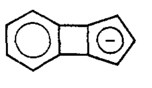
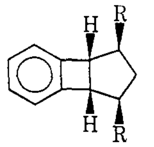
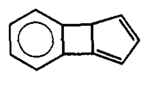
treatment with methyl iodide. Reaction of IX with potassium *t*-butoxide in *t*-butyl alcohol gave, after aqueous work-up, neither of the expected monomeric hydrocarbons X or XI, but rather a mixture of two crystalline dimers $C_{22}H_{16}$: dimer A, mp 132°, and dimer B, mp 201°. Whereas no color formation was observed during the *t*-butoxide elimination reaction of IX, a similar elimination reaction of IX using dimethyl sulfoxide anion in DMSO gave a stable deep brown solution (λ_{max} 590 mμ, shoulder at 500 mμ), the color of which we attribute to anion I. Addition of water to the brown solution caused immediate decolorization with the formation of dimers A and B; addition of D_2O led to the formation of dimers A and B, each containing two deuteriums.[4] In a control experiment, undeuterated dimer B was found not to give the brown anion with DMSO anion in DMSO and was recovered undeuterated after treatment with D_2O.



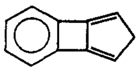
I



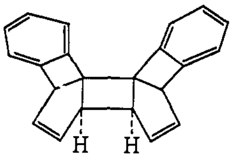
II, R = CO_2H
III, R = $CO_2C_2H_5$
IV, R = $CONHNH_2$
V, R = CON_3
VI, R = $NHCOOCH_2C_6H_5$
VII, R = NH_2
VIII, R = $N(CH_3)_2$
IX, R = $N(CH_3)_3I$



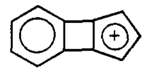
X



XI



XII



XIII

The above observations are consistent with the formation of the norbiphenylene anion (I) from IX by DMSO anion and its protonation by water at the predicted position of highest electron density[1] to give the highly strained, unstable monomer X. Cyclodimerization of X involving the strained central double bond could result in any of four possible dimers, all of which would have nmr spectra in general accord with those observed for dimers A and B. Such a dimeric structure was indeed determined by X-ray analysis for dimer B as explained below.

Dimer B crystallizes in the monoclinic system with unit cell parameters $a = 27.67 \pm 0.04$, $b = 6.015 \pm 0.009$, $c = 38.89 \pm 0.06$ Å, $\beta = 27.74 \pm 0.01°$. The observed and calculated densities ($Z = 8$) are 1.24 and 1.23 g/cc, respectively. Systematic absences are consistent with space groups I2/c and Ic. The intensities of 2187 independent data ($\theta_{Mo} \leqslant 22.5°$) were measured *via* the moving crystal–moving counter method with Mo Kα radiation on a Picker automatic four-circle diffractometer. The centrosymmetric space group was assumed to be the correct one, and iterative application of the Sayre equation[5] to the corrected intensities yielded the locations of all 22 carbon atoms. Preliminary isotropic least-squares refinement has yielded a crystallographic discrepancy factor, R_1, of 0.11.

The crystallographic results show dimer B to have the structure XII and to possess idealized C_s-m symmetry.

Work is in progress aimed toward the X-ray structure determination of dimer A and toward the generation of the ten-π-electron norbiphenylene cation XIII.[6]

Acknowledgment. Support of this work by the National Science Foundation (Grant GP-4931) and by the Petroleum Research Fund (PRF Grant 841-G), administered by the American Chemical Society, is gratefully acknowledged.

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(4) The two protons appearing at δ 4.48 in the undeuterated dimer B are completely absent in the nmr spectrum of the deuterated sample.

(5) D. Sayre, *Acta Cryst.*, **5**, 60 (1952); R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis (Part III), University of California at Los Angeles, 1965.

(6) R. Breslow, W. Washburn, and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 196 (1969), have very recently reported the detection of the cyclobutadienocyclopentadienyl anion, a species closely related to anion I. Protonation of the cyclobutadienocyclopentadienyl anion gave, *via* an unstable monomer, a material which was tentatively assigned the structure of a Diels-Alder dimer. However, subsequent work (private communication from Professor Breslow) shows that this was instead a difficultly separable mixture of two isomeric dimers formed by 2 + 2 cycloaddition of the strained double bond, as in our dimer XII.

(7) National Defense Education Act Fellow.

