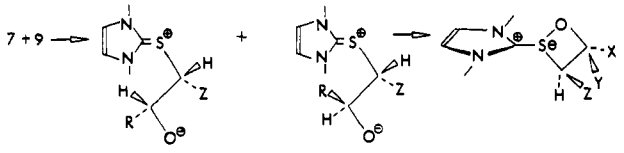
Table I. Products from Quasi-Wittig Reaction

9, R	*Z* isomer	*E* isomer	% yield
Ph	75	25	60
$CH_3CH_2CH_2$	71	29	31[a]
$(CH_3)_2C{=}CHCH_2CH_2CH_2$	75	25	42[a]
$CH_3CH{=}CHCH{=}CH$	35	65	12

[a] Molar ratio of aldehyde to **8** was 2:1.

aldehydes (**9**).[6] Improvement of the overall yield of acrylic ester from enolizable substrates was effected by increasing the ratio of **8** to substrate present in the reaction mixture.

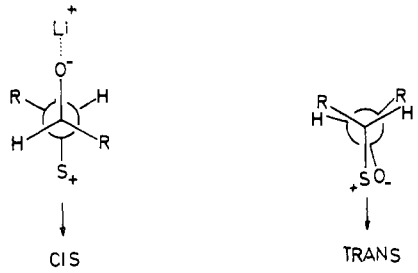
The stabilized thione *S*-methylide differs from its Wittig counterparts in that the former produces primarily the *Z* isomer (Table I). With this difference in mind, two pathways via **11** or **12** may be involved in the formation of the observed products. Considering the most favorable conformation, the



11 **12** **13**

	R	H	CO_2Me
a	X	Y	Z
b	Y	X	Z

erythro-betaine, **11**, arises from addition of the ylide to the carbonyl function with the changed centers diametrically opposed while the opposite is true for the development of the *threo*-betaine, **12**. If steps **11** + **12** → **13** → **10** are considered irreversible or faster than betaine dissociation the isomer distribution of **10** is determined by the ratio of **11** to **12** which, in turn, is a result of this conformational preference, i.e.,



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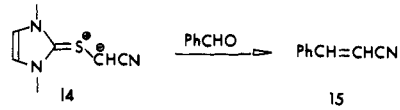
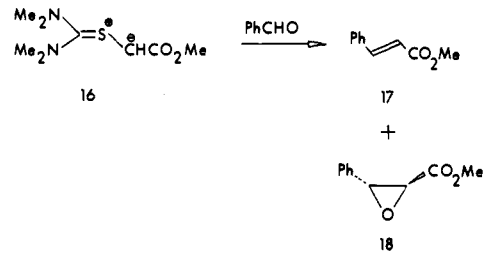
This must be the case as the predominant *Z* isomer arises from the sterically most encumbered hypervalent sulfurane **13b**.[7] Addition of a metal cation to the reaction should lower the transition state energy leading to **11** relative to **12** by ion pairing at the alkoxide site and increase the proportion of betaine **11** available for *Z*-alkene production. In fact, addition of LiI (3 equiv) to the ylide reaction with benzaldehyde raised the *Z* to *E* isomer distribution of the methyl cinnamate product to 92:8.[8] Thione *S*-methylides with sterically less-demanding groups at the carbonionic center yield a more nearly equal distribution of product stereoisomers. For example, **14** provides (50% isolated yield) a ratio of (*E*)- to (*Z*)-cinnamonitriles of



14 **15**

59:41. It should be noted also that the electron donating ability of the thione substituents is critical in determining both the partition of the reaction paths and the distribution of geometrical isomers.[9] The ylide **16** derived from tetramethylthiourea gave a 90:10 ratio of *E*- to *Z*-**17** along with **18** in an overall ratio of 1:1.



16 **17** **18**

Acknowledgments. We sincerely thank the National Science Foundation and the National Institutes of Health for research grants and Professors Kent Barefield and Charles Liotta for stimulating discussions.

References and Notes

(1) In one reported instance the reaction of an oxosulfonium ylide with an aldehyde gave a mixture of oxirane and alkene. This was a result of the large steric demand imposed on the transition state **3** by substituents about the C–C bond which led to the appearance of a competitive pathway (**4**): Y. Tamura, T. Miyamoto, and Y. Kita, *J. Chem. Soc., Chem. Commun.*, 531 (1974).
(2) An excellent review of both reactions may be found in H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, New York, N.Y., 1972, pp 682–733.
(3) Unlike **3** transition state **4** suffers a sulfur–oxygen lone-pair closed-shell destabilizing interaction.
(4) The magnitude of *E* is directly dependent upon the resonance integral developed between the reacting centers and inversely dependent upon the orbital energy difference.
(5) E. M. Burgess and A. J. Arduengo, *J. Am. Chem. Soc.*, **98**, 5020, 5021 (1976).
(6) The results were interpreted by comparing the IR and NMR (as well as GC retention times in some cases) of the products with those of independently synthesized authentic samples. An equivalent amount of 1,3-dimethylimidazole-2-thione was also isolated in all reactions.
(7) The stabilizing electronic features and geometry of tricoordinate hypervalent sulfuranes have been delineated: E. M. Burgess and A. J. Arduengo, *J. Am. Chem. Soc.*, **99**, 2376 (1977).
(8) The opposite effect occurs in the stereochemistry of Wittig reactions.
(9) The energetic placement of the acceptor orbital of the equatorial substituent governs the bond energy of the hypervalent system (see ref 5).

