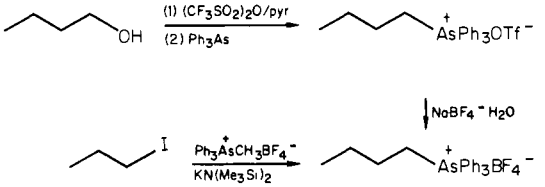
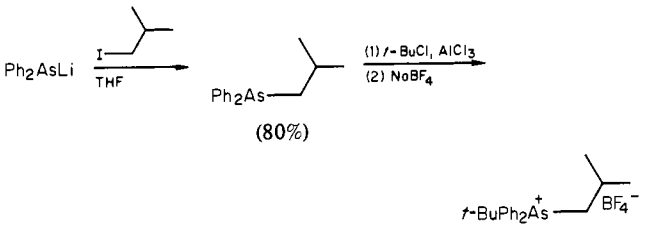
α branching turn out to be readily accessible by nucleophilic substitution of an alkyl triflate (CH_2Cl_2, 25 °C, 2–3 days) followed by fluoroborate exchange (100 equiv $NaBF_4/H_2O$ and extraction into CH_2Cl_2) or alkylation of an arsonium methylide (THF, −78–0 °C). Salts having α branches cannot be efficiently prepared by



mp 138–141 °C (87%)

using either of the two methods above due to competitive rearrangement or elimination. For these systems, highly nucleophilic lithiodiphenylarsine (from Ph_3As and Li/THF)[14] is reacted with the appropriate primary iodide (THF, −78 °C) and the resulting diphenylarsine is quaternized (*t*-BuCl, CH_2Cl_2, $AlCl_3$, or Et_2AlCl; 25 °C) and fluoroborate exchanged ($NaBF_4/H_2O$).



(80%)

mp 135–138 °C (72%)

These sequences are of considerable generality and proceed in good overall yield to produce the required arsonium tetrafluoroborates as stable, crystalline products. Experimental details are available as supplementary material.

Due to the unique capacity of unstabilized arsonium ylides to react with aldehydes to yield trans epoxides cleanly, it is expected that the above described reaction will find considerable application to the synthesis of acyclic molecules having adjacent chiral centers. Furthermore, we believe that the synthetic chemistry of the ylides will prove at least as rich as that associated with phosphorus ylides. Further work in this area will be reported in due course.[15]

Supplementary Material Available: Experimental details (6 pages). Ordering information is given on any current masthead page.

(14) A. M. Aguviar and T. G. Archibald, *J. Org. Chem.*, **32**, 2627 (1967); P. W. Clark, *Org. Prep. Proced. Int.*, **11**, 103 (1979).

(15) This work was supported by grants from NSF (CHE7801769) and NIH (R01 HL25634).

On the Nonconcertedness of Allylic Cation Promoted π-Cyclization Reactions[1]

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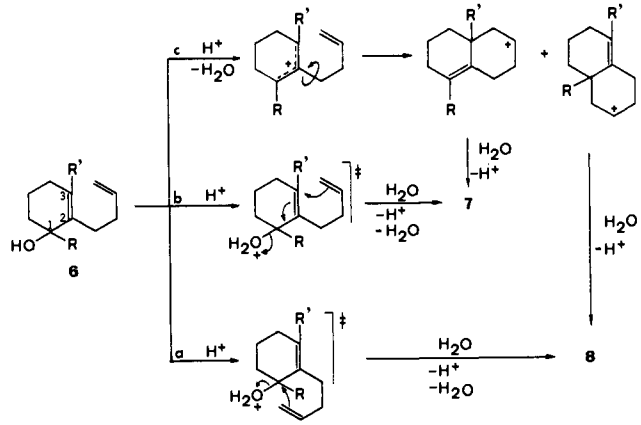
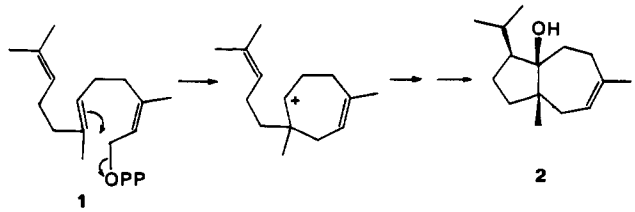
Allylic cations play a significant role in a number of biochemically important cyclization and condensation reactions. Thus, the biosynthesis of carotal (**2**) is thought to involve an anti-

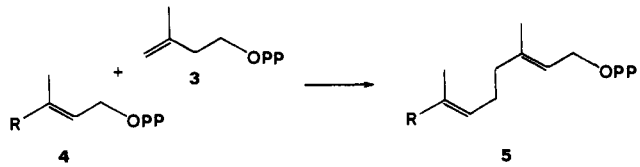
Scheme I



Markovnikov cyclization of the central double bond of *cis,trans*-farnesyl pyrophosphate[2] (**1**).



