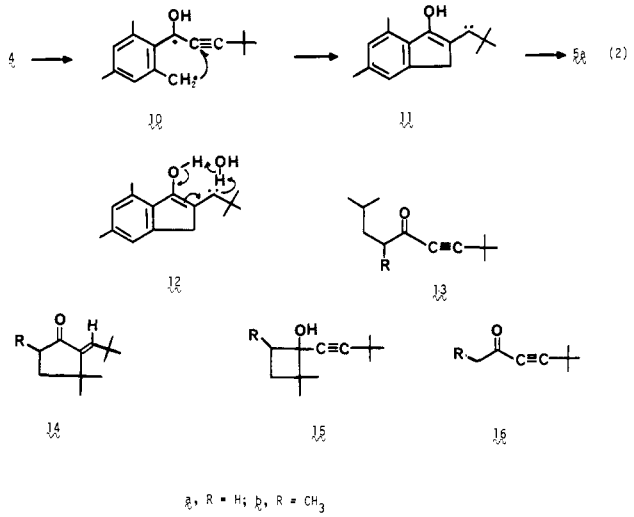
$k_q \tau \sim 0.29$ M^{-1}. The quantum yield for rearrangement of **4** in cyclohexane at 313 nm was ~0.097 as determined against concurrent formation of acetophenone from valerophenone.[13]

The simplest mechanism consistent with these findings is that of eq 2. As a mesityl ketone, **4** upon excitation should undergo



(2)

a, R = H; **b**, R = CH_3

intersystem crossing and abstraction of benzylic hydrogen[9] to furnish **10**. This triplet-derived alkyl propargyl biradical can cyclize (eq 1) to carbene **11**, and subsequent rearrangement of the hydroxylic hydrogen can yield **5a**. Thus, the benzylic hydrogen is transferred intramolecularly in two steps to the final olefinic position. Added water, however, should exchange[14] with the hydroxyl proton of **10** or **11** or alternatively protonate the carbene of **11** directly (as **12**), thereby leading to incorporation of solvent hydrogen at the olefinic position.

With **13a,b**[4,15] similar cyclization to **14a,b**[4] occurs in low yield on direct irradiation in competition with expected formation of cyclobutanols **15a,b** and favored fragmentation to **16a,b**.[16] The reactions of **13a,b** are efficiently sensitized by propiophenone (E_T = 74.5 kcal/mol)[18] but not by *m*-methoxyacetophenone (E_T = 72.4 kcal/mol),[18] consistent with a triplet energy of the alkynone chromophore of ~73-74 kcal/mol.[19] Ratios of the products **14-16** are the same on direct and sensitized reaction.

These novel rearrangements then furnished examples of all-carbon alkyl propargyl biradicals that close to a vinyl carbene. This is of some interest, since the earlier examples[1-3] contained an oxygen atom in the biradical chain, and such heteroatom substitution is known to influence dramatically both the behavior of biradicals[20] and also the rates and regiochemistry of cyclization of simple alkenyl radicals.[21] In addition to its mechanistic implications the photocyclization of **4** affords easy synthetic access to derivatives of 5,7-dimethyl-1-indanone. Preparation of this compound by classical procedures is laborious.[22]

In both the intermolecular [3 + 2] reactions[1-3] and the present type II abstractions, cyclization to a high-energy carbene (eq 1) competes successfully with formation of ground-state products through processes such as fragmentation or closure of a four-membered ring. Since this comes about specifically with triplet-derived intermediates, it is attractive to postulate that the triplet biradical closes directly to carbene in competition with the spin inversion necessary for collapse or fragmentation. Evidence already on record suggests that subsequent reaction of the carbene itself can take place in general from either a singlet or a triplet state.[3,23]

Supplementary Material Available: Melting point, IR, and NMR data and elemental analyses for **4**, **5a**, **6a**, **7**, **13a,b**, **14a,b**, **15a,b**, and **16a,b** (3 pages). Ordering information is given on any current masthead page.

