Chem. Pharm. Bull.
20(2) 300—303 (1972)

UDC 547.852.2.04 : 541.14

Photochemistry. VII.[1] Photolyses of Polyphenylpyridazine N-Oxides

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(Received July 29, 1971)

3,4,5,6-Tetraphenylpyridazine 1-oxide (II) was irradiated in acetone or dichloromethane with high pressure mercury lamp (200W) for 3 hr, affording tetraphenylfuran (III), dibenzoylstilbenes (IV and V), 1-(1,2,3-triphenylcyclopropenyl)-$\Delta^{3,6}$-bicyclo[3,2,0]-heptadien-2-one (VI), and the deoxygenated starting material (I). 3,4,6-Triphenylpyridazine 1-oxide (VIII) gave triphenylfuran (IX), *cis*-dibenzoylstyrene (X), 3-benzoyl-1,2-diphenyl-1-cyclopropene (XI), and the deoxygenated starting material (VII). The reaction mechanism is also discussed.

There have been many interesting reports[3] on the photolyses of aromatic amine N-oxides. But, as for pyridazines, only few reports were revealed, involving our report[4] on the photo-induced oxygenation reaction by the oxygen atom of the N-oxide, and the reports of Ogata, *et al.*[5] and Buchardt, *et al.*[6] on the photochemical formation of pyrazoles from pyridazine N-oxides *via* the corresponding oxaziridine intermediates.

Concerning the formation of pyrazoles by the photo-isomerization reaction, in the case of chloro-, methoxy-, and methyl-substituted pyridazines the yields were low (below 0.2%), whereas in the case of 3,6-diphenylpyridazine 1-oxide[6] the yield was considerably high (75%).

These findings prompted us to investigate the photolyses of triphenyl- and tetraphenylpyridazine N-oxides. As the interesting results, any of pyrazoles was not obtained, but three or four kinds of the oxygen containing compounds, formed by the rearrangement of the oxygen atoms of the N-oxides and by the elimination of nitrogen molecules, were obtained.

3,4,5,6-Tetraphenylpyridazine 1-oxide (II), mp 185—186°, obtained from 3,4,5,6-tetraphenylpyridazine[7] (I) by oxidation with H_2O_2 in AcOH, was irradiated in acetone or dichloromethane with high pressure mercury lamp (200 W) with pyrex filter for 3 hr. The reaction mixture was evaporated and the residue was separated by column chromatography on silica gel, affording[8] four kinds of the nitrogen free compounds having oxygen atoms and the deoxygenated starting material (I).

Thus, tetraphenylfuran[9] (III), *cis*-dibenzoylstilbene[9] (IV), *trans*-dibenzoylstilbene[10] (V), 1-(1,2,3-triphenylcyclopropenyl)-$\Delta^{3,6}$-bicyclo[3,2,0]heptadien-2-one (VI), and I were obtained in the yields shown in the Chart 1.

The irradiation time for 6 hr resulted in a decrease of the formation of III, and in turn, an increase of the formation of other compounds.

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[1] Part VI: T. Tsuchiya, H. Arai, and H. Igeta, *Chem. Pharm. Bull.* (Tokyo), **20**, 273 (1972).

[2] Location: *Hatanodai, Shinagawa-ku, Tokyo.*

[3] *a*) C. Kaneko, *Yuki Gosei Kagaku Kyokai Shi* (Japan), **26**, 758 (1968); *b*) G.G. Spence, E.C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970), and references cited therein.

[4] T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Letters*, **1969**, 2479; **1970**, 2213.

[5] M. Ogata and H. Kano, *Chem. Commun.*, **1967**, 1176.

[6] P.L. Kumler and O. Buchardt, *J. Am. Chem. Soc.*, **90**, 5640 (1968).

[7] R.A. Carboni and R.V. Lindsey, *J. Am. Chem. Soc.*, **81**, 4342 (1959).

[8] As for the photolyses of II, a part was already published: T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Letters*, **1971**, 2579.

[9] D.R. Berger and R.K. Summerbell, *J. Org. Chem.*, **24**, 1881 (1959).

[10] H.E. Zimmermann, H.G. Duerr, R.G. Givens, and R.G. Lewis, *J. Am. Chem. Soc.*, **89**, 1863 (1967).

