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KINETICS OF THE COPE REARRANGEMENT OF SOME TRICYCLO[5.2.1.0^{2,6}]DECA-4,8-DIENOLS

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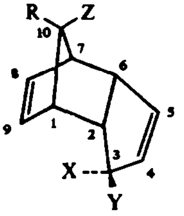
Abstract—The thermal rearrangement of α-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol(I) and of *syn*-tricyclo-[5.2.1.0^{2,6}]deca-4,8-dien-10-ol(III) in decalin was kinetically studied. Rate coefficients of the opposed reactions and equilibrium constants were determined in the temperature range 125–150°. The following activation parameters were found: reaction (I) → (III), $\Delta E_a = 34{\cdot}2$ kcal/mole, $\Delta S\ddagger = +\ 4{\cdot}3$ e.u.; reaction (III) → (I), $\Delta E_a = 36{\cdot}3$ kcal/mole, $\Delta S\ddagger = +\ 8{\cdot}3$ e.u. Kinetic runs at 125° were performed also on β-tricyclo-[5.2.1.0^{2,6}]deca-4,8-dien-3-ol(II) in the same solvent. Reactivities of the different isomers are compared and discussed.

The interest in valence isomerization reactions has given rise to several studies of the Cope rearrangement, both from the theoretical and the experimental points of view.[1] A well known example of such reaction is the rearrangement of the α- and β-isomers of tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol(I and II) to the *syn*- and *anti*-isomers of tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-10-ol(III and IV), respectively.[2]



I: X = R = Z = H; Y = OH (α-3-ol)
II: Y = R = Z = H; X = OH (β-3-ol)
III: X = Y = Z = H; R = OH (*syn*-10-ol)
IV: X = Y = R = H; Z = OH (*anti*-10-ol)

We took particular interest in isomer I, and the molecular structure of its *p*-bromobenzoic ester was determined by X-ray diffraction.[3] On the basis of such results and of previous computations,[4] the geometry of the transition state of reaction (I) ⇌ (III) (Fig 1) was deduced, and an activation entropy value was calculated.[3] Experimental results are available on the kinetics of reaction (II) → (IV),[5] but process (I) ⇌ (III) has not been kinetically studied. We have undertaken this study and the results are now reported.

RESULTS

Reactions were carried out in decalin, at temperatures in the range 125–150°, and their progress was followed by IR analysis. Process (I) ⇌ (III) being a case of opposed reactions,[2] a value of the equilibrium constant was needed in order to obtain the rate coefficients k_f and k_b (for forward and backward reactions) at each temperature. Although slow secondary reactions, accompanying the rearrangement, make the determination of the equilibrium position at "infinite" time uncertain, they do not

TABLE 1. RATE COEFFICIENTS AND ACTIVATION PARAMETERS OF THE REACTION (I) $\underset{k_b}{\overset{k_f}{\rightleftarrows}}$ (III) (SOLVENT: DECALIN)

Temperature (°C)	$10^4\bar{k}_f$ (sec^{-1})	$10^4\bar{k}_b$ (sec^{-1})	$\bar{k}_f/\bar{k}_b$
125	0·366 ± 0·004	0·185 ± 0·002	1·98
135	1·089 ± 0·012	0·561 ± 0·005	1·94
140	1·72 ± 0·04	0·968 ± 0·008	1·78
145	2·95 ± 0·16	1·64 ± 0·04	1·80
150	4·70 ± 0·03	2·78 ± 0·12	1·69

Forward reaction: log A = 14·3 ± 0·2; ΔE_a = 34·2 ± 0·4 kcal/mole; $\Delta H\ddagger$ = 33·3 ± 0·4 kcal/mole; $\Delta S\ddagger$ = +4·3 ± 1·0 cal/mole °K

Backward reaction: log A = 15·2 ± 0·2; ΔE_a = 36·3 ± 0·4 kcal/mole; $\Delta H\ddagger$ = 35·5 ± 0·4 kcal/mole; $\Delta S\ddagger$ = + 8·3 ± 0·9 cal/mole °K

TABLE 2. EXAMPLE OF KINETIC DETERMINATION
Temperature = 135°. Concentrations in mole/l; rate coefficients in sec^{-1}