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Isolation and Characterization of Two $C_{11}H_{11}$ Cationic Rearrangements

Sir:

Unsaturated substrates rearrange by some mechanisms that are cationic and by others that are not. The distinction is easier to recognize in principle than to resolve in practice. How can one isolate the rearrangement of an ionic intermediate from the competitive rearrangement of its covalent precursor or product?

We encountered this problem, as one might have expected, in trying to generate the bicyclo[4.3.2]undecatetraenyl cation[1] (**1**, Figure 1) from its covalent precursor under classic S_N1 conditions (2,6-lutidine-buffered 70% aqueous acetone hydrolysis of the 9-*syn*-*p*-nitrobenzoate (**2**)[2] at 80 °C). The problem was previously recognized in studies of apparently cationic C_9H_9 rearrangements.[3] Within the $C_{11}H_{11}$ series, some ten different rearrangements have already been reported.[4,5] Most of them appear to be cationic, but some clearly are not.[5a,b,d,e]

The S_N1 conditions which we selected generated only two products of kinetic control,[6] both rearranged: the anti-tetracyclic alcohol (**4**)[7a,b] and anti-pentacyclic alcohol (**5**).[7a,c] We

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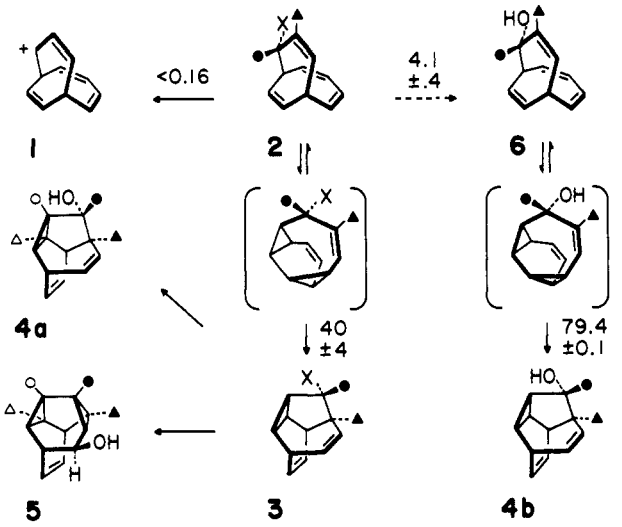


Figure 1. "Hydrolysis" mechanisms in 1,8-bis(dimethylamino)naphthalene-buffered 70% aqueous acetone at 80 °C: X = *p*-nitrobenzoate; ●, ▲, ○, △ = H or D. First-order rate constants are in units of 10^{-6} s^{-1}.

here resolve the covalent from the ionic parts of these rearrangements and separately characterize each of them. We also show that cation **1** (among others) is absent from the ionic part. Quantitative kinetic data are then used in the accompanying communication[8] to define the cationic part more closely. They are here used to set a maximum rate for the S_N1 process (**1** ← **2**) that was our original objective.

A useful experimental innovation was the analysis of aliquot samples by high pressure liquid chromatography rather than by acidimetry.[9] We thus discovered that anti-tetracyclic ester (**3**) is produced in a *pseudoequilibrium* (that is, its concentration rapidly rose to a subsequently stationary fraction (8 ± 1%) of that of its bicyclic precursor (**2**)). Parallel experiments in anhydrous acetone, however, showed that the rearrangement of **2** to **3** was both irreversible and not cationic. In that solvent, its rate (10^6k = 60 ± 20) was essentially identical with that in the buffered aqueous solution (Figure 1). An absence of catalysis is inferred: irreversible rearrangement of the corresponding alcohol (**6** → **4b**) was as rapid in unbuffered 70% aqueous acetone (10^6k = 79.8 ± 0.1) as in the buffered solvent (Figure 1).

