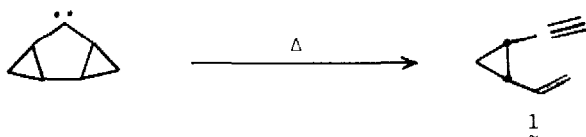


THERMOLYSIS OF SYN- AND ANTI-TRICYCLIC [5 1 0 0<sup>3,5</sup>]OCTAN-2-YLIDENE CIS-1-ALLYL-2-ETHYNYLCYCLOPROPANE

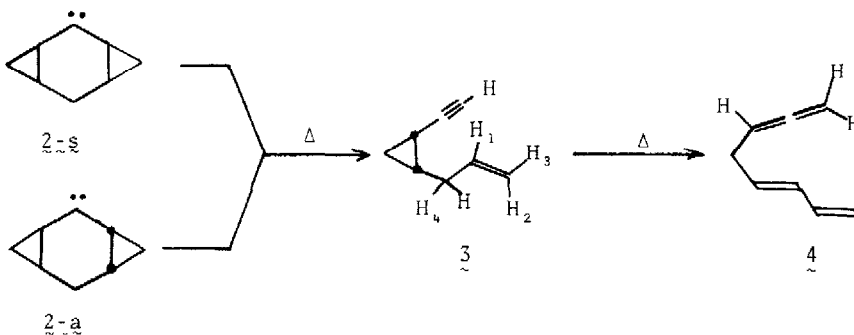
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An important fragmentation process of carbenes is that of the conversion of cyclopropyl carbenes to ethylenes and acetylenes<sup>3</sup> Recently we demonstrated the utility of this cleavage process in the synthesis of cis-1-ethynyl-2-vinylcyclopropane, 1<sup>4</sup>



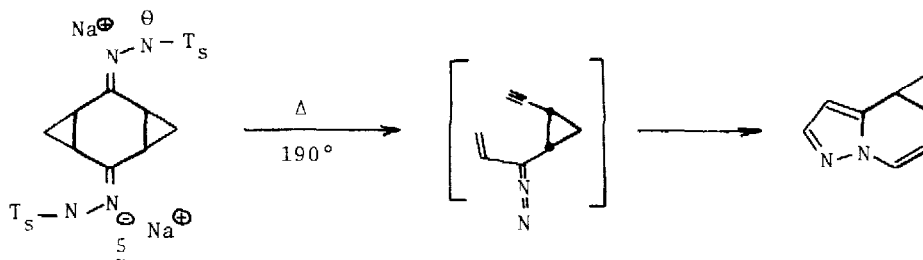
In this communication we report the similar fragmentation of the homologous carbenes, syn- and anti-tricyclo [5 1 0 0<sup>3,5</sup>]octan-2-ylidene, 2-s and 2-a, to produce cis-1-allyl-2-ethynycyclopropane, 3, and its facile thermal rearrangement to 1,2,5,7-octatetraene, 4



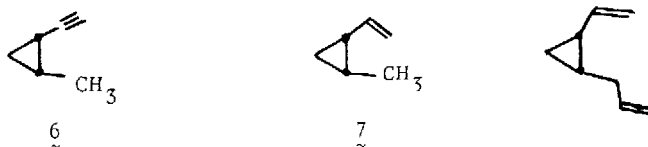
Carbenes  $\underline{2-s}$  and  $\underline{2-a}$  were generated from the pyrolysis of their respective tosylhydrazone sodium salts<sup>5</sup> in a drop-static pyrolysis system<sup>4</sup> at temperatures from 260-400°. Product ratios were relatively insensitive to the initial stereochemistry of  $\underline{2}$ . At 260°, essentially pure  $\underline{3}$  was obtained in 70% yield nmr (60MHz,  $\text{CDCl}_3$ ), cyclopropyl protons- $\delta$  0.47 (m,1H), 1.02 (m,2H), 1.38 (m,1H), acetylenic proton- $\delta$  1.81 (d,1H), allylic protons- $\delta$  2.23 (m,2H), vinyl protons-ABX pattern with multiplets  $\delta$  5.02, 5.10 and 5.95 with coupling constants  $J_{1,2}=17.4$ ,  $J_{1,3}=9.7$ ,  $J_{1,4}=6.4$  and  $J_{5,6}=2.0$  Hz. ir ( $\text{CCl}_4$ ) (inter alia), 3320, 2120, 3080, 1645, 990 and 910  $\text{cm}^{-1}$ .