Time (sec)	Forward reaction (c_I^0 = 0·417; c_{III}^0 = 0)		Backward reaction (c_I^0 = 0; c_{III}^0 = 0·417)	
	c_I	c_{III}	c_I	c_{III}
600	0·409			
1200	0·379	0·033	0·029	
1800	0·350	0·056	0·038	0·387
2400	0·339	0·081	0·049	0·380
3000	0·321	0·098	0·057	0·350
3600	0·308	0·116	0·064	0·343
4200	0·282	0·125	0·072	0·340
4800			0·080	
5400	0·257	0·151	0·078	0·336
6000'	0·257	0·172	0·091	0·328
21600 (∞)	0·147	0·251	0·139	0·261

Iterative computations:

Cycle No.	Employed K value	Results $10^4\bar{k}_f$	$10^4\bar{k}_b$	$\bar{k}_f/\bar{k}_b$
1	1·797[a]	1·1111	0·5375	2·0671
2	1·9321[b]	1·0906	0·5591	1·9505
3	1·9413[b]	1·0893	0·5607	1·9428
4	1·9420[b]	1·0892[c]	0·5608[c]	1·9422[c]

[a] average value of (c_{III}/c_I) from 'infinity' analyses

[b] average of K and ($\bar{k}_f/\bar{k}_b$) values of previous cycle

[c] final values

disturb the main reaction during kinetic runs, within experimental error. Therefore the experimental approximate equilibrium constant was used only to start the computation of k_f and k_b values, and subsequently average $\bar{k}_f/\bar{k}_b$ values were used to improve the values of the equilibrium constant. The computation was repeated until consistent results were obtained. Such iterative procedure, carried out by computer, gave rate coefficients and equilibrium constant values reported in Table 1. Activation parameters obtained from rate coefficients are also given in that Table.

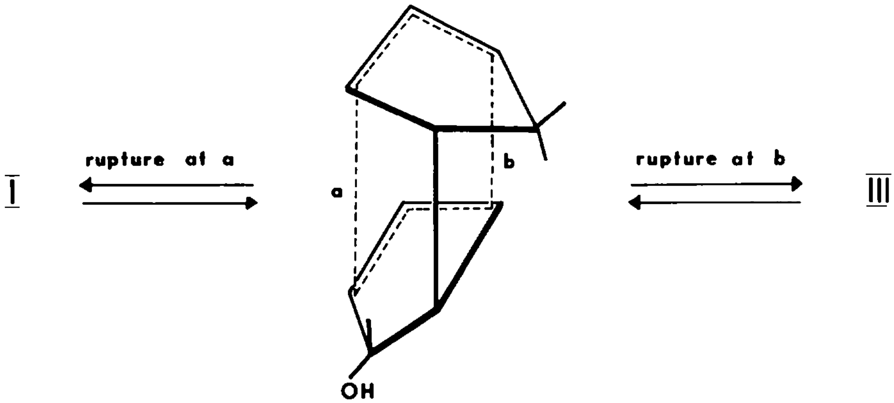


FIG 1. Scheme of the transition state for reaction (I) ⇄ (III).

The rate of reaction (II) → (IV) was measured in decalin for purpose of comparison since the literature measurements[5] had been done without solvent. No evidence for a significant reverse reaction was found. The average rate coefficient is $\bar{k} = (5{\cdot}09 \pm 0{\cdot}18) \times 10^{-4}\ \text{sec}^{-1}$ at 125°; this value is 2·2 times larger than the one measured with no solvent, at the same temperature.[5]

DISCUSSION

Experimental values of the activation entropy, for both (I) → (III) and (III) → (I) reactions (Table 1), are positive. This confirms the difference between Cope rearrangements in open and in cyclic, particularly multicyclic, dienes, foreseen by calculations,[3] and reported in other cases.[1] The figures ($\Delta S^\ddagger = +4{\cdot}3$ e.u. from $\bar{k}_f$; $+8{\cdot}3$ e.u. from $\bar{k}_b$) compare well with the calculated value of $+3{\cdot}5$ e.u.,[3] and with the value of $+5{\cdot}1$ e.u. obtained from the experimental rate coefficients[5] of the analogous process (II) → (IV).

Arrhenius activation energies of reactions (I) ⇄ (III) (34·2 and 36·3 kcal/mole from $\bar{k}_f$ and $\bar{k}_b$, respectively) are close to the value reported for the 1,1,6,6,[$^2H_4$]-hexa-1,5-diene (35·5 kcal/mole),[6] and to values reported for similar open-chain dienes.[1] Also the activation enthalpy of process (II) → (IV) (32 kcal/mole)[5] is close to values found for reactions (I) ⇌ (III) (Table 1).

