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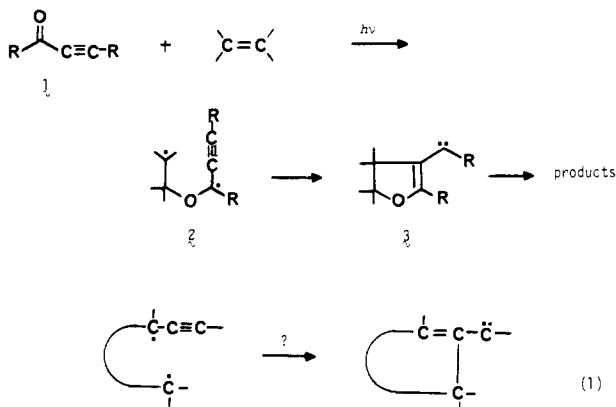
Novel Cyclization of Type II Biradicals from α,β -Acetylenic Ketones

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There is a good evidence¹ that the photochemical [3 + 2] cycloaddition between α,β -acetylenic ketones (**1**) and simple olefins proceeds through reaction of the ketone triplet with olefin to form biradical **2** that then closes to carbene **3**. Products are formed from **3** by way of various hydrogen shifts or cyclization to the cyclopropene.¹⁻³ Biradical **2** from the excited singlet of **1** closes in the [2 + 2] manner to form alkyneoxetane.¹ The closure of **2** to **3** implies that other types of alkyl propargyl biradicals could also cyclize to vinyl carbenes (eq 1). We have now confirmed



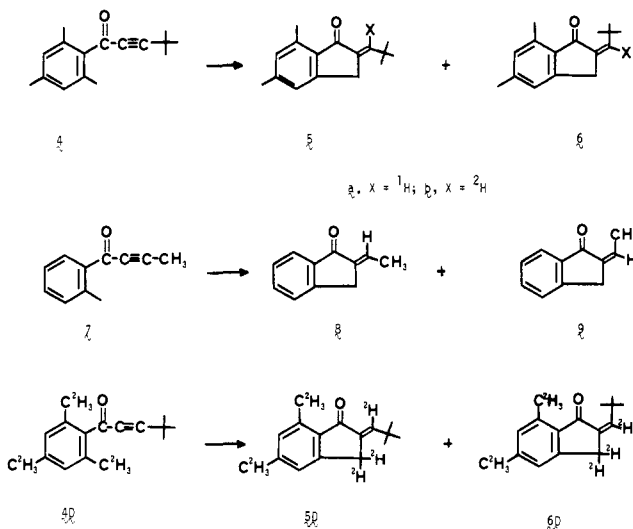
this possibility for several examples of the all-carbon system through a new photochemical reaction of α,β -acetylenic ketones. Irradiation of the mesityl alkynyl ketone **4** leads efficiently to indanone **5a**, and labeling experiments show that the simplest mechanism for this isomerization involves formation of the type II biradical and its cyclization according to eq 1. Details of this and analogous reactions are given below.

(1) Saba, S.; Wolff, S.; Schröder, C.; Margaretha, P.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 6902.

(2) Hussain, S.; Agosta, W. C. *Tetrahedron* **1981**, *37*, 3301.

(3) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 2363.

Ketone **4**,⁴ prepared by reaction of mesitaldehyde with the Grignard reagent from *tert*-butylacetylene and subsequent Jones oxidation,⁵ was irradiated in benzene solution (~ 0.02 M; $\lambda \geq 340$ nm) for 6 h to yield 74% of an 84:16 mixture of **5a**⁴ and **6a**⁴ which



were separated and purified by preparative gas chromatography. Photolysis of **7**,⁴ available through acylation⁶ of 1-(trimethylsilyl)propyne with *o*-toluyl chloride, yielded a 78:22 mixture of **8** and **9**.^{7,8}

We performed several experiments to clarify the mechanism of these transformations. In the first, irradiation of **4** as above, but in benzene saturated with deuterium oxide,¹⁰ furnished **5a** and **6a** carrying $\sim 45\%$ deuterium at the olefinic hydrogen (as **5b** and **6b**) and no deuterium at other positions. A second labeling experiment employed ketone **4D**, which was prepared from mesitoic acid-*d*₉.¹¹ Photolysis of **4D**, using glassware and solvent benzene that had been carefully dried, led to **5D** and **6D**, accompanied by some loss of the olefinic deuterium atom. Recovered **4D** had lost no deuterium. In dry solvent, then, the benzylic positions of **4** provide the olefinic hydrogen of **5a** and **6a**, but in the presence of water one of these benzylic hydrogens can be lost from some intermediate and the olefinic hydrogen is then derived from solvent. The time course of the rearrangement of **4** indicated that **5a** is a primary product but that essentially all of **6a** arises from secondary photolysis. The related isomerization of **8** to **9** under similar conditions is known to be efficient.⁷ Quenching of the isomerization of **4** (0.01 M in cyclohexane) at low conversion by 2,3-dimethyl-1,3-butadiene was examined over the range 0.0–3.2 M quencher and was found to follow Stern–Volmer kinetics¹² with