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(14) Cormier, R. A.; Agosta, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 618.
(15) Alkynones **13a** and **13b** were prepared by reaction of 4-methylpentanal and 2,4-dimethylpentanal, respectively, with (3,3-dimethylpropynyl)magnesium bromide, followed by oxidation of the intermediate alkynol.
(16) For 2-octyn-4-one quantum yields of these latter processes are known:[17] cyclobutanol, 0.12 ± 0.02; fragmentation, 0.32 ± 0.03.
(17) Engel, P. S.; Schroeder, M. E.; Schexnayder, M. A. *J. Am. Chem. Soc.* **1976**, *98*, 2683.
(18) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; and references cited therein.
(19) The reported triplet energy of 2-octyn-4-one is 73.1 kcal/mol.[17] We thank Prof. Paul S. Engel for useful correspondence on this matter. A triplet energy of 72.6 kcal/mol can be estimated for 5-decyn-4-one from its phosphorescence spectrum: Gerko, V. I.; Popov, L. S.; Alfimov, M. V.; Bardamova, M. I.; Trotsenko, Z. P.; Kotlyarevskii, I. L. *Opt. Spectrosc. (Engl. Transl.)* **1978**, *45*, 113; *Opt. Spektrosk.* **1978**, *45*, 203. Our earlier estimate[1] of 75-77 kcal/mol for this latter value was in error.
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(21) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4, p 192 and references cited therein.
(22) Kadesch, R. G. *J. Am. Chem. Soc.* **1944**, *66*, 1207. Similar convenient access to derivatives of the difficultly obtained 7-methyl-1-indanone (Elvidge, J. A.; Foster, R. G. *J. Chem. Soc.* **1963**, 590. Premasagar, V.; Palaniswamy, V. A.; Eisenbraun, E. J. *J. Org. Chem.* **1981**, *46*, 2974) from 2,6-dimethylbenzaldehyde should be possible.
(23) We are grateful to the National Science Foundation for support of this research.

Experimental Evidence of the Stepwise Mechanism of a Biomimetic Olefin Cyclization: Trapping of Cationic Intermediates

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There has been recorded very little direct evidence for deciding whether the mechanism of biomimetic olefin cyclization is "stepwise" or "synchronous".[1] The pioneering workers of this field explained their stereospecific results in a synchronous sense.[2] According to Johnson, the question of the mechanism has been open to debate, but the balance of the evidence is somewhat in favor of a synchronous process.[3] van Tamelen has indicated the stepwise mechanism involving a series of conformationally rigid cationic intermediates,[4] and Saito recognized their example to be a concerted reaction.[5] On the theoretical point of view, Dewar declared the existence of intermediate olefin-carbenium ion π-complexes on the basis of MINDO/3 calculation.[6] We herein wish to disclose clear experimental evidence for a biomimetic olefin cyclization that takes place *stepwise* via cationic intermediates with a flexible conformation.

We have developed an efficient olefin cyclization agent, mercury(II) triflate/*N*,*N*-dimethylaniline complex (**1**).[7] and reported its synthetic application to polycyclic terpenoids.[8-11] Recently, we have found that our cyclization agent **1** is stable but still reactive enough in the presence of water, and under such conditions, (*E*,*E*,*E*)-geranylgeranyl acetate (**2**) was converted to

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(2) Stork, G.; Burgstahler, A. W. *J. Am. Chem. Soc.* **1955**, *77*, 5068. Eschenmoser, A.; Ruzicka, L.; Jeger, O.; Arigoni, D. *Helv. Chim. Acta* **1955**, *38*, 1890.
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(5) Saito, A.; Matsushita, H.; Kaneko, H. *Chem. Lett.* **1983**, 729.
(6) Dewar, M. J. S.; Reynols, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 1744.
(7) Nishizawa, M.; Takenaka, H.; Nishide, H.; Hayashi, Y. *Tetrahedron Lett.* **1983**, *24*, 2581.