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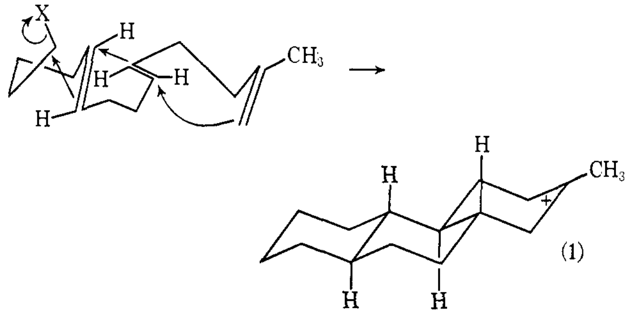
Nucleophilic Participation by a Carbon–Carbon Double Bond in an Intramolecular Analog to the SN2′ Displacement Reaction

Sir:

One rationale for the remarkable stereospecificity which attends the solvolytic cyclization of certain di- and trienyl sulfonate esters (*e.g.*, eq 1)[1] postulates that the cyclization is a concerted process in which *trans* addition occurs simultaneously at each double bond involved in the cyclization process.[1] If this mechanism were operative, it would necessitate nucleophilic attack by one carbon–carbon double bond upon another. The ability of carbon–carbon double bonds to function as nucleophiles in simple displacement reactions is now well established.[2] There is at present, however, little



(1)

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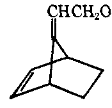
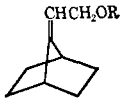
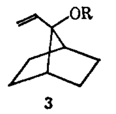
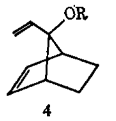
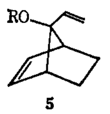
(1) A review: W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

(2) For a summary of leading references, see: (a) G. D. Sargent, N. Lowry, and S. D. Reich, *J. Am. Chem. Soc.*, **89**, 5985 (1967); (b) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *ibid.*, **89**, 880 (1967); (c) P. D. Bartlett, E. M. Nicholson, and R. Owyang, *Tetrahedron Suppl.*, **8**, Part II, 399 (1966), and previous papers in this series therein cited; (d) F. C. Uhle, *J. Org. Chem.*, **31**, 4193 (1966), footnote 26; (e) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms 1966," Interscience Publishers, New York, N. Y., 1967, pp 24–31; (f) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms 1965," Interscience Publishers, New York, N. Y., 1966, pp 37–42; (g) B. Capon, *Quart. Rev.* (London), **18**, 45 (1964); (h) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; *Chem. Rev.*, **56**, 571 (1956).

Table I. Rates and Products of Solvolysis of 3,5-Dinitrobenzoates[a]

	 1	 2	 3	 4	 5
k_1 (100°), 60% aqueous acetone, sec^{-1}	1.90×10^{-4}	1.01×10^{-5}			
k_1 (125°), 70% aqueous acetone, sec^{-1}		3.61×10^{-5}	1.13×10^{-5}	8.89×10^{-3}	1.38×10^{-5}
Solvolysis products[b]	96% **4a** 2.2% **1a**[c]	70% **2a**[d] 30% **3a**	64% **2a** 35% **3a**[d]	100% **4a**[e]	85% **4a** 10% **5a**[c] 4% **1a**[f] 1% unknown

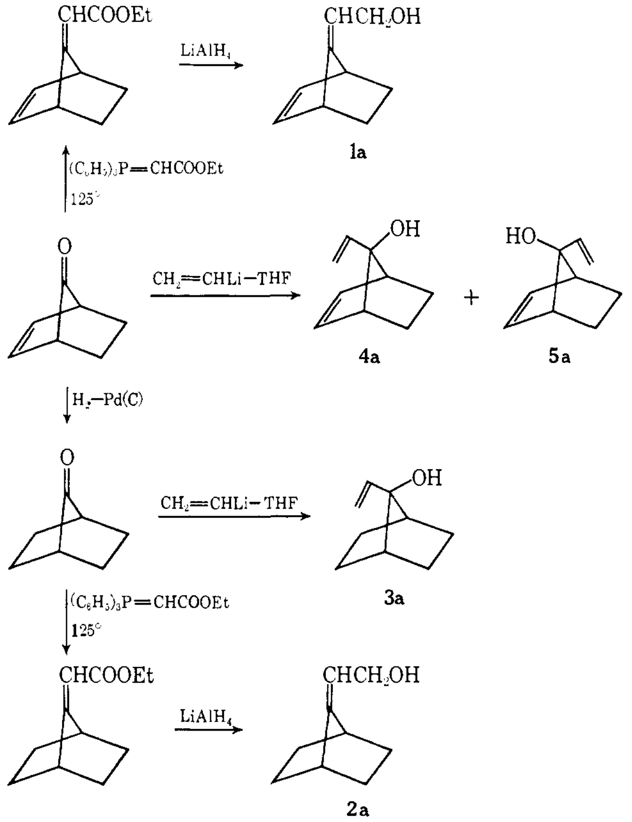
[a] Series **a**, R = H; **b**, R = 3,5-dinitrobenzoyl. [b] Absolute yields are reported. These were obtained by comparison of vapor phase chromatogram peak areas (suitably corrected for variations in molar response factors) to that of an internal standard, 1-decanol. In general, yields are reproducible to ±5% of the value reported. No volatile products other than those reported were observed. [c] May result in whole or in part from acyl oxygen cleavage or from partial equilibration under the reaction conditions. [d] A component (less than 15% of the total) may result from acyl oxygen cleavage. [e] Only volatile product. Absolute yields were inexplicably erratic. [f] May result in whole or in part from *in situ* formation of **1b** followed by some acyl oxygen cleavage or from partial equilibration under the reaction conditions.

