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THERMAL CIS-TRANS ISOMERIZATION OF 1,2-DIPHENYLCYCLOPROPANE

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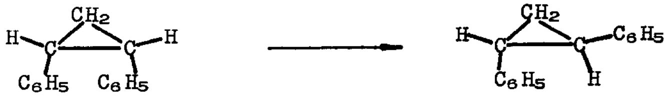
A variety of substituted cyclopropanes have been shown to undergo thermal structural and geometrical isomerizations [1-4].

We report here another example, the thermal, reversible cis-trans isomerization of 1,2-diphenylcyclopropane, proceeding without the accompanying structural isomerization noted in previous examples [1-4]. Kinetic determinations in the liquid state over the temperature range 161°-220°C. gave $k_{sec}^{-1} = A \exp[-Ea/RT] = 10^{11.2\pm0.5} \exp[-33,530\pm1070/RT]$ for reaction 1.



[I]

[1]

Table I contains some experimental rate parameters for vapor phase isomerizations given at the high pressure limit. Although strict comparison between these high pressure vapor parameters and the reported liquid phase parameters cannot be made, it seems unlikely that any differing medium effects would account for ~25 kcal/mole and that the much lower Ea for reaction

1 reflects stablization by the phenyls of a developing diradical intermediate [5]. Also pertinent in this respect is the quite small pre-exponential factor, log A = 11.2±0.5, reflecting a rather large negative $\Delta S^{\ddagger}$. Several attempts to trap a diradical intermediate were unsuccessful.

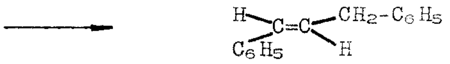
Table I

Arrhenius Parameters for Thermal cis-trans Isomerizations

Compound	E_a [kcal/mole]	log A
cis-1,2-dideutero-cyclopropane [1][a]	65.1	16.4
1,2-dideutero-3-methylcyclopropane [2][a]	60.5	15.4
cis-1,2-dimethylcyclo-propane [3][a]	59.4	15.3
cis-1-ethyl-2-methyl-cyclopropane [4][a]	58.9	15.1
cis-1,2-diphenyl-cyclopropane [I][b]	33.5±1.1	11.2±0.5
cis-1,2-[4-chlorophenyl]-cyclopropane[b]	36.4±0.8	12.5±0.4
cis-1-[4-chlorophenyl]-2-phenylcyclopropane[b]	36.8±1.0	12.5±0.5

[a] Vapor phase reaction with parameters given at high pressure limit. [b] Liquid phase reaction.

A rather interesting aspect of reaction 1 is the lack of competitive structural isomerization [reaction 2],

I  [2]

an analog of the familiar cyclopropane ⟶ propylene isomerization. No olefin could be detected after periods in excess of 25 half-lives of reaction 1.

Hammond and co-workers [6] have recently reported the sensitized photoisomerization analog of reaction 1.

We have also studied the rates of thermal geometric isomerization of *cis*-1,2-di[4-chlorophenyl]cyclopropane and *cis*-1-[4-chlorophenyl]-2-phenylcyclopropane and found that their rates are slightly slower than reaction 1. Their Arrhenius parameters are included in Table I and are seen to be the same within experimental error.

The equilibrium constants for each of the diaryl cyclopropane isomerizations are 10.0±0.5 at 193°C.

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