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PHOTOCHEMISTRY. III.⁽¹⁾ THE PHOTOLYSIS OF 3,4,5,6-TETRAPHENYLPYRIDAZINE N-OXIDES

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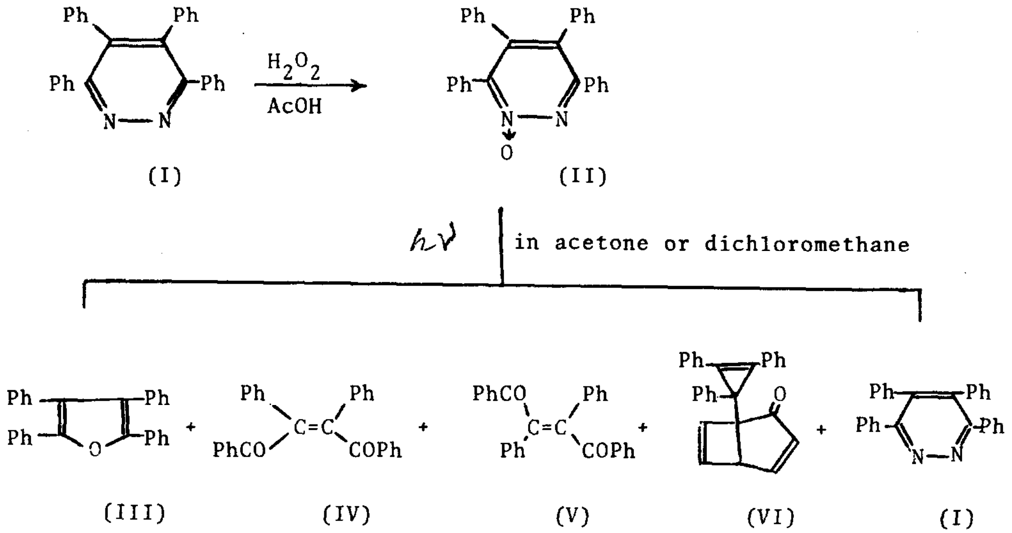
Concerning the photochemistry of pyridazine N-oxides, only a few reports were published, including our reports[2)] of photo-induced oxygenation reaction by the oxygen atom of the N-oxide and the papers reported by Ogata *et al*[3)] and Buchardt *et al*[4)], in which they reported the formation of pyrazoles *via* the corresponding oxaziridine intermediates.

The present paper deals with the photolysis of 3,4,5,6-tetraphenylpyridazine 1-oxide, affording interesting products of four kinds of the compounds which lack nitrogen atoms.

3,4,5,6-Tetraphenylpyridazine 1-oxide (II), m.p. 185-186°, obtained by oxidation of 3,4,5,6-tetraphenylpyridazine[5)] (I) with hydrogen peroxide in acetic acid, was irradiated in acetone or dichloromethane using pyrex filter[6)], and the reaction mixture was evaporated. The residue was separated by column chromatography on silica gel, affording four kinds of nitrogen-eliminated compounds, tetraphenylfuran[7)] (III), *cis*-dibenzoylstilbene[7)] (IV), *trans*-dibenzoylstilbene[8)], and 1-(1,2,3-triphenylcyclopropenyl)-$\Delta^{3,6}$-bicyclo[3,2,0]heptadien-2-one (VI), and also deoxygenated tetraphenylpyridazine (I) in the yields, respectively, shown in Chart 1. Besides these compounds, a few products were detected by thin layer and gas chromatography, but have not yet been isolated and identified on account of small quantities. No apparent difference was observed between the use of each solvent.



Irradiation time	Yields (Ca.)				
	(III)	(IV)	(V)	(VI)	(I)
3 hr	10%	10%	10%	25%	15%
6 hr	trace	20%	15%	30%	20%

Chart 1.

Among the products, I, III, IV, and V were known compounds and were proved to be identical (melting point, mixture melting point, i.r. and n.m.r. spectra) with authentic samples synthesized by alternative routes, respectively.

The structure of the compound (VI), $C_{28}H_{20}O$, m.p. 155-156^{0} was elucidated from the following spectral data: M^{+}; m/e 372, IR;νc=o(KBr),1710 cm^{-1}(five membered ring conjugated ketone), UV;λ_{max}^{EtOH} 231, 327 mμ, NMR;δ(CCl_4), 3.68(H_5, broad s.), 5.40(H_3, d., J=3.0 cps), 5.59(H_6 and H_7, broad, unassigned), 6.52 (H_4, d., J=3.0 cps), 6.8-7.4(15H, unassigned m.c., protons of three phenyl groups).

Furthermore, in the mass spectra, the appearence of fragment ions at m/e 344(M-CO, tetraphenylcyclopropenyl) and at m/e 267(additional loss of one phenyl group, triphenylcyclopropenyl) also supported the correctness of this structure. The data of this compound are well consistent with those of methyl-, methoxy-, and phenyl derivatives of $\Delta^{3,6}$-bicyclo[3,2,0]heptadienone[9].