or no evidence to support the hypothesis that one double bond can initiate nucleophilic attack upon another double bond which itself must serve as a reservoir of electronic stabilization for a developing cationic center. In order to seek evidence pertinent to this hypothesis we have investigated the possibility that a carbon–carbon double bond might be able to function in a manner analogous to that of the nucleophile in an S_N2′ displacement reaction.[3]

The synthesis of the model substrate employed, 7-(2′-hydroxyethylidene)norbornene (**1a**), together with those of other compounds pertinent to this investigation, is outlined in Chart I. The starting material for each of these syntheses, 7-norbornenone, was prepared by the method of Gassman and Pape.[4] The two tertiary alcohols, 7-vinyl-*anti*- (**4a**) and 7-vinyl-*syn*-7-norbornenol (**5a**), were prepared by the method of Berson and Jones.[5] Both 7-(2′-hydroxyethylidene)-2-norbornene (**1a**) [3,5-dinitrobenzoate (**1b**) mp 83.2–84.3°][6] and 7-(2′-hydroxyethylidene)norbornane (**2a**) [3,5-dinitrobenzoate (**2b**) mp 76.0–76.3°][6] are new compounds, as is 7-vinyl-7-norbornanol (**3a**) [3,5-dinitrobenzoate (**3b**) mp 144.5–145.0°].[6] The synthetic reactions employed in their preparation are straightforward and require no elaboration.

The kinetics of solvolysis of esters **1b**–**5b** in aqueous acetone were investigated utilizing standard ampoule and titrimetric techniques. The low solubility of esters **3b**–**5b** in 60% aqueous acetone required that their solvolyses be conducted in 70% aqueous acetone. The first-order solvolysis rate constants are summarized in Table I. The solvolysis of **2b** is characterized by a downward-drifting first-order rate constant, and the value reported in Table I represents the initial value. The first-order rate plot closely approaches linearity for nearly one half-life, but shows significant concave curvature over longer times. All other first-order rate plots show a good straight-line correlation over at least three half-lives. The downward drift in the rate constant for **2b** results from slow rearrangement to the less reactive tertiary ester **3b**, presumably *via* internal return.

Chart I. Synthesis



The products of solvolysis of esters **1b**–**5b** have been determined and are also reported in Table I. Product studies were conducted in the presence of 10% excess urea, a nonnucleophilic weak base, which is added to neutralize 3,5-dinitrobenzoic acid as it is formed. The product alcohols are unstable under the solvolysis conditions in the presence of 3,5-dinitrobenzoic acid, but are stable when sufficient urea is added to neutralize the acid. The presence of 10% excess urea caused no deviation in the rates of solvolysis greater than ±10%.

At 100°, the rate of solvolysis of **1b** is enhanced relative to that of **2b** by a factor of 18.8. This effect is substantial and clearly in the direction predicted were

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(3) Reviews: R. H. DeWolfe and W. G. Young in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, pp 681–738; *Chem. Rev.*, **56**, 753 (1956).

(4) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

(5) J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, **86**, 5019 (1964).

(6) All new 3,5-dinitrobenzoates gave correct elemental analyses.

the endocyclic double bond in **1b** to initiate nucleophilic attack at C-7 during heterolysis of the allylic ester. The influence of the endocyclic double bond on the kinetically controlled product distribution is even more dramatic. Both **2b** and **3b**, which lack the double bond, yield virtually identical product mixtures, in which the primary alcohol **2a** predominates over the tertiary alcohol **3a** by a factor of 2:1. Since the equilibrium distribution (acid catalysis) of **2a** and **3a** favors the tertiary alcohol by a factor of at least 12:1, the observed product distribution is clearly kinetically controlled and must derive from nucleophilic attack by water on a common cation. The predominance of primary product would seem to indicate that, unlike most unsymmetrically substituted allylic cations,[3] this cation is possessed of greater positive charge density at the primary than at the tertiary position.

