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(11) These studies were supported in part by a grant from the U.S. National Science Foundation and in part by Grant No. GM10040 from the National Institute of General Medical Sciences of the U.S. Public Health Services.

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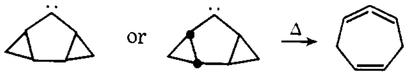
Thermolysis of *syn*- and *anti*-Tricyclo[4.1.0.0^{2,4}]heptan-5-ylidene. *cis*-1-Ethynyl-2-vinylcyclopropane

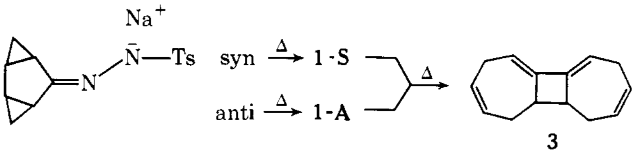
Sir:

Carbenes undergo a myriad of rather unique reactions, including a number of unusual unimolecular, σ-bond fragmentation processes.[1] These include the conversion of cyclopropylidene to allene[2] and the cleavage of cyclopropylcarbene into ethylene and acetylene.[3] Another potential fragmentation process is the conversion of cyclopentylidene into allene and ethylene. Heretofore such a process has been observed only in the case of oxycarbenes where a ketene rather than an allene is extruded.[4]

It was anticipated that *syn*- and *anti*-tricyclo[4.1.0.0^{2,4}]heptan-5-ylidene (**1S** and **1-A**) might fragment in such a manner to yield the highly strained 1,2,5-cycloheptatriene (**2**). Indeed, when the tosylhydrazone sodium salt precursors of **1-S** and **1-A**[5] were pyrolyzed using static (S), drop-static (D-S), or hot tube (T) techniques,[7] up to 94% yield of a dimeric hydrocarbon material was produced. This dimer was demonstrated spectroscopically to have the structure **3**.[9] Dimer **3** was a white crystalline solid, mp 46–47°, which showed only broad multiplets in the NMR at δ 5.55 (6 H), 3.02 (4 H), 2.90–2.45 (2 H), and 2.33 (4 H). **3** had a characteristic uv absorption at λ_{max} 254 nm (ϵ 8120)[10] and it absorbed 4 equiv of H_2 when subjected to catalytic hydrogenation.[12] Yields of **3** remained between 84 and 94% in the temperature range 250–500°, using the S or D-S techniques, the only other products being variable amounts of *trans*-1-ethynyl-2-vinylcyclopropane (*t*-**5**) (0–11%), obtained at relatively low temperatures (<300°), and 4-ethynylcyclopentene (**4**),[13] obtained only at high temperatures (4% at 500°). In cases where the hot tube technique was utilized at 500°, yields of **3** and **4** were 39 and 26%, respectively, while no *t*-**5** was detected.



1-S 1-A 2



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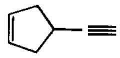

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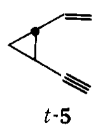
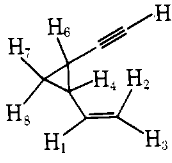


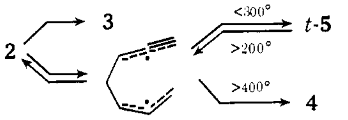
t-5

t-**5** evidenced characteristic ir absorptions at 3320 ($\equiv$C—H) and 2120 (C$\equiv$C) cm^{-1}, and its NMR ($CDCl_3$, 100 MHz) showed peaks at δ 1.40–0.80 (m) (H_6, H_7, H_8), 1.85 (d) (H_5) ($J_{5,6}$ = 2.0 Hz), and 1.94–1.58 (m) (H_4) and an ABX system with multiplets centered at δ 4.96 (H_3), 5.12 (H_2), and 5.40 (H_1) with $J_{1,2}$ = 16.8, $J_{1,3}$ = 9.5, $J_{1,4}$ = 7.5, and $J_{2,3}$ = 2.5 Hz:

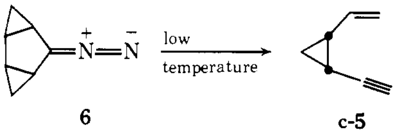


5

It seems probable that products **3**, **4**, and *t*-**5** derive from the highly strained cyclic allene, 1,2,5-cycloheptatriene (**2**), *t*-**5** being formed reversibly at temperature >200°. Indeed it was found that in solution at temperatures >200°, *t*-**5** converted quantitatively to dimer **3**.



