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THERMAL 1,5-HYDROGEN MIGRATION IN CIS-β-OCIMENE (1)

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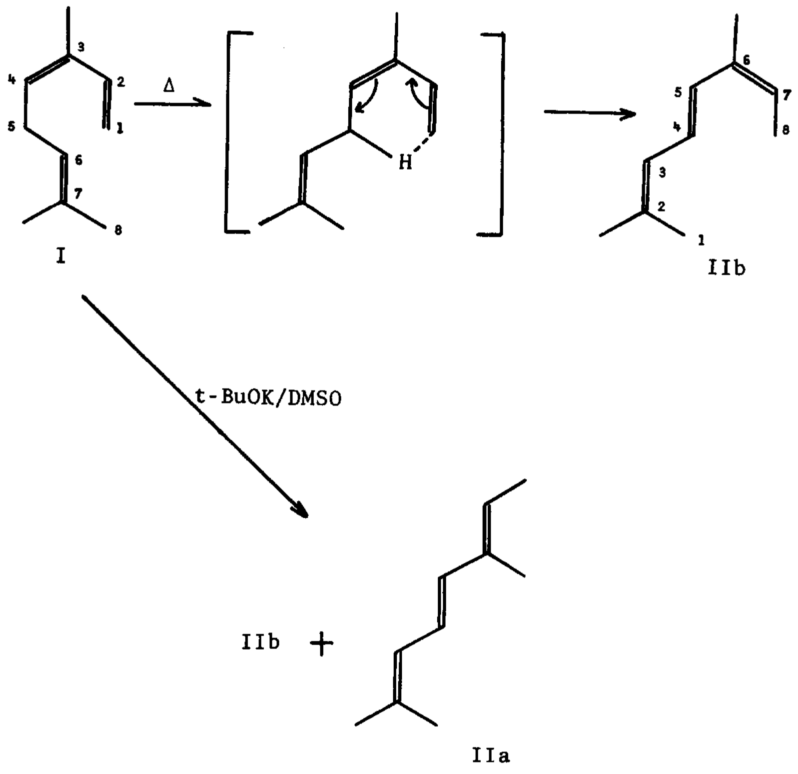
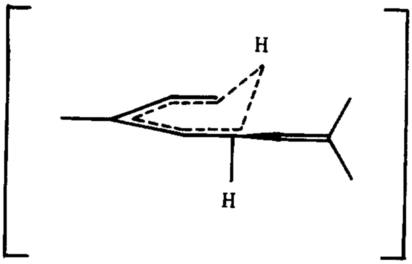
Although thermal 1,5-hydrogen migrations are well exemplified for a number of aliphatic dienes (2) as well as for cyclic systems (3), the mechanism of this type isomerizations has been investigated only recently (4). The thermal isomerization of cis-β-ocimene (I) (3,7-dimethyl-3-cis-1,3,6-octatriene) have been recognized for a long time (5), but the problem of the adequate characterization of the products remains unsolved and also, no kinetic study has been reported. In this communication, we wish to report kinetic results for the thermal 1,5-hydrogen migration of I.

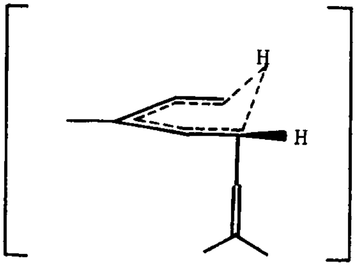
On heating at 185-190° for 0.5 hr under nitrogen atmosphere, I was converted to a 43:57 isomerization mixture of I and a sole product which was isolated by simple fractional distillation in 20% yield as a colorless oil, bp 82-85°/30 mm Hg, n_D^{20} 1.5406. The product was characterized as 4-trans-6-cis-alloocimene (IIb) (2,6-dimethyl-4-trans-6-cis-2,4,6-octatriene) on the basis of the following spectral and glpc analyses: the uv spectrum (cyclohexane) had λ_{max} 268 (ε 27,600), 277 (36,500), and 289 (28,000) nm, which was quite similar to those reported for IIb (6), ruling out the possibility of 4-trans-6-trans-alloocimene (IIa) and/or of 4-cis-6-cis-isomer. The glpc retention time (7) was also same as that of IIb and the nmr ($CDCl_3$, 60 MHz) signals at τ 3.37-4.30 (3H, ABX pattern m, C_3-H, C_4-H and C_5-H), 4.71 (1H, broad q, J=7.0 Hz, C_7-H), 8.25 (9H, broad s, C_2-Me_2 and C_6-Me), and 8.33 (3H, broad d, J=7.0 Hz, C_7-Me) (8) were compatible with assigned structure. No trace of the isomeric IIa was detectable in the reaction mixture, indicating the isomerization was stereospecific.

For obtaining kinetic information, the isomerization rate was measured at three reaction temperatures under nitrogen of 25 mmHg by the glpc analyses.

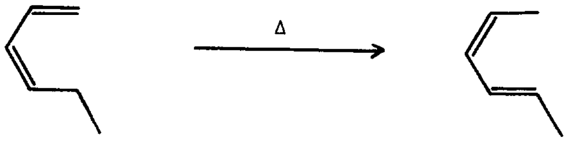




III



IV



V

VI

From the first order kinetic, the rate constants and kinetic parameters are calculated and are summarized in Table.

Table Rate Constants and Kinetic Parameters for Isomerization of I to IIb.

Temperature (°K)	433.0	423.0	413.0	
Rate const. (sec^{-1})	1.29×10^{-4}	6.19×10^{-5}	2.69×10^{-5}	
Kinetic parameters	Log A (sec^{-1})	Ea,kcal/mole	ΔH^{*},kcal/mole	ΔS^{*},e.u.
(from Arrhenius plot)	10.41	28.3		
(from absolute rate theory, at 423.0°K)			27.0	-14.7

It is reported that the log A values for 1,5-hydrogen migration of other dienes are low as 10.8-11.2 similar to those for the Cope rearrangement, and the activation energies fall in the range of 31-37 kcal/mole (9). These characteristic values are rationalized by the concerted intramolecular shift via a six-membered transition state. The log A value (or ΔS^{*}value) obtained for the present system was very similar to 10.8 (or ΔS^{*}-12.0 e.u.) in the isomerization of cis-hexa-1,3-diene (V) to cis,trans-hexa-2,4-diene (VI) (10), suggesting similar transition state. However, the Ea (or ΔH^{*}) value for I ⟶ IIb isomerization was considerably lower than 32.5 kcal/mole for V ⟶ VI isomerization (10). This indicates clearly that the proton migration is much easier in I compared to V, which is rationalized by the fact that the migrating proton in I is bisallylic while that in V is allylic.

Thus, two possible transition states III and IV could be depicted for the thermal 1,5-hydrogen migration of cis-β-ocimene (I), following to the allowed suprafacial 1,5-proton sigmatropic rearrangement by the Woodward-Hoffmann rule (11). However, it is evident that the thermal isomerization of I to only 4-trans-6-cis-alloocimene proceeds exclusively via the transition state III on the basis of the observed stereospecificity. This preference of III to IV could be explained by less steric repulsion of the large isobutenyl group in less crowded equatorial position than more crowded axial.

The above thermal isomerization reaction of I to IIb is very useful for obtaining pure IIb, since alloocimene is available only as a mixture of IIa and IIb to be hardly separated (6), and also, an alkaline isomerization of I gave only a mixture of several products including IIa and IIb.

References and Notes

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