogenation. III. Kinetics of Iodination of Azulene. Amplification of Isotope Effects by Steric Hindrance[1]

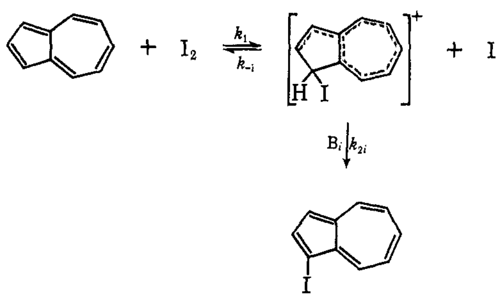
Sir:

Azulene reacts with iodine at 25° in dilute aqueous solutions of sodium iodide (0.1 *M*) to give 1-iodoazulene in good yield[2] and at a convenient rate for determination of the velocity of the reaction from spectroscopic measurement of the triiodide concentration. Since 1-iodoazulene reacts with additional iodine to give diiodoazulene at a rate which is about one-tenth that of monoiodination, a threefold or greater molar excess of azulene over iodine was employed in the present kinetic measurements to ensure monoiodination. Under these conditions iodination was found to obey the rate law

$$\frac{d[\mathrm{AzI}]}{dt} = \frac{[\mathrm{AzH}][\mathrm{I_2}]}{[\mathrm{I^-}]}\sum_i k_i[\mathrm{B}_i]$$

where AzI and AzH represent iodoazulene and azulene, respectively, B_i is a general base, and the quantities in brackets refer to the actual concentration of the species indicated. Similar kinetic expressions have been found previously for the iodination of phenol,[3] 4-nitrophenol,[1] and aniline,[4,5] except that for the neutral hydrocarbon azulene the extent of protonation of the reactant does not complicate the kinetics at the low acidities (pH 5.2–7.5) used nor does the azulene molecule function as an effective general base. In accord with the proposed mechanism of iodination of 4-nitrophenol[1] and aniline,[5] the mechanism in Scheme I seems likely for azulene. This mechanism can be shown to be in agreement with the observed kinetics provided that the steady-state approximation is applicable to the intermediate iodoazulenium cation and provided that $k_{-1}[\mathrm{I^-}] \gg \Sigma k_{2i}[\mathrm{B}_i]$; under these conditions, the individual catalytic constant k_i in the experimental rate expression corresponds to the product k_1k_{2i}/k_{-1} in the derived mechanism. The indicated inequality of the rates of the step k_{-1} *vs.* step k_{2i} is found to hold at [I⁻] of 0.04–0.20 *M* with the solvent water as general base and at 0.1 *M* [I⁻] with up to 0.15 *M* of a general base such as chloroacetate anion.

Scheme I



Since the mechanism of electrophilic aromatic substitution upon azulene has been studied in detail previously only for proton exchange,[6] we deemed it of interest to study iodination in more detail. Azulene-1,3-d_2 (>95% of the theoretical deuterium content according to analysis by nmr) was prepared from azulene by deuterium exchange with 1 *M* D_2SO_4 in a modification of the procedure of Gruen and Long.[6] The iodination of this material was performed under the same conditions as those of the protium compound. The catalytic constants $(k_i)_H$ for the protium compound and the ratios of the catalytic constant of protium compound to those of the deuterium compound $(k_i)_H/(k_i)_D$ are recorded in Table I for various bases along with literature values for the acidity of the conjugate acids of these bases. It is immediately obvious that the iodination of azulene has an appreciable isotope effect of sufficient size to be classified as a primary isotope effect. The general mechanism of iodination suggested above is therefore confirmed; in particular, cleavage of the C–H bond is part of the rate-determining step. Moreover, the position of iodination is confirmed since the location of deuterium in the reactant is well established by nmr analysis[7] and only if deuterium is being replaced would such a large isotope effect be expected.

Table I. Catalytic Constants for Iodination of Azulene and Azulene-1,3-d_2 in Aqueous Solution at 25.0°, μ = 0.3

Base	pK_a of base	$(k_i)_H$, M^{-1} sec^{-1}	$(k_i)_H/(k_i)_D$
Water	-1.7^a	6.1^a	3.2 ± 0.1
Chloracetate	2.85	4.4×10^3	3.0 ± 0.3
Acetate	4.75	3.1×10^4	3.0 ± 0.1
Pyridine	5.23	2.9×10^4	2.0 ± 0.2
HPO_4^{2-}	7.21	2.5×10^5	3.2 ± 0.1
2,4,6-Trimethylpyridine	7.59	5.0×10^3	6.5 ± 1.3

[a] Based on the assumption that the effective concentration of H_2O in water is 55.6 *M*.