At temperatures  $>400^\circ$ , the product mixture consisted largely of  $\underline{4}$  (yield  $\approx 37\%$ ) nmr (100MHz,  $\text{CDCl}_3$ ), pseudo heptuplet at  $\delta$  2.84 and a complex vinyl region,  $\delta$  4.74 (m,1H), 4.84-5.32 (m,3H) and 5.50-6.60 (m,3H), ir ( $\text{CCl}_4$ ) (inter alia), 1955, 3090, 3005, 1645, 1605, 995, 910, 345 and 740  $\text{cm}^{-1}$ , uv (EtOH),  $\lambda_{\text{max}}$  225 nm ( $\epsilon$  27,100). Moreover  $\underline{3}$  was found to rearrange smoothly to  $\underline{4}$  either via gas phase flow pyrolysis at 410° (78%) or via static pyrolysis in isooctane (essentially quantitative).

A fragmentation related to that of  $\underline{2}$  has been hypothesized to rationalize the results of thermal decomposition of  $\underline{5}$ <sup>6</sup>



Rearrangement of  $\underline{3}$  to  $\underline{4}$  involves a 1,5-hydrogen shift, and the reaction is closely analogous to the previously reported rearrangement of cis-1-ethynyl-2-methylcyclopropane,  $\underline{6}$ , to 1,2,5-hexatriene<sup>7</sup>



A kinetic study of the reaction in the temperature range of 150-171° led to five rate constants which gave an reasonable Arrhenius plot, the equation of which was obtained by a least squares analysis

$$\log k/\text{sec}^{-1} = 8.2 \pm 0.5 - 25,100 \pm 1,000 \text{ cal mole}^{-1}/2.303RT$$

The small pre-exponential factor is strong indication of a concerted H-shift mechanism being involved. However, in order to effectively evaluate the enthalpic and entropic factors involved in this hydrogen-shift process, one would need to have available activation parameter data for molecules 6, 7, and 8. Unfortunately such data is available only for 7.<sup>8,9</sup>

A comparison, nevertheless, of the activation parameters of 3 and 7 reveals a probable significantly enhanced entropic demand of an ethynyl

Table<sup>a</sup>

	$k_{170^\circ}$ (sec <sup>-1</sup> )	Log A	$E_A$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta F^\ddagger$
3	$6.1 \times 10^{-5}$	8.2	25.1	24.3	-24	34.7
7	$3.9 \times 10^{-5}$	10.9	31.1	30.2	-12	35.4

<sup>a</sup>units of  $E_A$ ,  $\Delta H^\ddagger$  and  $\Delta F^\ddagger$  are kcal/mole while those of  $\Delta S^\ddagger$  are eu/group which is involved as the termination site for [1,5] hydrogen migration, an observation which is reminiscent of our earlier observed enhanced entropic demand of an ethynyl group involved in the Cope rearrangement of 1 as compared with cis-1,2-divinylcyclopropane.<sup>10</sup>

Additional quantitative studies of the kinetic effect of an ethynyl group on sigmatropic processes are needed to elucidate this interesting phenomenon.

References

- 1 Department of Chemistry, College of Sciences, University of Baghdad, IRAQ
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- 3 T Sasaki, F Eguchi, M Ohno and t Umemura, J Org Chem , 38, 4098 (1973), and references therein
- 4 W. R Dolbier, Jr , O T Garza and B H Al-Sader, J Amer Chem Soc , 97, 5038 (1975)
- 5 J B Lambert, F R Koeng and J W Harnersa, J Org Chem , 36, 241 (1971)
6. C B Chapleo and A S Dreiding, Helv Chim Acta, 57, 873 (1974)
- 7 V Dalacker and H. Hopf, Tetrahedron Lett , 15 (1974)
- 8 R J Ellis and H M Frey, J Chem Soc , 5578 (1964)
- 9 W R Roth and J Konig, Ann , 688, 28 (1965)
- 10 J M Brown, B T Golding and J J Stofko, Jr , J Chem Soc , Chem Comm , 319 (1973).