(4) Characterization data for **4**, **5a**, **6a**, **7**, **13a,b**, **14a,b**, **15a**, and **16b** have not been reported previously; each gave appropriate infrared and ¹H nuclear magnetic resonance spectra, as well as satisfactory elemental analysis or molecular ion in its high-resolution mass spectrum. Complete data are available as supplementary material.

(5) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemm, A. *J. Chem. Soc.* **1953**, 2548. Djerassi, C.; Engle, R. R.; Bowers, A. *J. Org. Chem.* **1956**, *21*, 1547.

(6) Birkofer, L.; Ritter, A.; Uhlenbrauk, H. *Chem. Ber.* **1963**, *96*, 3280.

(7) The spectroscopic properties and mp's of **8** and **9** agreed with those recorded for these substances: Newsoroff, G. P.; Sternhell, S. *Aust. J. Chem.* **1972**, *25*, 1669 and references cited therein.

(8) The yield of **8** and **9** was $\sim 10\%$. It is well-known in other cases that *o*-tolyl ketones undergo reversible photoenolization rather than the photochemical reactions typical of similar 2,6-dimethylphenyl ketones; for details, see ref 9.

(9) Wagner, P. J. *Pure Appl. Chem.* **1977**, *49*, 259 and references cited therein.

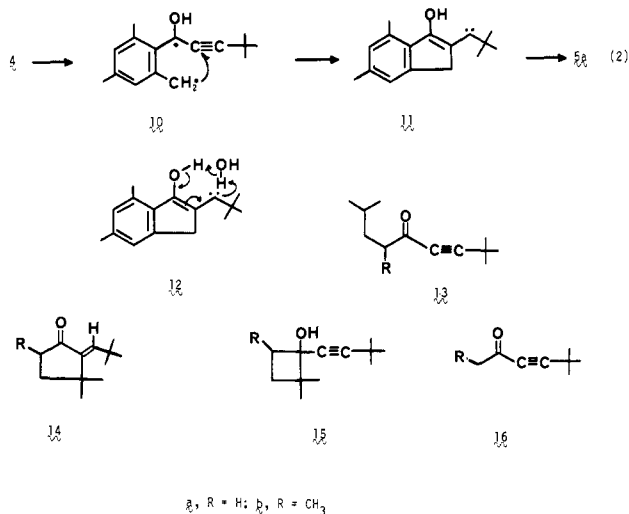
(10) The solubility of water in benzene at 20 °C is 0.021 M: Joris, G. G.; Taylor, H. S. *J. Chem. Phys.* **1948**, *16*, 45.

(11) This was available ($\sim 95\%$ *d*₉) through base-catalyzed exchange of sodium mesitoate with deuterium oxide: Atkinson, J. G.; Csakvary, J. J.; Herbert, G. T.; Stuart, R. S. *J. Am. Chem. Soc.* **1968**, *90*, 498. Hydride reduction and reoxidation furnished labeled mesitaldehyde.

(12) Wagner, P. J. In "Creation and Detection of the Excited State"; Marcel Dekker: New York, 1971; Vol. 1, Part A, p 173.

$k_q \tau \sim 0.29 \text{ M}^{-1}$. 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



intersystem crossing and abstraction of benzylic hydrogen⁹ 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 exchange¹⁴ 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**,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 ($E_T = 74.5 \text{ kcal/mol}$)¹⁸ but not by *m*-methoxyacetophenone ($E_T = 72.4 \text{ kcal/mol}$),¹⁸ consistent with a triplet energy of the alkynone chromophore of $\sim 73\text{--}74 \text{ kcal/mol}$.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 biradicals²⁰ 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

(13) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.

(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 alkyne.

(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 estimate¹ of $75\text{--}77 \text{ kcal/mol}$ for this latter value was in error.

(20) Lewis, F. D.; Turro, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 311.

(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.

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.

(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

(1) Bartlett, P. A. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p 341.

(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.

(3) Johnson, W. S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 9; *Bioorg. Chem.* **1976**, *5*, 51.

(4) van Tamelen, E. E. *J. Am. Chem. Soc.* **1982**, *104*, 6480.

(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.