The significance of these results revolves around the question of the role played by the 1,2,5-cycloheptatriene. Is it formed *directly* from **1-A** and **1-S** via synchronous C_2–C_4 and C_1–C_6 fragmentation or does it derive from another pathway? The total lack of dependence of product ratios upon the syn or anti nature of **1** speaks against a synchronous pathway for formation of **2**. Strong evidence in favor of a more conventional pathway was obtained when significant amounts of *cis*-1-ethynyl-2-vinylcyclopropane, *c*-**5** were isolated from low-temperature (160–200°) static pyrolyses of either salt. The isolation of *c*-**5** apparently derived from the ability to distill the diazo compound **6** from the hot region *prior* to its loss of N_2. Condensed on the sublimator cold finger at −80°, the reddish species then decomposed slowly yielding the highly unstable *c*-**5** in up to 25% yield with the remainder of the products consisting of dimer **3** and azine formed from **6**.



6 c-5

cis-1-Ethynyl-2-vinylcyclopropane gave an ir spectrum similar to that of the trans isomer (i.e., peaks at 3310 and 2120 cm^{-1}) and an NMR spectrum (100 MHz, $CDCl_3$) which showed two one-proton multiplets at δ 0.78 (H_8) and 1.20 (H_7), a two-proton multiplet region at 1.48–1.84 (H_4 and H_6), doublet at 1.88 (H_5), and an ABX pattern with multiplets centered at δ 5.10 (H_3), 5.24 (H_2), and 5.64 (H_1). Coupling constants were $J_{1,2}$ = 15.8, $J_{1,3}$ = 8.5, $J_{1,4}$ = 7.5, $J_{2,3}$ = 2.5, and $J_{5,6}$ = 2.0 Hz.

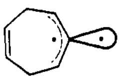
It was found that *c*-**5** underwent conversion rapidly ($t_{1/2}$ = 4.3 hr at 30°) to the dimer **3**, ostensibly via a Cope rearrangement to 1,2,5-cycloheptatriene. The kinetics were followed in the uv at five temperatures between 30 and 48° in ethanol. Plots of log Co/C vs. time were found to be linear through three half-lives with the sole observable product being dimer **3**. Thus the reaction appears to be first order with rate-determining Cope rearrangement being followed by very rapid bimolecular dimerization. An Arrhenius plot of the data yielded a good straight line the equation of which was obtained by a least-squares analysis:

$$\log k/\mathrm{sec}^{-1} = (9.98 \pm 0.22) - (19{,}893 \pm 310)\mathrm{cal\ mol}^{-1}/2.303RT$$

This corresponds to $\Delta H^{\ddagger} = 19.3$ kcal/mol and $\Delta S^{\ddagger} = -15$ eu at 39°, activation parameters which are certainly compatible with a rate-determining Cope process.

It thus appears that *cis*-1-ethynyl-2-vinylcyclopropane rearranged to 1,2,5-cycloheptatriene with a facility equal to that of conversion of *cis*-1,2-divinylcyclopropane (**7**) to 1,5-cycloheptadiene ($\Delta H^{\ddagger} = 19.4 \pm 1.8$ kcal/mol and $\Delta S^{\ddagger} = -5 \pm 7$ eu).[14] While the overall process of dimer formation should be very exothermic ($\Delta H_0 = -40$–50 kcal/mol of *c*-**5**)[15] the rate-determining formation of **2** should be *endothermic* by ~12 kcal/mol.[15] This is in contrast to the exothermicity of ~23 kcal/mol for the *cis*-1,2-divinylcyclopropane rearrangement.[15] Moreover, it appears that the Cope process of *cis*-1,2-diethynylcyclopropane, which could lead initially to an even more strained diallenic intermediate, occurs with a rate constant similar to those of *c*-**5** and **7**.[16]