Table I further shows that the catalytic constant depends upon the nature of the base. A Brønsted plot of

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(1) Part II: E. Grovenstein and N. S. Aprahamian, *J. Am. Chem. Soc.*, **84**, 212 (1962).

(2) The yield of iodoazulene was determined by vapor phase chromatography with an Apiezon L on Chromosorb column; it was assumed that the product of slightly longer retention time than 1-iodonaphthalene was 1-iodoazulene. The ultraviolet absorption spectrum of this product was very similar to that of 1-chloroazulene [F. A. Long and J. Schulze, *ibid.*, **86**, 327 (1964)]. Attempts to isolate pure 1-iodoazulene resulted in a green-black product of very different ultraviolet spectrum which appears to be a polymer of iodoazulene. For a similar report of an unsuccessful attempt to isolate pure 1-bromoazulene see A. G. Anderson, J. A. Nelson, and J. J. Tazuma, *ibid.*, **75**, 4980 (1953).

(3) F. G. Soper and G. F. Smith, *J. Chem. Soc.*, 2757 (1927); B. S. Painter and F. G. Soper, *ibid.*, 342 (1947); E. Berliner, *J. Am. Chem. Soc.*, **73**, 4307 (1951).

(4) E. Berliner, *ibid.*, **72**, 4003 (1950).

(5) F. M. Vainstein, E. I. Tomilenko, and E. A. Shilov, *Kinetika i Kataliz*, **4**, 357 (1963).

(6) L. C. Gruen and F. A. Long, *J. Am. Chem. Soc.*, **89**, 1287 (1967).

(7) The doublet assigned [W. G. Schneider, H. J. Bernstein, and J. A. Pople, *ibid.*, **80**, 3497 (1958)] to H_1 and H_3 in azulene is absent and the triplet assigned to H_2 is reduced to a singlet, as expected in azulene-1,3-d_2.

log k_i *vs.* pK_a of the various bases has a slope, β, of about 0.4 for both azulene and azulene-1,3-d_2; however, water and especially 2,4,6-trimethylpyridine deviate considerably from the linear relationship and are less effective catalysts than predicted from their basic strengths. The low catalytic activity of 2,4,6-trimethylpyridine can reasonably be attributed[8] to a steric effect involving the 2,6-dimethyl groups on approach of the basic nitrogen to the iodoazulenium cation. Paralleling the decrease in $(k_i)_H$ there is a still larger decrease in $(k_i)_D$ such that with 2,4,6-trimethylpyridine the isotope effect $(k_i)_H/(k_i)_D$ is over three times as great as in the case of pyridine. We believe that the large increase in the isotope effect here is due in good part to proton tunneling in the transition state for the same reasons which Funderburk and Lewis[9] have advanced to explain the 2.5-fold greater isotope effect (k_H/k_D) upon ionization of 2-nitropropane by 2,4,6-trimethylpyridine as compared to pyridine. Lewis and Funderburk[11] have recently pointed out that steric effects may also increase the isotope effect by bringing about a larger than usual loss of zero-point vibrational energy in a more stretched transition state.

In contrast to the nitrogen bases, the oxygen bases of Table I give an almost constant isotope effect $(k_i)_H/(k_i)_D$ in spite of 7 pK units difference in basicity over the range of bases examined. In the ionization of aliphatic C–H bonds by bases of various strength Bell and coworkers[10] found a maximum in the isotope effect when the ionizing acid and the attacking base had about equal pK_a. In terms of this correlation and the likely approximation that iodoazulenium cation is some 2 pK units more acidic than azulenium cation, the bases of Table I should give decreasing isotope effects with increasing pK_a of the base (*i.e.*, in going from water to 2,4,6-trimethylpyridine). The trend in isotope effect from water to pyridine is in qualitative accord with this expectation; however, the near constancy in isotope effect among the oxygen bases suggests that a factor is operating here in opposition to the basicity effect of Bell. We suggest that this is a steric effect, qualitatively like that mentioned earlier for 2,4,6-trimethylpyridine, which increases about in proportion to the basicity of the base and which has its possible origin in the increased solvation of the ions of greater basicity.

