Tetrahedron Letters No. 35, pp 3707 - 3708, 1972. Pergamon Press. Printed in Great Britain.

THERMAL RACEMISATION OF [6], [7], [8] and [9]HELICENE.

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(Received in UK 26 July 1972; accepted for publication 30 July 1972)

We wish to report that [6], [7], [8] and [9]helicene undergo thermal racemisation when heated, in evacuated sealed tubes, slightly above the melting points of the respective pure antipodes[b]. [9]Helicene $[\alpha]_{579}$-1430° is thus completely racemised in 10 minutes at 380°. Pure optically inactive [9]helicene (NMR and IR) was recovered by chromatography in over 85% yield.

Following this rather surprising observation, we have undertaken the kinetic study of these racemisations, starting with [6]helicene (vide infra).

Newman and Lednicer[1] briefly reported, in 1956, that "partial racemisation of [6]helicene occurred during the melting point determination" (of the pure antipode). Kinetic data on the racemisation of [5]helicene[2] and [6]heterohelicenes containing thiophene rings[3], all of which racemise in solution at room temperature, have been published recently.

Kinetic study : [6]helicene. Rates of racemisation of [6]helicene $[\alpha]_{579}$+2850°, dissolved in naphthalene[c], were measured at 187.6°, 205.2° and 221.4°C. The solutions (6% w/w) were carefully degassed *in vacuo* (melt-and-freeze technique) and sealed in pyrex tubes at a residual pressure of 5.10^{-4} Torr.

For the determination of the residual optical activity, the naphthalene was sublimed under reduced pressure, the residue dissolved in $CHCl_3$ and the solution percolated through a micro alumina column. The helicene concentrations were controlled by UV and the purity of the recovered material checked by IR and VPC.

From the first order plots (no concentration effects were observed) the racemisation rate constants $k_r (=2k_i)$, the inversion rate constants k_i and the half-lifes $t_{1/2}$ were determined. The results are collected in Table 1. The activation parameters are given in Table 2, together with the data pertaining to the racemisation of [5]helicene.

Table 1.

t°C	T°K	k_r (min^{-1})	k_i (sec^{-1})	$t_{1/2}$(rac.)(min)
187.6	460.76	$3.68\ 10^{-3}$	$3.08\ 10^{-5}$	187
205.2	478.36	$1.43\ 10^{-2}$	$1.20\ 10^{-4}$	48
221.4	494.56	$5.2\ 10^{-2}$	$4.13\ 10^{-4}$	13.4

$$(1)\quad \log \frac{k_i}{T} = 10.319 + \frac{\Delta S^{\ddagger}}{4.574} - \frac{1}{T} \cdot \frac{\Delta H^{\ddagger}}{4.574}$$

Table 2.

Helicene	E_a (x) (Kcal mole^{-1})	A (xxx)	$\Delta H^{\ddagger}$ (Kcal mole^{-1})	$\Delta S^{\ddagger}$ (xx) (e.u.)	$\Delta G^{\ddagger}$ (Kcal mole^{-1})
[6]	35	$1.26\ 10^{12}$	33.8	-6.7	37.0 at 478°K
[5] 2)	23.5	$2.58\ 10^{12}$	22.9	-4.1	24.1 at 293°K

(x) E_a = 34.75 Kcal mole^{-1} at 478.36°K is found using eq. (1) and the relation $E_a = \Delta H^{\ddagger} + RT$; the direct Arrhenius plot yields an average value of E_a = 35.4 Kcal mole^{-1}.

(xx) The average $\Delta S^{\ddagger}$ value of -6.70 e.u. results from plotting eq. (1); the very close value of -6.75 is obtained by computing the data at 478.36°K.

(xxx) The somewhat low pre-exponential factor A agrees with the negative entropy of activation and indicates a definite loss of degrees of freedom in the transition state; i.e., the reaction is not likely to proceed by a bond-breaking mechanism.

We will not attempt to discuss the present results before having collected kinetic data for the racemisation of the higher benzologues.

Acknowledgements. The authors are indebted to Dr. S. Boué for helpful discussions and advices. The financial support of the "Fonds de la Recherche Fondamentale Collective" (contract No. 994) is gratefully acknowledged.

Footnotes.

a) Author to whom correspondence should be addressed.

b) The "spontaneous" resolution and optical rotations of [6], [7], [8] and [9] helicenes will be reported in a forthcoming publication.

c) For the thermal stability of naphthalene under the conditions used, cf. 4).

References.

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