While the source of the bulk of the dimer from these pyrolyses has not been unambiguously ascertained,[17] it does appear reasonable that the major, if not only, primary fragmentation product is *cis*-1-ethynyl-2-vinylcyclopropane,[18] and that this then rearranges to 1,2,5-cycloheptatriene[20] which rapidly dimerizes. The structure of this highly reactive allenic intermediate is a matter of some significance. The question yet unanswered experimentally is whether this allene is a planar diradical or dipolar species, such as **8**, or a twisted, strained-but-bonded allene. Calculations by Dillon and Underwood indicate that a *planar* structure may be most stable and that a triplet, biradical species may be the ground state.[22]



8

The unexpected, low-activation-energy Cope rearrangement of *cis*-1-ethynyl-2-vinylcyclopropane is presently receiving further attention in our laboratories, as are probes of the nature of 1,2,5-cycloheptatriene.

Acknowledgment. We wish to acknowledge with thanks partial support of this research by the National Science Foundation.

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(10) This compares favorably with the $\lambda_{\max}$ 252 nm (ϵ 8600) for the dimer of the relatively stable allene, 1,2,6-cyclononatriene,[11] which dimerized at 120°.

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(12) The dimers from **1-S** and **1-A** appear to be identical in all respects although the stereochemistry of the cyclobutane ring has not yet been elucidated. **3** was extremely air sensitive and subject to facile thermal decomposition in solution. Thus, no Diels–Alder adducts could be obtained with either tetracyanoethylene or maleic anhydride.

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(15) Approximations of heats of formation of **2, 3,** and **5** were made utilizing Benson's group values: S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968. $\Delta H_f°$ for **2** was approximated by assuming no unusual ring strain but a structure similar to **8** (vide infra) and assuming an allenic π bond energy of 60 kcal/mol—8 kcal/mol usual allene strain—15 kcal/mol allyl radical resonance stabilization.

(16) M. B. D'Amore, Ph.D. Thesis, California Institute of Technology, 1972; and personal communication from R. G. Bergman. See also T. J. Henry and R. G. Bergman, *J. Am. Chem. Soc.*, **94,** 5103 (1972).

(17) Such ambiguities are common in flash pyrolytic studies of tosylhydrazone sodium salts. Localized high pressure zones may be the cause of such extensive dimer formation with little evidence of monomeric species.

(18) A similar fragmentation was observed in the pyrolysis of tetracyclo[3.2.1.$0^{2,7}$.$0^{4,6}$]octan-3-ylidene, although in this case there was no evidence of subsequent conversion to an allene species.[19]

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Book Reviews

Introduction to Organic Electrochemistry (Techniques and Applications in Organic Synthesis Series). By M. R. RIFI and FRANK H. COVITZ (Union Carbide, Research and Development Department). Marcel Dekker, Inc., New York, N.Y. 1974. vii + 417 pp. $26.50.

This book is designed to initiate organic chemists into the mysteries of electrochemical synthetic methods.

The first chapter includes a frank discussion of the advantages and disadvantages of the method and a historical background. The second chapter covers the basic principles in about 60 pages, touching on the Nernst equation and diffusion as well as such esoterica as double layer capacitance, adsorption, *iR* drop effects, junction potentials, etc. It includes a particularly lucid discussion of charge-transfer rate constants. The third chapter covers apparatus and techniques. The discussion of electrode materials and their pretreatment, solvents, supporting electrolytes, and practical synthetic cells is excellent. The authors also discuss measurement and recording devices, coulometers, and potentiostats and provide a