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The Mechanism in the Photolysis of 5-Phenyl-tetrazole Derivatives

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5-Phenyl-tetrazole의 光分解反應과 그 메카니즘에 관한 研究

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要 略

5-Phenyl-tetrazole은 光分解하면 질소 한 分子를 放出하며 1, 3-dipole인 C-phenyl-nitrilei-mine을 形成한다. 그러나 이 때 dipolarophile의 存在下에서 1, 3-dipole-cyclo-addition은 일으키지 않으며 二重合體인 3, 6-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine(Ⅲ)을 거쳐 最終產物로서 3, 6-diphenyl-1, 2, 4, 5-tetrazine(Ⅳ), 2, 5-diphenyl-1, 2, 4-triazole, 4-amino-3, 5-diphenyl-1, 2, 4-triazole, benzonitrile, ammonia 그리고 nitrogen을 生成한다.

Abstract

The main object of this experiment is to provide a systematic approach to the reaction mechanism in the photolysis of 5-phenyl-1, 2, 3, 4-tetrazole during which the formation of C-phenyl-nitrile-imine of 1. 3-dipole was expected. So the occurrence of 1, 3-dipole-addition was examined but not observed despite the formation of nitrile-imine. 3, 6-diphenyl-1, 2, 4, 5-tetrazine (Ⅳ); 3, 6-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine (Ⅲ); 3, 5-diphenyl-1, 2, 4-triazole; 4-amino-3, 5-diphenyl-1, 2, 4-triazole; benzonitrile; ammonia and nitrogen were isolated as final products of this reaction.

Introduction

In the thermolysis of 5-phenyl-tetrazole(I), nitrile-imine of 1, 3-dipole has been taken as reaction intermediate.⁽¹⁾ But 1, 3-dipole addition has not been detected as yet. Nitrile-imine thus formed dimerized to form 2, 3-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine which in turn thermolyzed to 4-amino-3, 5-diphenyl-1, 2, 4-triazole(V); 3, 5-diphenyl-1, 2, 4-triazole; 2, 4, 6-triphenyl-1, 3, 5-triazine; benzonitrile; ammonia and nitrogen⁽²⁾. The aim of our experiment was focused upon the result obtained by varing the operating condition, that is, U. V. light was used as energy source in the place of heating which cased the rupture of intramolecular bonds. The existence of nitrile-imine as intermediate resulting from the photolysis of 5-phenyltetrazole and the occurrence of the 1, 3-dipole-addition frequently observed in nitrile-imine reaction were both examined.

Experimentals

A. Synthesis of Starting Materials

(a) Synthesis of 5-phenyltetrazole

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This was synthesized by the method of R. Huisgen⁽⁴⁾. 51.5gr of benzonitrile (500mM), 48.8 gr of sodium azide (750mM), 31.8 gr of LiCl (750mM) were dissolved in 500ml of distilled methylglycole and heat for 120 hrs. with refluxed. The reaction mixture was cooled and dissolved in 1500 ml of water then clear solu'n appeared, to which 430 ml of 2N-HCl was added. And there crystallized 5-phenyltetrazole in needle form. Settling for one day in ice-box and it was recrystallized in ethanol. Finally the substance of needle form decomposing 214—215°C was obtained.

(b) Synthesis of 2-acetyl-5-phenyl-tetrazole⁽⁴⁾

3gr of tetrazole, 15ml of distilled acetylchloride were heated for 2 hrs. with refluxed. Even slight addition of water hydrolyzing the acetylchloride careful treatment was required not to hydrolyze the acetylchloride. The excess of this compound unreacted was evaporated at 40°C by vacuum distillation. The reaction product of colorless crystalls was settled with solid sodium hydroxide in decicator.

(c) Synthesis of 3, 5-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine⁽¹⁾

15 gr of benzonitrile (145.5mM), 4, 65 gr of water free hydrazine (145.5mM) were heated to 100°C, 31/2 days with the passage of nitrogen to inhibite the oxidation. Crystalls of golden color began to appear after two days reaction. The reaction product was composed of dihydrotetrazole(Ⅲ) and 4-amino-triazole (V). (Ⅲ) was extracted from the mixture by the Soxhlet method with benzene solvent.