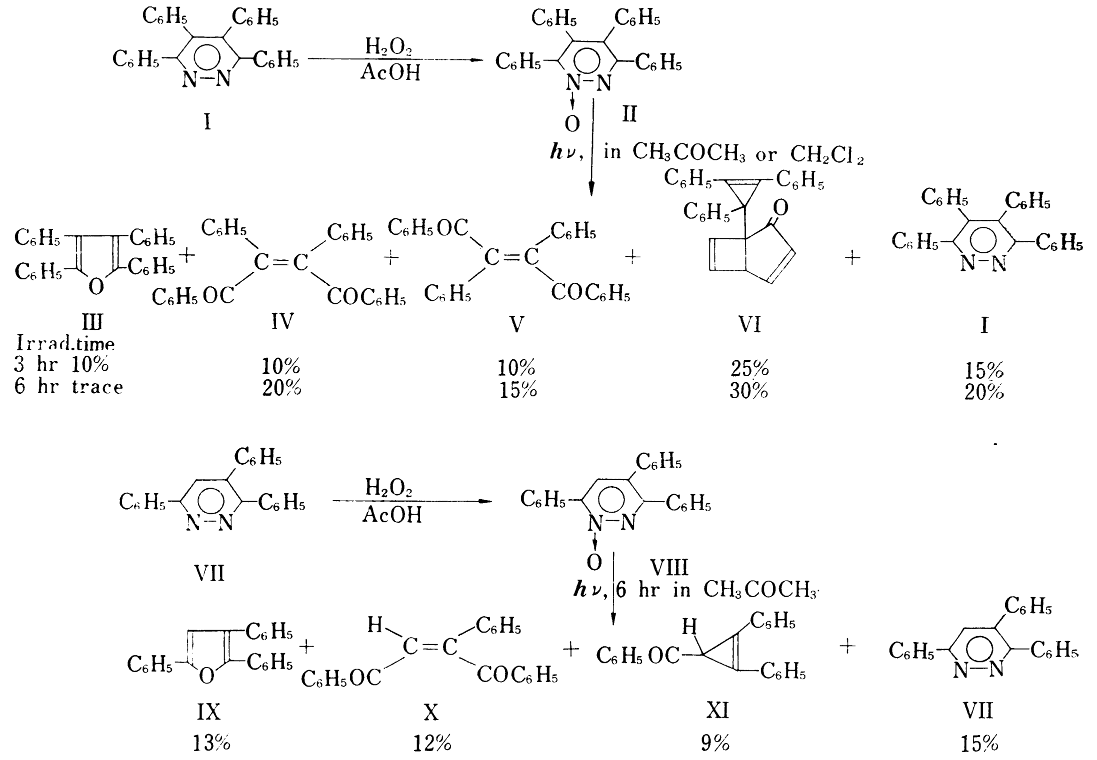

Chart 1

As for the products and yields, there were no appreciable diffrences between the use of two kinds of the solvents.

Next, 3,4,6-triphenylpyridazine 1-oxide[11] (VIII), mp 170—171°, derived by the reaction of 3,4,6-triphenylpyridazine[7] (VII) with H_2O_2 in AcOH, was irradiated for 3 hr in the same condition as described for II and worked up as usual. Thus, three kinds of the nitrogen free compouhds, *i.e.*, 2,3,5-triphenylfuran[12] (IX), *cis*-α,β-dibenzoylstyrene[13] (X), 3-benzoyl-1,2-diphenyl-1-cyclopropene (XI), and the deoxygenated starting material (VII) were obtained in the yields shown in the Chart 1.

In both cases of II and III, a couple of the compounds other than the products mentioned above, were detected by thin-layer and gas chromatography, whose isolations and identifications were not yet carried out on account of small quantities.

Except for VI and XI, these products were the known compounds, and were confirmed in comparison with the samples synthesized according to the methods given in the literature.

The structure of the compound (VI), $C_{28}H_{20}O$, mp 155—156°, was elucidated from the following spectral data; M^+ *m/e*: 372, IR $\nu_{C=O}$ (KBr); 1710 cm^{-1} (five membered ring conjugated ketone), UV λ_{max}^{EtOH}; 231, 327 mμ NMR (CCl_4) δ; 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 appearance of fragment ions at *m/e* 344 (M—CO, tetraphenylcyclopropenyl) and *m/e* 267 (additional loss of one phenyl group, triphenylcyclopropenyl) also supported the correctness of this structure.

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11) The position of the N-oxide group was confirmed by the photolysis to afford XI.

12) F. Klingemann, *J. Chem. Soc.*, 57, 674 (1895).

13) F.R. Japp and F. Klingemann, *J. Chem. Soc.*, 47, 662 (1890).