We think that the phenomenon of steric amplification of isotope effects[12] may prove a useful tool in chemistry especially in cases where the normal isotope effect is either too small to detect or so small that it might be confused with a secondary isotope effect.

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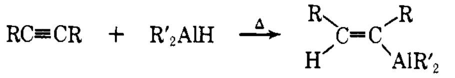
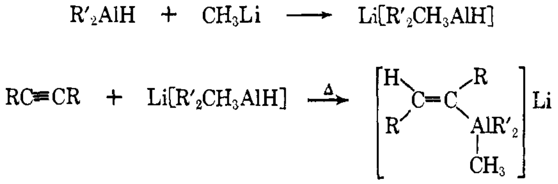
A Novel Method for the Synthesis of *cis*-α,β-Unsaturated Derivatives *via* *trans*-Hydroalumination of Disubstituted Alkynes with Lithium Diisobutylmethylaluminum Hydride[1]

Sir:

The hydroalumination of disubstituted alkynes with diisobutylaluminum hydride is a highly stereoselective process giving excellent yields of *cis*-vinylalanes (1)[2] which may readily be converted into a variety of isomerically pure α,β-unsaturated derivatives.[3] In view of the increasing interest in vinylalanes as synthetically useful intermediates we have been investigating possible routes for the preparation of *trans*- as well as *cis*-vinylaluminum derivatives. We now wish to report that the hydroalumination of disubstituted alkynes with lithium diisobutylmethylaluminum hydride[4] in ether solvents apparently results in a *trans* addition of the aluminum–hydrogen bond to the triple bond (2). Evidence for the *trans* addition was obtained by hydrolysis of the intermediate vinylalanates which revealed the formation of *trans*-olefins.[5]



(1)



(2)

The possibility that the hydroalumination of disubstituted alkynes with lithium diisobutylmethylaluminum hydride produces initially the *cis*-vinylalanates, which subsequently isomerize on heating to the *trans* compounds,[6] was ruled out on the basis of the following experiment. The *cis*-vinylalane derived from the reaction of 3-hexyne with diisobutylaluminum hydride was treated with methyllithium and the *cis*-vinylalanate thus formed was heated under conditions similar to the one used for the preparation of the *trans*-vinylalanate. Hy-

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(8) H. Zollinger [*Helv. Chim. Acta*, **38**, 1623 (1955)] has noted similarly that 2-methylpyridine and especially 2,6-dimethylpyridine are less effective catalysts than expected from their base strengths in the azo coupling of 2-naphthol-6,8-disulfonic acid with *p*-chlorobenzenediazonium ion, and he has attributed this result to steric effects involving the methyl groups. While the factor appears not to have been studied, we would anticipate that these catalysts would show larger isotope effects in azo coupling than the unhindered pyridine bases, in accord with the present observations on iodination.

(9) L. Funderburk and E. S. Lewis, *J. Am. Chem. Soc.*, **86**, 2531 (1964); see also ref 10.

(10) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.* (London), **A294**, 273 (1966;) R. P. Bell and J. E. Crooks, *ibid.*, **A286**, 285 (1965); see also J. L. Longridge and F. A. Long, *J. Am. Chem. Soc.*, **89**, 1292 (1967).

(11) E. S. Lewis and L. H. Funderburk, *ibid.*, **89**, 2322 (1967).

(12) The effect under discussion is different from another type of steric effect where, in a complex mechanism, a bulky substituent may shift the rate-determining step from one not directly involving the isotope to one involving the isotope, *e.g.*, nitration of 2,4,6-tri-*t*-butylnitrobenzene [P. C. Myhre and M. Beug, *ibid.*, **88**, 1569 (1966)]; however, even here direct steric effects in the rate-determining step may be responsible in part for the isotope effects observed.

(1) This work was supported by the National Science Foundation, Grant No. GP-6633.

(2) G. Wilke and H. Müller, *Ann.*, **629**, 222 (1960).

(3) G. Zweifel and R. B. Steele, *J. Am. Chem. Soc.*, **89**, 2754 (1967).

(4) The reagent is readily prepared by adding methyllithium to diisobutylaluminum hydride.

(5) The progress of the reaction was followed by withdrawing samples at different time intervals and quenching them in dilute sulfuric acid. Glpc analysis of the upper phase formed indicated that only the *trans* olefin was formed.

(6) The isomerization of *cis*-vinylalanes to the corresponding *trans* compounds has been reported by J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, 2213 (1966).