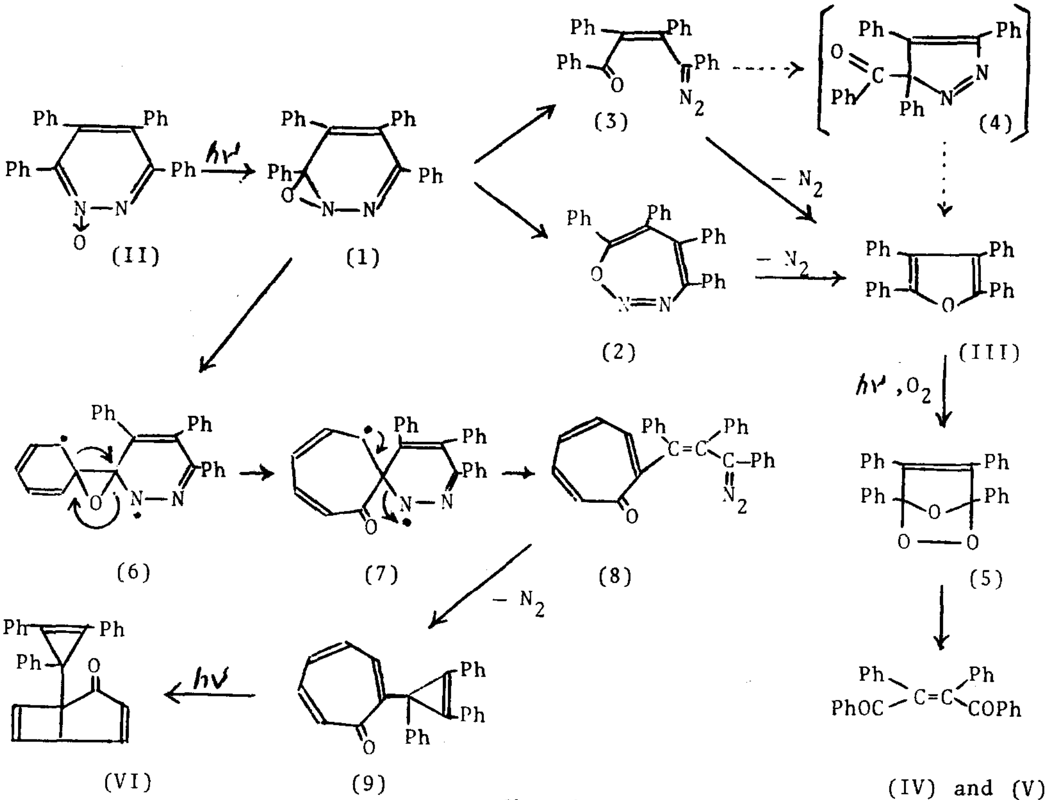


Chart2

The tentative reaction mechanism to account for the formation of these products is presented in Chart 2. An irradiation of II affords oxaziridine (1), similar to other aromatic amine N-oxides[10], and (1) is then converted into oxadiazepine (2) in either a photochemical or a thermal process, followed by elimination of the nitrogen molecule to form a furan derivative (III).

Buchardt[4] has also presented the plausible mechanism of the formation of 3-benzoyl-5-phenylpyrazole from 3,6-diphenylpyridazine 1-oxide and of 1,3-diphenylisobenzofuran from 1,4-diphenylphthalazine N-oxide by irradiation, and he explained that they were formed via the diazo compounds (3). This seems to be applicable to our mechanism.

It has been already reported that dibenzoylstilbenes (IV and V) were formed via (5) by photo-sensitized oxygenation with oxygen molecules presented in the solvent[11]. This seems to be true for our experiments.

The yield of III was considerably decreased by an irradiation for 6 hr., compared with that for 3 hr., and subsequently the yields of IV and V were increased for the prolonged irradiation time. And in the atmosphere of nitrogen, the yields of IV and V were notably decreased. These findings also support the validity of the present mechanism.

Oxygen atom of the oxaziridine (1) rearranges to the phenyl group in the 6-position of the pyridazine ring, and the radical thus formed again rearranges to (7), which leads to the formation of the tropone ring, followed by the fission of the pyridazine ring and the elimination of the nitrogen molecule to form the cyclopropenyl ring. 2-(1,2,3-Triphenylcyclopropenyl)-tropone (9) thus formed seems to be converted into the valence isomer (VI). Photochemical conversion of tropones and tropolones into their valence isomers, $\Delta^{3,6}$-bicycloheptadienones, is already reported[12)], but it is interesting that the rearrangement of the oxygen atom of the oxaziridine (1) to the substituent to form the radical is scarcely known in the cases of other aromatic amine N-oxides, details of which are now under investigation. As for the formation of the deoxygenated compounds, it is generally known that oxygen atoms of N-oxides are deoxygenated photochemically, and this fact is also recognized in the case of pyridazine N-oxides[2,3)].

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