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SYNTHESIS AND THERMAL ISOMERIZATION OF CIS N-METHYL-2,3-DIVINYL AZIRIDINE.

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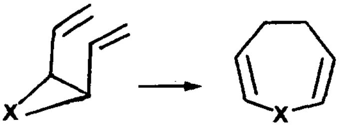
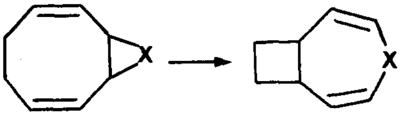
Until recently, all attemps to prepare cis-1,2-divinylcyclopropane I_b [1,2] and cis N-alkyl-2,3-divinylaziridines I_c [3] have failed, although cis-2,3-divinyloxirane I_a [4,5] has been isolated at room temperature. These three-membered rings I undergo the thermal Cope expansion to seven-membered dienes $II\_$. It had even been suggested that the compound I_b could not be isolated at a temperature as low as -40°C. [1,2] If we consider the activation energy for the similar isomerizations of III_{a-c} to IV_{a-c} [6] (table I) we could expect an acceleration for the Cope rearrangement of I_c relative to I_b, contrary to indications published, [7] and consequently a lower stability for that compound. The isolation of I_b, recently published by Brown and coworkers, [8] prompts us to report the synthesis and thermal isomerization of the hitherto unknown I_c (R:methyl) which permits a quantitative comparison of the thermal valence isomerization of these cis-divinyl three-membered rings.



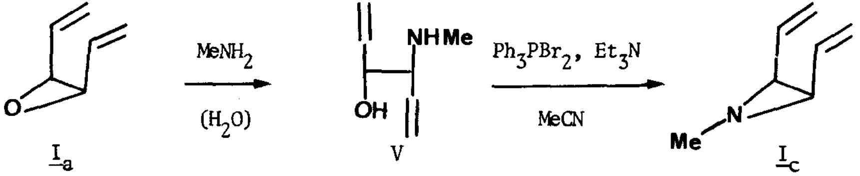
I_{a-c} II_{a-c}

a : X = O
b : X = CH_2
c : X = N - R



III_{a-c} IV_{a-c}

Cis N-methyl-2,3-divinylaziridine I_c was prepared from the oxirane I_a [4] through aminolysis with $MeNH_2$ and cyclisation of the threo-aminoalcohol V with Ph_3PBr_2 [9] at -15°C. The proton N.M.R. spectrum at this temperature indicated that I_c was free from trans isomer [10] and that less than 4 % of II_c was present. The compound I_c rearranges quickly and completely at 40°C. N.M.R. : I_c $\delta(CCl_4)$ 2.37 (s, 3H), 1.92 (m, 2H), 4.9 to 5.8 (m, 6H) ; II_c $\delta(CCl_4)$ 2.97 (s, 3H), 2.32 (m, 4H), 5.6 (d, 2H), 4.47 (m, 2H).



I_a V I_c

The kinetics of the Cope rearrangement were followed by N.M.R. spectroscopy in benzene solvent. Analysis of the product distribution was based on methyl (δ C_6H_6 2.52) and methylene peaks (δ 2.42) of II_c and methine peaks (δ 1.74) of I_c respectively. The reaction is cleanly first order (up to 70 % extent) with respect to starting material. The calculated rate constants are obtained by a least squares analysis of fifteen to twenty experimental data : k 11.1°C = 3.21 x 10^{-3}mn^{-1}, k 13.8°C = 4.94 x 10^{-3}mn^{-1}, k 16.5°C = 6.57 x 10^{-3}mn^{-1}, k 21.3°C = 10.85 x 10^{-3}mn^{-1}, k 24.8°C = 15.80 x 10^{-3}mn^{-1}.

Thus the enthalpy of activation of the nitrogen heterocycle $\underline{I}_c$ (ΔH^{*} = 18.5 Kcal mole^{-1}) is lower than that of the cyclopropane $\underline{I}_b$ [8] (table I) and the stability of cis-divinyl substituted three-membered rings decreases in the order oxygen, carbon, nitrogen (table I). This sequence parallels that observed by Grimm with cis-bicyclo |6,1,0| nona-2,6-dienes [6] ;

Table I Activation parameters

	ΔH^{*}(Kcal.mole^{-1})	ΔS^{*}(cal d°$^{-1}$ m.$^{-1}$)		$E_a$$^{(c)}$(Kcal.mole^{-1})
$\underline{I}_a$	22.7 ± 1.0$^{(a)}$	-15.2 ± 2.9	$\underline{III}_a$	28.6 ± 0.85
$\underline{I}_b$	19.4 ± 1.8$^{(b)}$	- 5.30± 6.75	$\underline{III}_b$	25.0 ± 0.50
$\underline{I}_c$	18.5 ± 1.5$^{(d)}$	- 3.8 ± 5.0	$\underline{III}_c$	21.3 ± 0.60

(a) ref 4 ; (b) ref 8 ; (c) ref 6 ; (d) this work

it is in good agreement with what is known about the relative stability of azanorcaradiene [7], norcaradiene [11], benzene oxide [5] on the one hand and seven-membered trienes on the other. In these series, to our knowledge, no satisfactory explanation seems to have been given for the variation of the reactivity with the nature of the ring atom. Finally, the synthesis of cis-divinylaziridines with various substituents on the nitrogen atom should permit a study of the ways by which the activation energy for this fascinating Cope isomerization may be modified.

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