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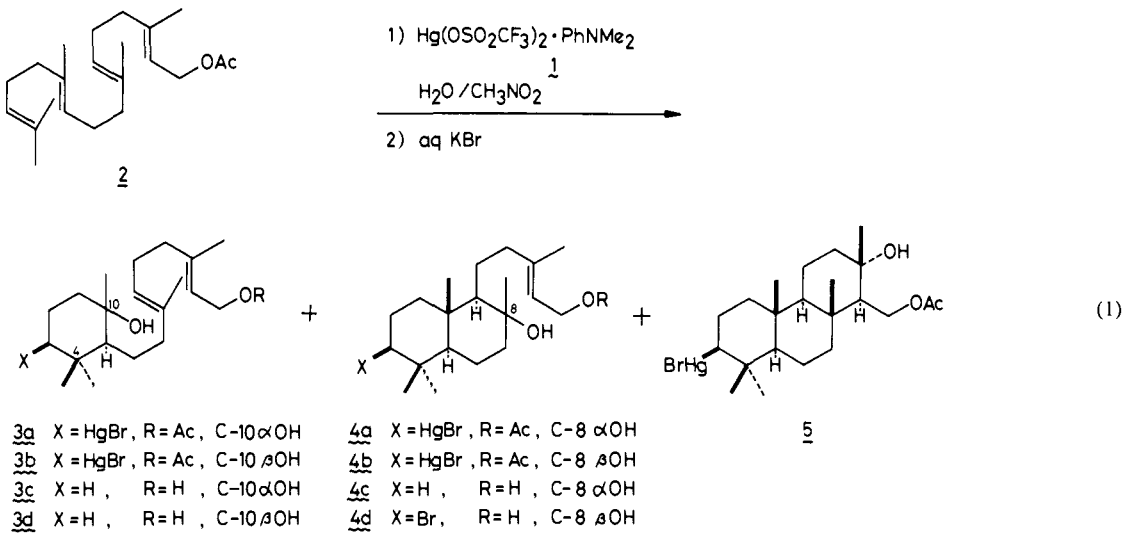
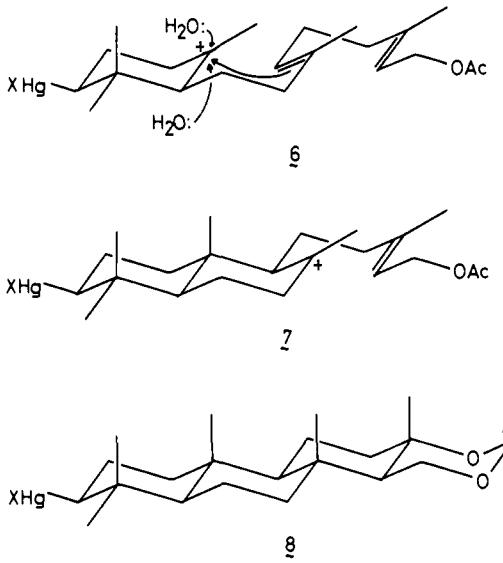


mono-, bi-, and tricyclic *tert*-alcohols via trapping of the cationic intermediate of each step.

The acetate **2** (6.0 mmol) was treated with **1** (1.2 equiv) in nitromethane (90 mL) in the presence of water (12 equiv) at −20 °C for 2 h, and the resulting mixture was directly treated with aqueous KBr solution. Silica gel column chromatography of the crude product gave *tertiary* alcohols **3a**, **3b**, **4a**, **4b**, and **5** in 4.9%, 0.8%, 9.0%, 2.9%, and 8.8% yields, respectively (eq 1), along with 40% of the recovery starting material. The tricyclic product **5** was identified with the authentic material prepared in this laboratory.[11] The structure of bicyclic product **4a** was established by the conversion of (±)-(13*E*)-13-labdene-8,15-diol (**4c**),[12] and that of **4b** was confirmed by the completion of the total synthesis of (±)-aplysin-20 (**4d**)[13] according to the Hoye's bromination.[14] The structure of monocyclic products **3a** and **3b** was determined by the spectral analyses (especially ^{13}C NMR spectra) of both compounds and their demercuration products **3c** and **3d**.[15] The cyclization of **2** with **1** in the presence of 1.2 equiv of water also afforded mono-, bi-, and tricyclic alcohols (**3ab**, **4ab**, and **5**), but the ratio was changed to 1.3:5.4:11.2 (5.7:11.9:8.8 for 12 equiv of water).[16]

The results obtained by this cyclization clearly showed the existence of cationic intermediates such as **6**, **7**, and **8**. These intermediates should maintain sufficient stability via solvation and were slowly converted to each hydroxylation product under the competition with the subsequent ring closure. Important is the



predominant formation of α-equatorial alcohols (**3a**:**3b** = 6:1, **4a**:**4b** = 3:1). If the conformation of the alkyl side chain of the cationic intermediates is fixed via π-complexation as stated by Dewar[6] or van Tamelen,[4] the α-side of the cations should be entirely shielded and the trapping by nucleophile should result in the predominant formation of the β-alcohols. Thus, the alkyl side chain of the cationic intermediates should be conformationally flexible, and the real intermediates of this biomimetic olefin cyclization should be solvated classical cations.

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Supplementary Material Available: IR, ^1H NMR, ^{13}C NMR, and mass spectra of compounds **3a–d** and **4a–d** (8 pages). Ordering information is given on any current masthead page.

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(15) β-Axial methyl groups at C-10 of **3a** and **3c** and C-8 of **4a** and **4c** gave signals at δ 23.1, 23.2, 23.9, and 24.1, respectively, in ^{13}C NMR spectra (in $CDCl_3$), whereas the corresponding α-equatorial methyl signals of **3b**, **3d**, **4b**, and **4d** appeared at δ 30.6, 30.7, 30.8, and 30.7, respectively.
(16) The numbers represent the isolation yields of each ring system product. The proportional change of the ratio of mono-, bi-, and tricyclic products depending on the quantity of water suggests that the single intermediate could be responsible for hydroxylation and subsequent ring closure.