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THERMAL CYCLIZATION OF A VINYLALLENE TO A CYCLOBUTENE

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Thermal cyclization of 1,3-dienes to cyclobutenes has recently been observed for 1,3-cyclooctadiene and 1,3-cyclononadiene.[1] We wish now to report the formation under thermal conditions of a cyclobutene derivative from an open chain 1,3,4-triene. The ring closure in this case involves an allenic double bond and it should be recalled that allenes undergo cycloaddition to suitably substituted olefins to yield cyclobutenes.[2]

Continuing our studies on the reactions and equilibrium isomerizations of cycloolefins,[3] we have pyrolyzed 1-methyl-3-methylenecyclobutene (I) in pentane solution at 350 and 400°C. As expected, the vinylallene, 2-methyl-1,3,4-pentatriene, was formed. Surprisingly, however, when increasing the time of pyrolysis, the proportions of I to II remained constant, pointing to the formation of an equilibrium. The reversibility of the reaction was established by pyrolyzing the vinylallene and finding in the product practically the same ratio of I/II as above (see Table I). The semicyclic double bond stabilizes the cyclobutene ring since no opening of I occurs below 350°, while alkylcyclobutenes are cleaved already at 160°-200°C, under otherwise similar conditions.[3a]

I was prepared by isomerization of 1,3-dimethylenecyclobutane[4] at room temperature using a sodium on alumina catalyst.[5] The equilibrium mixture contained 99.2% I and 0.8% 1,3-dimethylenecyclobutane.

After pyrolysis two peaks appeared on the chromatogram (see Table I) in addition to the solvent peak. The compounds corresponding to the two peaks were isolated with a preparative GLC column (1m x 2cm) using 30% $AgNO_3$/glycol as stationary phase, and were shown to be pure I and II, respectively.

Table I

Pyrolysis[a] of 1-Methyl-3-methylene-cyclobutene (I) and 2-Methyl-1,3,4-pentatriene (II)

No. of pass	% in product[b]	
	I	II
	T=350°C	
Starting from I:		
1	49.2	50.8
2	49.6	50.4
3	49.2	50.8
4	49.7	50.3
Starting from II:[c]	48.2	51.8
	T=450°C	
Starting from I:		
1	53	47
2	49	51
3	44.7	55.3
4	44.7	55.3
Starting from II:[c]	52.0	48.0

a. The pyrolysis was carried out in a vertical 30cm x 1cm pyrex tube, packed with pyrex beads; the isothermal zone had a length of about 15cm. Contact time was about 11 sec. per pass.

b. As shown by GLC on two different columns of equal dimensions (2m x 4mm), containing 10% $AgNO_3$/glycol and 20% β,β'-oxydipropionitrile, respectively, as the stationary phase.

c. Isolated by preparative GLC from pyrolysate of I.

I exhibited absorption bands at 1605 and 1680 cm^{-1}. The n.m.r. spectrum showed a singlet at 6.05 p.p.m., a doublet at 4.4 p.p.m., a singlet at 2.83 p.p.m. and another singlet at 1.95 p.p.m. with relative intensities in the ratio of 1:2:2:3. These data are in agreement with the literature.[4] Mass spectrometry gave a molecular weight of 80.

II absorbed three molecules of hydrogen (10%Pd/charcoal catalyst at room temperature) yielding 2-methylpentane. The infrared spectrum showed the specific allene absorption at 1940 cm^{-1}. The assigned structure was further confirmed by the n.m.r. spectrum, which showed a triplet at 5.9 p.p.m. (J=6.5 cps), a multiplet between 4.7 and 5.1 p.p.m. and a slightly broadened singlet at 1.81 p.p.m. with intensities in the ratio 1:4:3. The triplet and multiplet are assigned respectively to the single proton on C_3 and the four terminal protons on C_1 and C_5. Both the chemical shift and the coupling constant of these protons are in good agreement with literature data for allenic compounds.[6] The ultraviolet spectrum (in ethanol) had a λ_{max} at 220 mμ (log ε 4.24), as compared with λ_{max} 216 mμ (log ε 4.14) for 1,3,4-pentatriene[7] and λ_{max} 225 mμ (log ε 4.39) for 2,7-dimethyl-3,5,6-octatriene.[8]

The scope of the reaction will be the subject of further studies. The investigation of compounds, suitably substituted, for permitting to follow the steric course of the conversion, will be of particular interest in view of the recent theory of electrocylic transformations of Woodward and Hoffmann.[9]

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