B. 1, 3--Dipole-Addition of Nitrilimine

1gr of 5-phenyltetrazole (6.85mM) was dissolved in 20mM of absolute dioxane and divided into two fraction to each them 1gr of styrene (9.61mM) and 1 gr of P-N-dimethylaminobenzaldehydephenylhydrazone 4.22mM were added respectively. Having exposed to U.V. light in the quartz tube for 48 hrs. they were analyzed. The formation of pyrazoline or triazoline was expected when adding C-phenylnitrileimine to C=C or C=N double bond containing compounds. The extraction of above two compounds was attempted by NaOH solu'n but neither of their existences were detected. It was therefore conceived that the reaction didn't proceed in 1, 3 dipoleaddition.

C. Photolysis of 5-Phenyl-Tetrazole

5-phenyl-tetrazole dissolved in absloute dioxane was exposed to U.V. light for 48 hrs. in above way. During the reaction nitrogen was evolved and the colorless reaction mixture changed to yellow and lastly to red. The oxygen passed completely through the solu'n to oxidize the 3, 6-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine(Ⅲ) to red color of 3, 6-diphenyl-1, 2, 4, 5-tetrazine(Ⅳ) (mole-extinction; 530). The total quantity of 3, 6-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine (Ⅲ) was calculated by measuring the optical density at the wavelength of 545 mμ. After separation of organic solvent. benzonitril was distilled by vacuum distillation. The residue was extracted by 5%-$NaHCO_3$, 2N-NaOH, 2N-HCl, in this order, from which some compound was expected to isolate. When neutralizing the slou'n extracted from the residue by the above three reagents, there adpeared precipitates which was identified later as 5-phenyl-tetrazole (by 5%-$NaHCO_3$) 2, 5-diphenyl-1, 2, 4-tetrazole (by NaOH) 4-amino-2, 5-diphenyl-1, 2, 4-triazole(by 2N-HCl), by the I.R. spectrum. The final residue chemically neutral was dried and absorbed to Al_2O_3 neutral column chromatograph, from which 3, 6-diphenyl-1, 2, 4, 5-tetrazine(Ⅳ) and yelow color of unknown compound were isolated by the eluation of cyclohexane and ethanol respectively.

D. Photolysis of 2-Acetyl-5-Phenyl-1, 2, 3, 4, Tetrazole(Ⅶ)

Dissolving 1gr of 2-acetyl-5-phenyl-1, 2, 3, 4. -tetrazole in absolute dioxane, it was exposed to U.V. light for 48 hrs., during which nitrogen was evolved. After evaporation of the solvent by vacuum distillation, the residue dissolved in cyclohexane was absorbed to Al_2O_3 neutral column the portion of which eluated by cyclohexane was obtained. The compound in that portion was identified as 2-phenyl-5-methyl-1.2.4-oxidazole by comparison of its I.R. spectrum with that of the same compound synthesized different way.

E. Photolysis of 3, 6-Diphenyl-1, 4-Dihydro-1, 2-4, 5-Tetrazine(Ⅲ)

Solution of 1 gr of the sample dissolved in absolute dioxane in quartz tube was exposed to U.V. light for 48 hrs. Evolution of nitrogen was observed and the original yellow color of the solu'n gradually changed to red. Then the oxygen was passed completely to oxidize the starting material unreacted during the exposure to red color of 2, 5-diphenyl-1, 2, 4, 5-tetrazi-

Table 1. Photolysis 3, 6-Diphenyl-1, 4-Dihydro-1, 2, 4, 5-Tetrazine(Ⅲ)

Number of experiment	m·Mol of Ⅲ	reaction-time (Temp.)	Ⅲ m·Mol (%)	Ⅳ m·Mol (%)	Ⅴ m·Mol (%)	Ⅵ m·Mol (%)
Ⅰ	2.12	48hrs. (30°C)	1.45 (68, 5)	0.624 (26.4)	0.064 (3.02)	0.2405 (11.4)
Ⅱ	2.12	51hrs. (30°C)	1.48 (69.9)	0.601 (27)	0,0635 (2.86)	0.263 (12.4)