The prenyl transferase catalyzed 1′,4 coupling reaction between isopentenyl pyrophosphate (**3**) and an allylic pyrophosphate (**4**) is also known to include cationic intermediates.[3]



Recent synthetic applications of biomimetic polyene cyclizations[4] sustained the interest in the elucidation of mechanistic details in these reactions.[5] The important question regarding the stepwise or concerted nature of cation-induced cyclizations still remains to be answered.[4,6]

Poulter et al.[7] presented compelling evidence that reaction **3** + **4** → **5** proceeds by an ionization–condensation–elimination mechanism, but it is not at all certain that this mechanism also applies to cases such as **1** → **2** where the allylic moiety and the double bond are parts of the same molecule.[8] Here the remote double bond could directly assist the departure of the leaving group without intervention of the allylic π system. We addressed ourselves to this problem by studying the formic acid catalyzed cyclization of cyclohexenol derivatives **6a,b**.

Deuterium labeling introduces a convenient perturbation of symmetry, and the mechanistic implications of investigating the course of this well-known reaction[9] by means of labeled substrates are the following (Scheme I): (a) direct displacement of the leaving group by the double bond (π participation) should afford

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(1) This investigation was supported by research grants from the Research Council of Croatia and the National Institutes of Health (02-011-1/PL 480).

(2) Souček, M *Collect. Czech. Chem. Commun.* **1962**, *27*, 2929.
(3) Poulter, C. D.; Rilling, H. C. *Acc. Chem. Res.* **1978**, *11*, 307.
(4) (a) Johnson, W. S. *Angew. Chem., Int. Ed., Engl.* **1976**, *15*, 9. (b) Amupitan, J.; Sutherland, J. K. *J. Chem. Soc. Chem. Commun.* **1980**, 398.
(5) Garst, M. E.; Cheung, Y-F.; Johnson, W. S. *J. Am. Chem. Soc.* **1979**, *101*, 4404.
(6) Eschenmoser, A.; Ruzicka, L.; Jeger, O.; Arigoni, D. *Helv. Chim. Acta* **1955**, *38*, 1890.
(7) Poulter, C. D.; Satterwhite, D. M.; Rilling, H. C. *J. Am. Chem. Soc.* **1976**, *98*, 3376. Poulter, C. D.; Argyle, J. C.; Marsh, E. A. *J. Biol. Chem.* **1978**, *253*, 7227.
(8) For other examples, see: Coates, R. M. *Prog. Chem. Org. Nat. Prod.* **1976**, *33*, 73.
(9) (a) Johnson, W. S.; Lunn, W. H.; Fitzi, K. *J. Am. Chem. Soc.* **1964**, *86*, 1972. See also: Johnson, W. S. *Acc. Chem. Res.* **1968**, *1*,1. (b) Marshall, J. A.; Cohen, N. *J. Am. Chem. Soc.* **1965**, *87*, 2773. Marshall, J. A.; Cohen, N.; Hochstetler, A. R. *Ibid.* **1966**, *88*, 3408.

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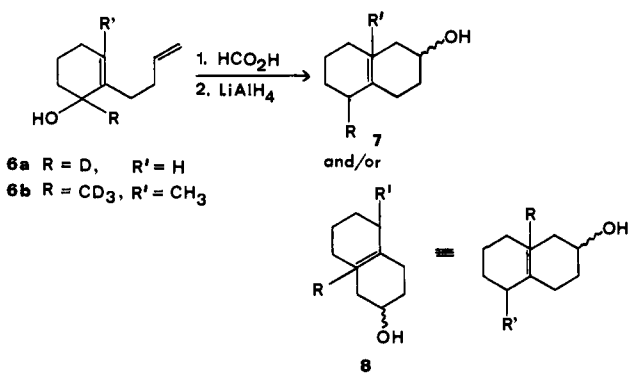

6a R = D, R' = H
6b R = CD_3, R' = CH_3

only **8**; (b) concerted ionization–condensation by a "zipper" mechanism (S_N2') would give only **7**;[10] (c) stepwise ionization–condensation via a resonance-stabilized allylic cation (S_N1) should result in a mixture of equal parts of **7** and **8**.

The required alcohols **6a** and **6b** were prepared in a straightforward manner and subjected to formolysis as described in the supplementary material. The resulting product mixtures were reduced with $LiAlH_4$ in ether and the alcohol was isolated by filtration through a silica gel column. The product composition was determined by taking NMR spectra of the purified mixture and comparing them with spectra of products obtained from unlabeled cyclohexenols. They show well-resolved signals for C_3-H, C_1-CH_3 and C_3-CH_3 centered at δ (relative to Me_4Si) 5.35, 1.59, and 1.04 respectively. The cyclization was practically quantitative, and the product alcohols from either **6a** or **6b** showed a 50% reduction in peak intensities for the respective hydrogens in **7a** and **8a** and the respective methyl groups in **7b** and **8b**.[11]

On the basis of these results one can confidently conclude that in intramolecular cationic π-cyclization reactions of Δ^2-cyclohexenol derivatives, the allylic cation is the first formed intermediate (mechanism C). It is sufficiently stable to permit rotation of the side chain and a subsequent indiscriminate attack of the double bond on either one of the equivalent carbon atoms of the allylic system. It is interesting to note that in this respect the less substituted cation derived from **6a** behaves identically with the tertiary allyl cation derived from **6b**.[12]

Reports on kinetic and isotope effect studies of π-cyclization reactions on a series of similar substrates will appear elsewhere.[13]

Supplementary Material Available: Preparation of **6a** and **6b** and their deuterated derivatives (7 pages). Ordering information is given on any current masthead page.

