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THERMAL REARRANGEMENT OF 3-PHENYLCYCLOBUTENE

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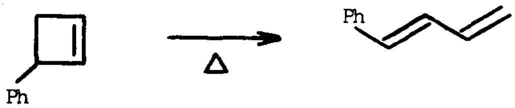
Because of the interest in the valence isomerization of cyclobutenes to 1,3-butadienes (2,3,4,5) we decided to examine the thermal isomerization of 3-phenylcyclobutene (I) to 1-phenyl-1,3-butadiene (II) to see what effect a single phenyl group, at the 3-position, would have on the activation energy. It is known that four phenyl groups have a large effect on the rate (5).



I II

3-Phenylcyclobutene was synthesized by a photochemical electrocyclic ring closure reaction of 1-phenylbutadiene as described previously (6).

The kinetics of isomerization were followed by gas chromatographic analysis (corrections being made for differences in thermal conductivities) using conditions which did not isomerize the starting material appreciably. The reactions were run in either nonane or o-xylene using 1-10% solutions, over a temperature range of 74 to 119°. The reaction was shown to be first order and was not catalyzed by powdered glass. The product was demonstrated to be exclusively (> 95%) <u>trans</u>-1-phenylbutadiene.

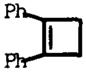
The energy of activation was determined to be 26 kcal/mole with the log of the pre-exponential factor (log A) being 12.4. (Table I lists the experimental rate constants).

TABLE I

Temp. (°C)	$k \times 10^3$ (sec^{-1})
74.2	0.11
80.5	0.28
84.8	0.44
92.8	0.6
97.6	1.5
109.1	3.1
118.6	9

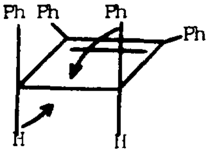
These results are to be compared with the activation energies for isomerization of cyclobutene (III) (2), 1,2-diphenylcyclobutene (IV) (4), cis-1,2,3,4-tetraphenylcyclobutene (V) (5), and trans-1,2,3,4-tetraphenylcyclobutene (VI) (5) as indicated in Table II.

TABLE II

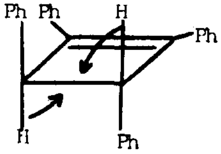
Compound		E_a(kcal/mole)	log A
	(III)	32.5	13.1
	(IV)	32	12.8
	(V)	25	(12.8)[a]
	(VI)	21	(11.1)[a]
	(I)	26	12.4

(a) Calculated in ref. 4 from data in ref. 5

If it is assumed that the difference between the activation energies of V and VI are due in large measure to the greater increase in steric crowding in the transition state for conrotatory ring opening of compound V over compound VI then the difference of 11 kcal/mole between III and VI (or IV and VI) represents the lowering of the activation energy due to two allylic phenyl groups. The activation energies of III and IV indicate very little, if any, additional stabilization of the transition state over starting cyclobutene for phenyl substituents on the double bond.



V



VI

Our data, taken with the data of Freedman, indicate that the phenyl substituents reduce the activation energy by stabilizing the transition state for the electrocyclic (conrotatory) ring opening much more than the ground state. The observation that each phenyl substituent in the 3 and 4-positions stabilizes the transition state by *ca*. 5-6 kcal/mole requires that the "radical character" or hybridization at carbon atoms 3 and 4 be the same in the transition state which then must have, except for the substituents, C_2 symmetry as postulated (7). The modest negative entropy of activation points up the constraint of the phenyl ring in the transition state due to overlap of the ring with the developing π-system.

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