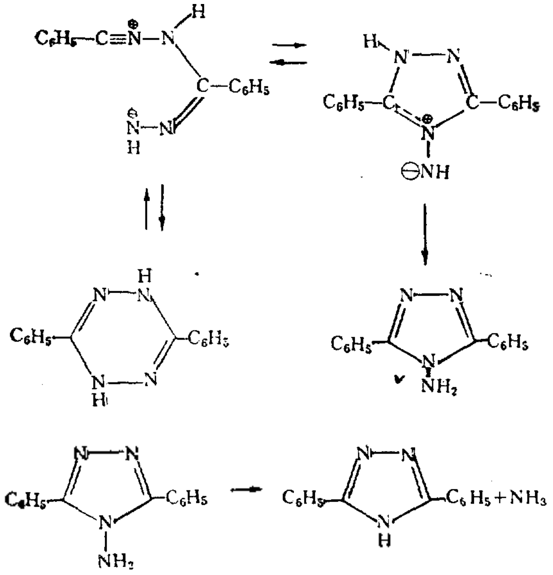

Illustration-3

Table 2. Photolysis of 5-Phenyl-1, 2, 3, 4-Tetrazole (Ⅰ)

Number of experiment	m·Mol of Ⅵ	reaction-time (Temp.)	Ⅲ m·Mol (%)	Ⅳ m·Mol (%)	Ⅴ m·Mol (%)	Ⅵ m·Mol (%)
Ⅰ	3.43	48hr. (30°C)	0.5075 (14.8)	0.2184 (6.38)	0.0224 (0.654)	0.0842 (2.455)
Ⅱ	3.43	48hr. (30°C)	0.5475 (15.8)	0.2224 (6.5)	0.0235 (0.685)	0.0973 (2.84)

Ⅲ: 3, 6-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine
Ⅳ: 3, 6-diphenyl-1, 2, 4, 5-tetrazine
Ⅴ: 4-amino-3, 5-diphenyl-1, 2, 4-triazole
Ⅵ: 3, 5-diphenyl-1, 2, 4-triazole.

3, 6-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine in which the compounds previoulsly mentioned were yielded in much higher proportion.

In the conversion of 5-phenyl-tetrazole(Ⅰ) to dihydrotetrazine(Ⅲ) via nitrile-imine intermediate or in the formation of diphenyltriazole and aminotriazole (Ⅴ), the polymerization of styrene added to reaction media was not appreciated. Consequently, the mechanism of the reactions above, at least, didn't involve radical process was concluded. Though not clearly established the mechanism was supposed to proceed in ionic one as in the case of thermolysis⁽³⁾. Refer to Illus. -3.

Upon exposure of 2-acetyl-5-phenyl-tetrazole in which

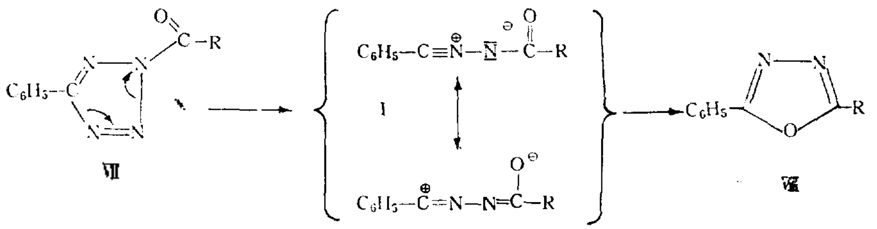

Illustration-4

by the experimental data of the direct photolysis of H is substituted by acetyl group at N-position to U. V. light nitrogen began to evolve and 2-methyl-5-phenyl 1, 3, 4-oxidiazole was obtained as reaction product. The transformation of (Ⅶ) to (Ⅷ) through thermolysis has already known nd the mechanism is as following⁽⁴⁾. *N*-acetyl-*C*-phenyl-nitrile-imine appeared as intermediate and (Ⅷ) was formed through intramolecular nucleophilic addition. Conclusively, in the photolysis the reaction does proceed in ionic mechanism in the place of radical one.

References

(1) R. Huisgen, J. Sauer and M. Seidel. Liebigs *Ann. Chem.* **654**
(2) Young Bog Chae. Dissertation, München (1965)
(3) R. Huisgen, Young Bog Chae. In preparation.
(4) R. Huisgen, J. Sauer, H. J. Sturm and J. H. Arkgraf. *Chem. Ber.*, **93**, 2106 (1960)

ne. The total quantity of starting materrial unreacted was known through measurement of the mole-extinction at the wavelengh $545 m\mu$. Then the solvent was evaporated and benzonitrile detected by use of I. R. spectrum. The residue was treated with 2N-NaOH 2N-HCl from which acidic 2, 5-diphenyl-1, 2, 4-triazine, alkaline 4-amino-3, 5-diphenyl-1, 2, 4, 5 triazole were idtentified by I. R. spectrum. These were precipitated when neutralizing the each extraction. Finally the neutral substance dissolved in cyclohexane was absorbed to Al_2O_3 column. Tetrazine of red color was eluated by cyclohexane and unknown compound of white color probably thought as triphenyltetrazine obtained by eluation of ethanol. So microscopic its quantity, it was nearly impossible to identify the compound.

