

THERMODYNAMIC SECONDARY DEUTERIUM ISOTOPE EFFECT
IN THE THERMAL REARRANGEMENT OF BIALLYL

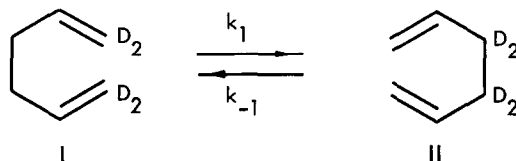
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The thermodynamic deuterium isotope effect was measured in the degenerate Cope rearrangement of biallyl-1,1,6,6-d₄ (I) and of biallyl-3,3,4,4-d₄ (II).



Compounds I and II were prepared in a similar manner as described by Vogel et al. (1) for 1,2-divinylcyclopropane. I was obtained by heating 1,6-bis(dimethylamino)hexane-N,N'-dioxide-1,1,6,6-d₄ while the dioxide labeled in the 3 and 4 positions afforded II**.

Samples of I and II were heated in sealed ampoules in the presence of small amounts of diphenylamine. The equilibrium constants $K = \frac{[II]}{[I]}$ i.e. the thermodynamic isotope effects were determined from the integrals of the nmr spectra of the equilibrium mixture. The results are given in Table***.

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** The experimental details will be published elsewhere.

*** The temperature readings were rather crude and have to be taken as approximate.

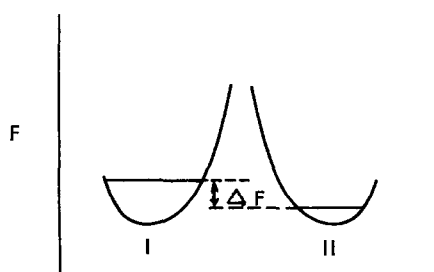
TABLE
Thermodynamic Secondary Deuterium Isotope Effects in the
Rearrangement of Biallyl

Compound	Temp. °C	K^a [II] / [I]	$k_1 \times 10^7$ sec ⁻¹	$k_{-1} \times 10^7$ sec ⁻¹
I	220	1.25 ^b		
I	200	1.20		
I	200	1.23	123 ^c	100 ^c
II	200	1.25		
I	150	1.27	1.88 ^c	1.48 ^c
I or II ^d	25	1.41 ± 0.02 ^e		

a) K represents the isotope effect. b) One experiment for the appropriate temperature. c) Calculated from: $(k_1 + k_{-1})t = \ln \frac{[I]_0 - [I]_{eq}}{[I] - [I]_{eq}}$ and $\frac{k_1}{k_{-1}} = K$. d) Calculated from data at higher temperatures. e) The uncertainty is standard error.

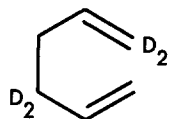
The thermodynamic isotope effect of 1.41 at 25° amounts to a free energy difference ΔF of 204 cal/mole.

FIGURE



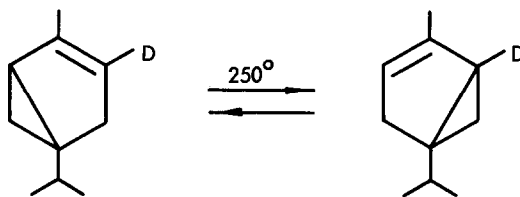
As can be seen from Figure only the difference in the ground state energies is responsible for the preference of compound II in the equilibrium mixture (2). Therefore an isotope effect of about 10% per deuterium is due to the change in vibrational energy in going from the trigonal to tetrahedral geometry of the isotopically substituted carbons. This is in agreement with the kinetic α -isotope effect observed in the same type of rearrangement (3).

By inspecting the Woodward-Hoffmann correlation diagrams (4), bialllyl can rearrange in a thermal concerted intramolecular reaction which is the low energy path. The energy of activation of 33 kcal/mole is in agreement for this type of rearrangement and the entropy of activation of -14 e.u. indicates a cyclic transition state. The high energy photochemical rearrangement should yield the crossover product III. If the formation of allyl radicals competes with the thermal rearrangement it should be possible to detect the presence of III in the equilibrium mixture.



Nmr is not suitable for this purpose since the spectrum of III is identical to that of a mixture of I and II. It was therefore necessary to degrade the reaction products to succinic anhydride by ozonolysis followed by oxidation with hydrogen peroxide and treatment of the succinic acid with acetic anhydride. Succinic anhydrides obtained from compounds I, II and III have molecular weights 100, 104 and 102 respectively. These three different masses are easily distinguishable by mass spectrometry. It was shown that succinic anhydrides derived from the equilibrium mixture obtained at 200° contained only undeuterated and tetradeuterated molecules while dideuterated species were practically absent.

A similar case of degenerate rearrangement has been reported by Doering and Lambert (5) for deuterated α -thujene:



The nmr spectrum of the equilibrium mixture showed the presence of one half of one vinyl proton. Within the limits of error of this method one can conclude **there is no isotope effect**. The apparent discrepancy between this result and ours can be explained by the special nature of the cyclopropane ring. Because C-D bonding orbitals in cyclopropane are considered as nearly sp^2 -hybridized only a negligible difference in the ground state vibrational energy levels can be expected.

REFERENCES

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