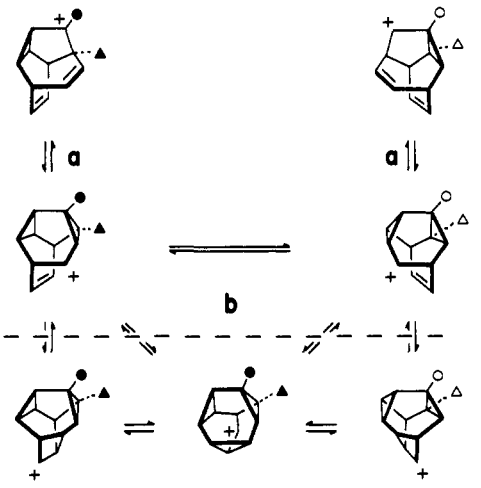
The thermal rearrangement of bicyclic to tetracyclic ester was then shown to be consistent with a two-step sequence: intramolecular Diels–Alder cycloaddition followed by Cope rearrangement.[10] Precursor samples of **2**, separately labeled in the α (●) and β (▲) positions, provided the deuterated tetracyclic ester that was labeled only as shown in **3**.

Subsequent hydrolysis of the tetracyclic ester (**3**) must proceed cationically. One alternative, thermal rearrangement of tetracyclic ester (**3**) to the corresponding ester of the pentacyclic alcohol (**5**), is both stereochemically implausible and experimentally precluded by the stability of **3** in anhydrous acetone. In 10% enriched [$H_2{}^{18}O$]acetone, the alcohols incorporated 100 ± 11% and 98 ± 8% of the maximum isotopic enrichment.

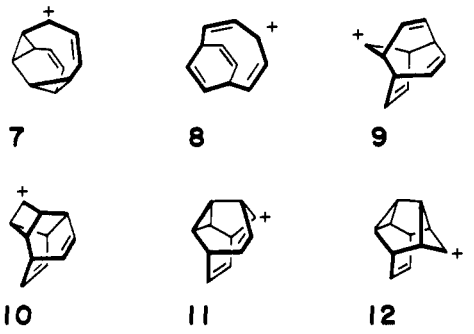
Scheme I segregates two different cationic processes: (a) carbocyclic rearrangement; and (b) redistribution of the two deuterium labels, each one between two nonequivalent sites in the isolated alcohols.[11] The cations displayed above the dashed line are each stabilized by both an adjacent cyclopropane ring and an adjacent homoallyl function. Those below the line lack such added stabilization; experimentally, they are neither required nor excluded.

In contrast, **1** *is* excluded because its element of structural symmetry does not correspond to the symmetry plane of label distribution. Also excluded, and for the same reason, are the

Scheme I



symmetrical cations **7**, **8**, **9**, **10**, **11**, and **12** (among others). Not one of them can serve as a necessary intermediate or even be encountered in a peripheral equilibrium. It is sobering to consider how easily empirical analogy might otherwise have anticipated their production.

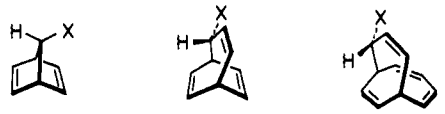


Such extraordinary selectivity strengthens the mechanistic view that cyclobutyl cation formation is more difficult than allylcarbinyl–cyclopropylcarbinyl equilibration,[12] but the observed selectivity reflects experimental constraints as well. Chromatographic analysis had earlier revealed an acid-catalyzed equilibration of the two alcohol products, unsuppressed even by 10 equiv of 2,6-lutidine (pK_a = 6.75).[13] Under these conditions, more isomers appeared at longer reaction times; they appeared at even shorter times in still less adequately buffered solutions. Subsequent use of 1,8-bis(dimethylamino)naphthalene (pK_a = 12.34)[14] solved both problems and provided the kinetically controlled conditions of isotope-label and product analysis.[15]

Unfortunately, the stronger base also stimulated the production of bicyclic alcohol (**6**) as the product of acyl–oxygen fission (⇢, Figure 1). When isolated from incomplete hydrolysis in 10% enriched [$H_2{}^{18}O$]acetone, **6** had incorporated <21 ± 16% of the maximum isotopic enrichment. More precisely, α-deuterated bicyclic ester (**2**, ●) provided alcohol **4b** with its label 100 ± 4% intact.