Result and Discussion

When adding 1, 3-dipolarophill substances such as acetonitrile, benzonitrile, benzaldehyde, styrene, p-tolunitrile to C-phenyl-nitrile-imine derived from the photolysis of 5-phenyl-tetrazole(I) no addition compounds were identified, which might have been produced as products of cycloaddition reaction. Our experiment confirmed that 1, 3-dipole-addition was not induced, as in the case of thermolysis in the reaction involving the phenyl-nitrile-imine as intermediate produced from photolysis. Because of faster reaction rate of dimerization than that of 1, 3-dipole-cycloaddition, the formation of 3, 6-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine (Ⅲ) predominated over that of addition compounds was to be predicted. Illustration-1 shows such facts graphically.

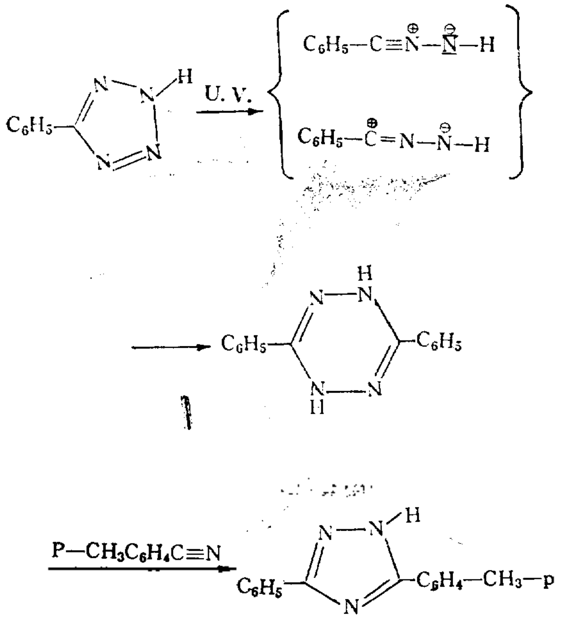

Illustration-1

In analyzing the reaction mixture of photolyzed tetrazole, 3, 6-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine (Ⅲ);3, 6-diphenyl-1. 2. 4. 5-tetrazine(Ⅳ); 3, 5-diphenyl-1, 2, 4-triazole; benzonitrile; ammonia; nitrogen were identified. These were the natural off spring of the photolysis of the 3, 6-diphenyl-1, 4-dihydro-1, 2, 4, 5-tetrazine primarily formed through the dimerization of nitrile-imine. Illus. -2 would lead you to more clear underatanding.

Clear-cut evidence of the above was to be provided

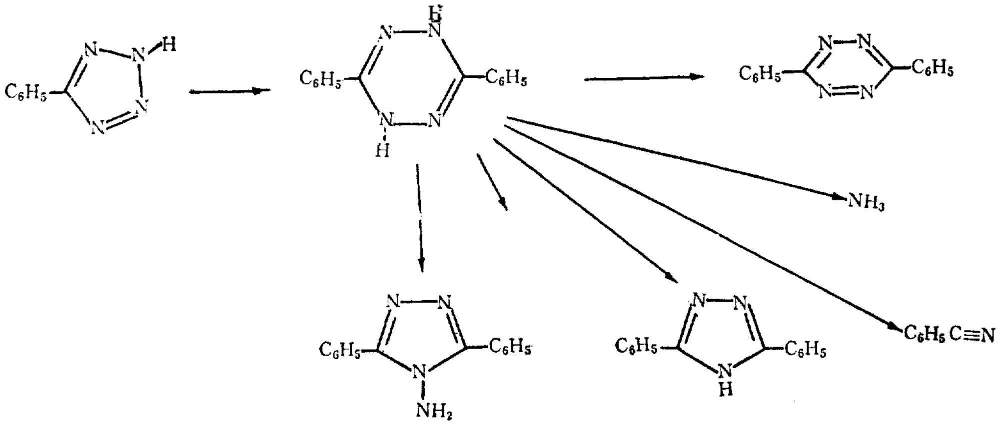

Illustration-2