The relatively low values of the activation energy in cases where a "boat-like" transition state is required, imply that although such transition state is one of high energy,[4,7] this is compensated by relief of steric strain in the reactants. The activation entropy appears as the really distinctive feature of rearrangements of open-chain or cyclic dienes.

A comparison of the forward and backward reactions of process (I) ⇌ (III) shows that isomer III is slightly favoured, the equilibrium constant reaching the value of 2 at the lowest temperature of the experiments. The standard free energy difference that favours III is made up of a negative ΔH° value, prevailing on a positive ($-T\Delta S^\circ$) value. Therefore isomer III is favoured by a lower enthalpy, that may be related to the presence in its structure of the nucleus of *syn*-2-norbornen-7-ol: the OH group *syn* to a double bond is probably π-H-bonded to it in sterically favourable cases, as in 2,5-norbornadien-7-ol.[8] The extra-stability of III in terms of enthalpy corresponds to a more rigid structure, with a consequent lower entropy.

A similar, but not identical, relation exists between isomers II and IV, the latter being definitely more stable, since the rearrangement is a substantially complete reaction. Here a relatively high energy can be attributed to II, an *endo*-hydroxy derivative, the configuration of which was initially assigned on the basis of its lower stability when compared with isomer I.[2] Indeed reaction (II) → (IV) is about 14 times faster than reaction (I) → (III), at 125° in decalin, according to our results. The effect of solvent on reaction (II) → (IV) is small, in line with what is known of this type of reaction.[9]

An examination of all the data available about isomers (I)–(IV) suggests that I is a good model of tricyclo[5.2.1.0^{2,6}]deca-4,8-diene and was rightly chosen[3] to define the behaviour of cyclopentadiene dimer.

EXPERIMENTAL

Commercial decalin was purified by a standard method[10] and fractionated. Compounds I–IV were prepared as described.[2] The alcohols had correct m.ps, and presented characteristic absorption bands in the IR region. Specific bands were at 11·01 and 13·73 μm(I), 13·09 μm(II), 13·16 and 14·10 μm(III), 12·17, 13·33 and 14·97 μm(IV); these wavelengths are close to literature values,[2,5] when available.

IR spectra were scanned on Perkin–Elmer 21 equipment with NaCl optics.

Kinetics. A weighed amount of reagent was dissolved in decalin: initial concentration was 0·417 M for I, 0·409 M for III and 0·284 M for II.

Runs were carried out in sealed Pyrex tubes (internal diameter 4 mm; content of each tube *ca* 150 μl of soln) in a thermostat accurate to ± 0·15°. At known times, a tube was withdrawn, and reaction quenched by cooling. The content was examined by IR analysis in NaCl cells (0·1 mm) at wavelengths corresponding to specific bands of reagents and products. For a given reaction, usually both reagent and product, sometimes only product, were analysed. Two different systems of reading the peak height for a given band were often used. Concentrations were obtained from absorbance values by means of calibration graphs. The latter were linear. All kinetics were followed up to about 50–80% reaction progress towards equilibrium. The IR bands used as the most suitable for quantitative analysis were at 13·73 μm(I), 13·16 μm(III), 13·33 and 14·97 μm(IV). The latter two bands had already been employed in a kinetic study of the (II) → (IV) reaction.[5]

Reaction (I) ⇌ (III) was studied starting from both sides. Rate coefficients were computed from the appropriate equations. For instance for reaction (I) → (III) coefficient k_f was obtained by plotting *vs* time the function

$$[-2{\cdot}303\,K/(1 + K)]\log[c_I(K + 1) - (c_I^0 + c_{III}^0)]$$

where K is the equilibrium constant and c_I, c_I^0 and c_{III}^0 have the usual meaning; analogous expression was used when c_{III} was the result of the analyses.

For each run, rate coefficients were obtained from 2 to 4 independent analyses, and ultimately averaged to give $\bar{k}_f$ and $\bar{k}_b$; an example is given in Table 2. The approximate experimental value of the equilibrium constant was improved by iterative calculation, by using the relation $K = \bar{k}_f/\bar{k}_b$, until the difference between successive values of a rate coefficient was less than 0·1% of the value, both for $\bar{k}_f$ and $\bar{k}_b$ (Table 2). Rate coefficients so calculated were used for computation of activation parameters (Table 1) by a standard computer program.

Reaction (II) → (IV) was studied at 125 ± 0·15°. The usual plots for first order rate coefficients were employed and four values of the coefficient were averaged (2 independent analyses for two independent runs).

All rate coefficients are given with their probable error of the mean. Probable errors were computed for activation parameters.

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