We therefore think it prudent to set 4% of the basic hydrolysis rate as an upper limit to the undetected S_N1 rate constant that we had originally hoped to measure. The resulting order of Chart I might well appear to be inconsistent with that suggested by any simple π-electron model. Complete neglect of homoconjugative stabilization suggests **14** ≈ **2** ≫ **13**. A variant of the homoaromatic model[16] that minimizes the contribution of the syn-unsaturated bridge[17] suggests **13** ≫ **14** ≈ **2**. The bicycloaromatic model[1] suggests **13** ≈ **2** ≫ **14**. An obvious flaw, common to all such deductions, is the faith that S_N1 activation free energies might reflect only the stability of

Chart I. S_N1 Rate Constants (10^6k, s^{-1}, 80 °C, *p*-Nitrobenzoates in 70% Aqueous Acetone)



13	14	2
6.3[a]	11.1[b]	<0.16

[a] C. L. Deyrup, Ph.D. Dissertation, Boston University, 1970, as cited in ref 18; extrapolated from higher temperatures (E_a = 25.5 kcal/mol). [b] Extrapolated from higher temperatures (E_a = 25.0 kcal/mol)[17] and from 80% aqueous acetone assuming m = 1,[19] whence $k_{70\%}/k_{80\%}$ = 6.35.

the cationic product. This view neglects many other factors, especially the differing stabilities of the reactants.

The remaining rate constants of Figure 1 were best determined indirectly. The kinetic parameters that govern cationic processes were extracted from an independent hydrolytic study of tetracyclic ester (**3**).[8] Independent thermal rearrangement of authentic bicyclic alcohol (**6**) provided the rate constant of this irreversible and uniquely simple first-order process. All of these parameters were next incorporated into an exact solution of the full kinetic network. Only then were the remaining two parameters—the rate constants for basic hydrolysis and for thermal rearrangement of the starting bicyclic ester (**2**)—fitted by a nonlinear least-squares program to the chromatographic area ratios observed during hydrolysis of **2.**

Acknowledgment. Financial support was provided by U.S. Public Health Service Grant No. 10495 from the National Cancer Institute.

Supplementary Material Available: ^{1}H NMR structural analysis of **4** and **5** (2 pages). Ordering information is given on any current masthead page.

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(6) ^{1}H NMR and chromatographic analysis of the crude product (105% isolated yield) revealed significantly less than 5% contamination by **6**, by its epimer, or by the epimers of **4** and **5.** Recovered internal chromatographic standard (borneol) was equally uncontaminated.
(7) (a) Elemental analyses of reactants and products agreed with expectation to ±0.3%. (b) *anti*-Tetracyclo[5.4.0.0^{2,11}.0^{4,10}]undeca-5,8-dien-3-ol,[5d] stereochemistry required by Pr(fod)$_3$-shifting slopes and by $^3J_{3,4}$ < 0.5 Hz. (c) *anti*-Pentacyclo[5.4.0.0^{2,11}.0^{4,10}]undec-8-en-6-ol, mp 166 °C, structure and stereochemistry assigned by analysis of the completely resolved Pr(fod)$_3$-shifted spectrum.
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(20) Presented in part at the 26th International Conference of Pure and Applied Chemistry, Tokyo, Sept 4–10, 1977.
(21) Taken in part from the Ph.D. Thesis of D. P. Warren, Cornell University, 1978.

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Quantitative Analysis of Two $C_{11}H_{11}$ Homoallyl Cationic Rearrangements

Sir:

A long anticipated experimental characteristic of the "nonclassical homoallyl" hypothesis[1] has only recently been reported. The identical mixture of solvolytic products was obtained from stereochemically appropriate allylcarbinyl and cyclopropylcarbinyl precursors, apparently via a common cation.[2] Previous discrepancies from product-mixture identity were admittedly minor,[3] and the experiments that provided them were less sophisticated in technology and design. Such discrepancies are easily attributed to minor deviations from ideal experimental prerequisites (kinetic control under precisely identical conditions, absence of competing mechanisms, etc.). The more recent report[2] strengthens this view and, with it, the reliability of the original hypothesis.

We now must report the observation of a *non*identical product composition, obtained in comparably well-controlled experiments. We analyze the necessary mechanistic consequences of this observation and test them by isotopic labeling. Finally, we indicate some of the more general conclusions that can and cannot be drawn from a realistic kinetic analysis of such data.

The preceding communication[4a] introduced the anti-tetracyclic ester (**4E,** Figure 1). It was the thermal rearrangement product of its syn-bicyclic isomer as well as the ionic precursor of tetracyclic and pentacyclic alcohol products (**4A, 5A**). Here we begin with separate hydrolytic studies of anti-tetracyclic and anti-pentacyclic esters (**4E, 5E**). Under identical conditions, each ester provided the other as a transient intermediate whose concentration rose, and then fell, during hydrolysis. Esters other than these could not be detected, nor could any alcohol other than **4A** and **5A.**[4b,5] The data consisted of 48 chromatographic area ratios: three different ratios[6] for each of 16 aliquot samples, eight samples from each of the two reactants.

Six of the seven independent mechanistic parameters of Figure 1 were fitted to these data by a nonlinear least-squares program (R factor = 0.042).[7] The seven include the two S_N1 rate constants that govern formation of each cation (**4C, 5C**)

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