In sharp contrast, the product mixture derived from solvolysis of **1b** consists largely of the tertiary alcohol, 7-vinyl-*anti*-7-norbornenol (**4a**), which predominates over the primary alcohol **1a** by a factor of at least 43:1. No 7-vinyl-*syn*-7-norbornenol (**5a**) could be detected in the product mixture. Clearly the intermediate involved in solvolysis of ester **1b** must distribute a much greater percentage of the positive charge density to C-7 than does the intermediate derived from **2b** and **3b**. In addition, the absence of **5a** from the **1b** solvolysis product mixture is strongly reminiscent of results obtained with the 7-norbornenyl cation,[7] for which there is strong evidence for interaction between the endocyclic double bond and the vacant p orbital at C-7, but contrasts markedly with the lack of stereospecificity observed in the product distribution from the 7-*p*-anisyl-7-norbornenyl cation,[8] in which interaction between the double bond and the electron-deficient center appears to be absent. Both observations point to the interaction of the π electrons of the endocyclic double bond with the electron-deficient allylic π system in the cation resulting from ionization of ester **1b**. The fact that the rate of solvolysis of **1b** is accelerated by a factor of 18.8 strongly suggests that this interaction is already well developed in the transition state for bond heterolysis. For these reasons, we conclude that the endocyclic double bond does, indeed, participate during solvolysis of ester **1b** in a manner directly analogous to the behavior of the nucleophile in an S$_N$2′ displacement reaction.

The solvolytic behavior of esters **4b** and **5b** is of interest in its own right and will be discussed elsewhere.

Acknowledgment. We are grateful to the National Science Foundation for financial support. J. A. H. thanks the National Science Foundation for two summer stipends provided by the Undergraduate Research Participation Program.

(7) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(8) P. G. Gassman, J. Zeller, and J. Trevor Lumb, *Chem. Commun.*, 69 (1968).

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A Kinetic Probe for Basicity and Its Application to Mixed Aqueous Solvents[1]

Sir:

The cyanocarbons constitute a class of RC–H acids of high stability and with widely varying acid strength.[2] Recent work with 1,4-dicyanobutene-2, a cyanocarbon acid of pK = 21, has demonstrated that the detritiation of a tritium-labeled species shows general base catalysis in the Brønsted sense which, along with other properties, establishes that the detritiation step measures the rate of proton removal from the weak acid.[3] Studies have now been made with two stronger acids of this series, malononitrile and *t*-butylmalononitrile. The detritiation of tritium-labeled molecules again exhibits general base catalysis. However, these acids are sufficiently strong (pK values of 11.2[4,5] and 13.10,[6] respectively) that, in addition to measurable detritiation rates with general bases and with hydroxide ion, there is an easily measured reaction with the solvent water. The consistency of the rate of this water reaction with that of other bases and the normal behavior of the rate of the reverse reaction make it clear that in this reaction water is acting as a base species attacking the acidic proton of the molecule and that the rate of detritiation, except for an isotope effect, measures the rate of this proton removal. At 25° the first-order rate coefficients for detritiation in aqueous solution by the "water" path are 3.2×10^{-4} sec^{-1} for *t*-butylmalononitrile and 8.5×10^{-3} sec^{-1} for malononitrile.

The existence of this slow reaction in which the solvent water is acting as a base offers the opportunity for a kinetic probe of the basicity of mixed solvents in which water is one component. This basicity probe has now been applied to three solvent mixtures: water–dioxane, water–ethanol, and water–dimethyl sulfoxide.

All studies were made with tritiated *t*-butylmalononitrile in solutions which were 0.001 *M* in hydrochloric acid, previous work having shown that at this acidity only the water reaction occurs; *i.e.*, the hydroxide ion reaction is negligible and there is no acid catalysis. The experimental procedure was to let the reaction proceed at 25°, remove aliquots at intervals, extract the *t*-butylmalononitrile and subject it to scintillation counting. Rates were reproducible to ±3%. The results are given in Figure 1 as plots of logarithm of the observed relative rates for detritiation *vs.* mole fraction of water in the two-component solvent system.

The gross over-all trend for all three systems is that, as expected, the replacement of water by the nonaqueous component leads to decreased basicity. However, there are two notable features. One is the very considerable specificity; the change in basicity with mole fraction of nonaqueous component is significantly different for each of the three solvent mixtures. The second remarkable feature is the rate maximum which is exhibited by each of the three systems, implying that initial addition of the nonaqueous components to water causes an *increase* in basicity.

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(1) Work supported by a grant from the Atomic Energy Commission.

(2) R. H. Boyd, *J. Phys. Chem.*, **67**, 727 (1963).

(3) E. A. Walters and F. A. Long, submitted for publication.

(4) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

(5) R. H. Boyd and C. H. Wang, *ibid.*, **87**, 430 (1965).

(6) F. Hibbert and F. A. Long, unpublished work.