(10) For an excellent discussion of this "nonstop" mechanism, see: Cornforth, J. W. *Angew. Chem.* **1968**, *80*, 977.

(11) Identical results were obtained in preliminary experiments where the product formation was followed directly in the NMR tube.

(12) One referee raised the question of possible label scrambling *prior* to cyclization which would make the mechanisms a–c undistinguishable. Such internal return is highly improbable on the following grounds: (i) the cyclization in formic acid is almost instantaneous; (ii) solvolysis of unsymmetric substrates (R = H, R' = CH_3) which upon ion-pair return would yield more reactive derivatives shows clean first-order kinetics and normal α-deuterium isotope effects.[13]

(13) The greater part of the, as yet unpublished, material can be found in the Ph.D. Thesis of M. Ladika (University of Zagreb, 1978).

Gas-Phase Oxidation Catalysis by Transition-Metal Cations

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We wish to report the observation, using ion cyclotron resonance (ICR) spectroscopy, of catalytic oxidation cycles involving transition-metal cations and their oxides in the gas phase. For example,

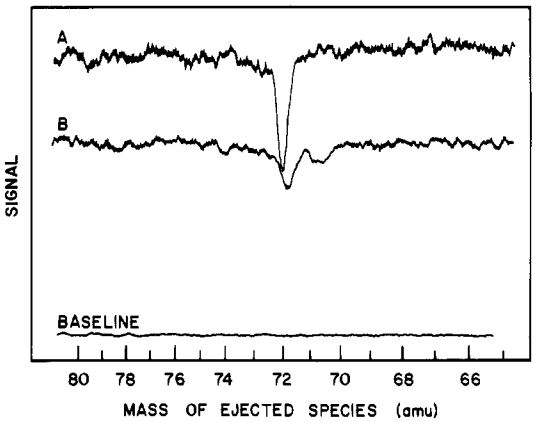
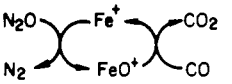


Figure 1. Shown is the ICR signal obtained for Fe^+ while scanning the double-resonance oscillator to eject ions of a given mass from the cell. Trace B is obtained with only N_2O present ($P_{N_2O} = 4.0 \times 10^{-6}$ torr). Trace A results when CO is added to the system ($P_{N_2O + CO} = 4.7 \times 10^{-6}$ torr). The increase in Fe^+ signal after adding CO is due to regeneration of Fe^+ by reaction 2. This is evidenced by the double resonance at m/e 72 (FeO^+) which indicates that FeO^+ is reacting to Fe^+.

Scheme I



oxidation of CO to CO_2 by N_2O is catalyzed by iron cations (Scheme I). This occurs in a two-step process. Fe^+ accepts an oxygen atom from N_2O to give FeO^+ (reaction 1),[1a] and FeO^+

$$Fe^+ + N_2O \rightarrow FeO^+ + N_2,\ k = 0.7 \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1} \quad (1)$$

transfers the oxygen atom to CO to produce CO_2, regenerating Fe^+ (reaction 2). The net result is transfer of an oxygen atom

$$FeO^+ + CO \rightarrow Fe^+ + CO_2,\ k = 9 \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1} \quad (2)$$

from N_2O to CO (reaction 3). This overall process is exothermic

$$N_2O + CO \rightarrow CO_2 + N_2,\ \Delta H^\circ = -107\ kcal\ mol^{-1} \quad (3)$$

by 107 kcal mol^{-1} but does not occur directly at room temperature to any measurable extent.[1b]

The experimental arrangement used for this study has been previously described.[2] A pulsed YAG laser is used to produce atomic metal cations inside the ICR cell. Reactions of these ions with neutral gases are investigated by conventional ICR techniques.[3] When Fe^+ is generated in the presence of N_2O, first-order decay of the Fe^+ signal is observed with a corresponding increase of the FeO^+ signal. The observed half-time indicates a rate constant of $k = 0.7 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} for reaction 1. Thus at 4×10^{-6} torr of N_2O, 80% of the Fe^+ is converted to FeO^+ after 180 ms. Addition of CO to this system increases the Fe^+ signal and decreases the FeO^+ signal with respect to their previous values with only N_2O present. At 180 ms, for example, the Fe^+ signal is 50% larger than with only N_2O present when 0.7×10^{-6} torr of CO is added. Double-resonance spectra (Figure 1) show that the relative increase in Fe^+ is due to a reaction by FeO^+ that occurs only in the presence of CO. The slight dou-

(1) (a) Reaction 1 was reported by Allison, J., Ph.D. Thesis, University of Delaware, 1978, p 123. (b) The standard enthalpy change for this reaction was calculated from heats of formation given in: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(2) (a) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794–3798. (b) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4144–4149.

(3) For a general description of ICR, see: Lehman, T. A.; Bursey, M. M. "Ion Cyclotron Resonance Spectrometry"; Wiley: New York, 1976.

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