Tetrahedron Letters No.49, pp. 4395-4398, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE SELECTIVE DECOMPOSITION OF 3,7-DIPHENYL-1,2-DIAZA-1-CYCLOHEPTENE IN THE SOLID STATE.

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(Received 29 September 1965)

We wish to report the selective formation of cis-1,2-diphenylcyclopentane (II) from the solid state photolysis of 3,7-diphenyl-1,2-diaza-1-cycloheptene[1] (I).

Both the thermal and the photolytic decompositions of I in solution yielded a mixture of cis-(II) and trans-(III) 1,2-diphenylcyclopentanes, in addition to cis- and trans-1,5-diphenyl-1-pentene (IV). At temperatures below 110°, isomerization of I to 3,7-diphenyl-1,2-diaza-2-cycloheptene (V) competes with the decomposition.

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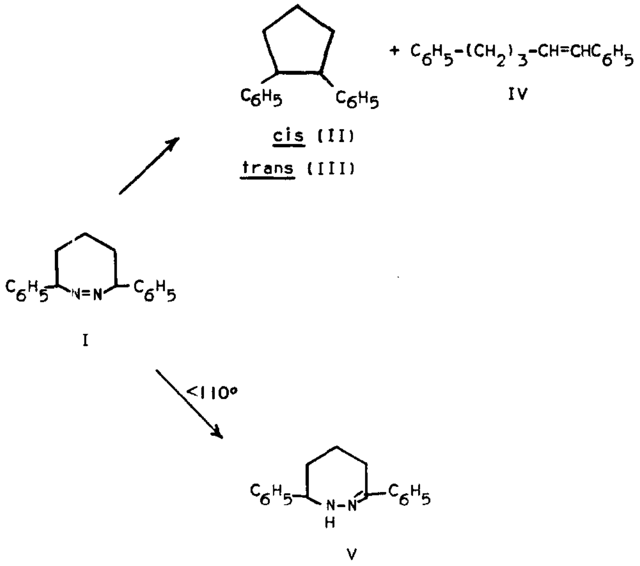

The solutions or solids were irradiated in n.m.r. tubes using a Hanovia high-pressure mercury lamp. The completion of the decomposition was evidenced by the absence of the absorption of the azo group at 389mμ. The thermal decompositions were carried out in reaction flasks and were continued until gas evolution stopped.

The hydrazone (V) was determined by the nitrogen content of the mixture. The amounts of olefins and of cis- and trans-1,2-diphenylcyclopentanes were obtained from the n.m.r. spectral analysis of the hydrocarbon fraction by measuring the area under the peaks of the olefinic protons (3.5-4.0τ) and the α-protons of the cyclic products[2] (6.68τ for II and 7.00τ for III). Vapor phase chromatography on a D.C. 200 silicone oil column at

200° gave the ratio of the olefinic to cyclization products. The ratio of the *cis*- and *trans*-1,2-diphenylcyclopentanes could be established by v.p.c. on a UCON LB 550-X column.

The distribution of products obtained in the decomposition of I in solution and in the solid state is presented in Table I. Thermal decomposition in solution at 132°, yielded *trans*-1,2-diphenylcyclopentane as the main cyclization product. A slight preference for the *cis* isomer was observed in the photolytic decomposition in solution. Solid state photolysis at 25° gave *cis*-1,2-diphenylcyclopentane as the exclusive cyclization product. Two factors may control the decomposition in the solid state: (a) the rigid medium, which prevents the radicals from "flipping" and changing configuration before coupling occurs, namely the density factor of the crystalline state and (b) the topochemical effect[3], in which preference of product formation is dictated by common elements

TABLE I

Decomposition of 3,7-Diphenyl-1,2-diaza-1-cycloheptene

Decomposition Products	Mode of Decomposition		
	Thermal(a)	Photolytic(b) in solution %	Photolytic(c) in the Solid State
Cis-1,2-diphenylcyclopentane (II)	35	25	72
Trans-1,2-diphenylcyclopentane (III)	45	23	-
1,2-Diphenyl-1-pentene (IV)	20	39	23
Hydrazone (V)	-	13	5

(a) In xylene, at 132°. (b) In tetrahydrofuran, at 14°. (c) At 25°.

of symmetry with reactants. The available physical and chemical data[1,4] were not conclusive evidence for the establishment of the configuration of the phenyl groups. The results of the solid state decomposition strongly suggest that the phenyl substituents have the cis configuration.

This view was supported by the results of the solid state photolysis of trans-3,5-bis-(p-chlorophenyl)-1-pyrazoline[5] (VI) and of cis-3,5-bis-(p-methoxyphenyl)-1-pyrazoline (VII)[6]. Trans-1,2-bis-(p-chlorophenyl) cyclopropane was the sole product of the decomposition of VI while 86% of cis-1,2-bis-(p-methoxyphenyl) cyclopropane was formed from the decomposition of VII (in contrast to the photolysis in solution of VII which gave 57% of the cis cyclopropane[6]). No isomerization of the p-chlorophenyl cyclopropanes occurred in the solid state.

Olefin formation in the solid state decomposition of I might be attributed to a favorable conformation of I in which ring carbon atom 3 and the C-H bond of ring carbon 6 are close enough to allow a disproportionation reaction in the rigid medium.

We are continuing our studies of the solid state decomposition of cyclic azo compounds.

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