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.[14]

The compound (XI), $C_{22}H_{16}O$, mp 152—153°, was elucidated from the following spectral data; M^+ *m/e*; 296, IR $\nu_{C=O}$ (KBr); 1667 cm^{-1} (benzoyl group), NMR ($CDCl_3$) δ; 3.83 (1H, s, cyclopropene 1-H), 7.28—7.8 (13H, unassigned m.c., usual phenyl protons), 8.09—8.25 (2H, unassigned m.c., two ortho ring protons at phenyl group of benzoyl).

The tentative reaction mechanism to account for the formation of these products is presented in the Chart 2.

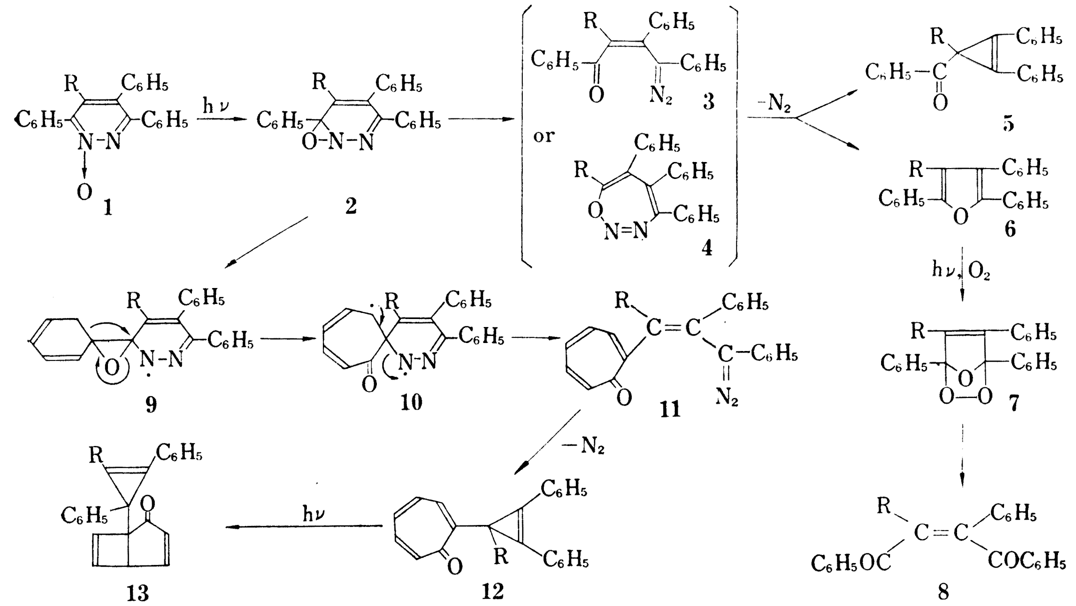

Chart 2

Similar to other aromatic amine N-oxides, the oxygen atom of the N-oxide (**1**) is rearranged by irradiation to form oxaziridine (**2**), which is then converted into the diazo compound (**3**) or oxadiazepine (**4**), followed by the elimination of nitrogen molecule to give benzoylcyclopropene (**5**, XI) and furan derivative (**6**, III, IX).

Concerning the intermediates (**3** and **4**), Kaneko, *et al.*[3] considered that the isomerization reaction of aza-aromatic N-oxides proceeds through the oxazepine, while Buchardt, *et al.*[6] presented the mechanism of the formation of 3-benzoyl-5-phenylpyrazole from 3,6-diphenylpyridazine 1-oxide *via* **3**. Both routes are reasonably considered to explain our present reaction, although the definite pathway remained uncertain.

It is already known[14] that the furan derivatives (III, IX) are oxidized by oxygen molecules presented in the solvent to give the dibenzoyl compounds (IV, V, and X), *via* the peroxide (**7**). And the present reaction seems to proceed similarly, since the irradiation of II for 6 hr results in a decrease of the formation of III and alternatively an increase of those of IV and V.

Furthermore, the fact that the irradiation in the atmosphere of nitrogen gas leads to a decrease of the formation of the dibenzoyl compounds, also supports the pathway of the reaction.

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[14] M.J. Martel and M.C. Dufraisse, *Compt. Rend.*, **244**, 626 (1957); N.M. Bikales and E.I. Becker, *J. Org. Chem.*, **21**, 1405 (1956).

The oxygen atom of **2**, rearranges to the phenyl group at the 6-position of the pyridazine ring, followed by the fission and the elimination of nitrogen atoms of the pyridazine ring to form the cyclopropene ring.

Thus, the compound (**12**) is formed and is converted photochemically into $\Delta^{3,6}$-bicycloheptadienone derivative (**13**).

The photochemical conversion of tropones and tropolones to their valence isomers, $\Delta^{3,6}$-bicycloheptadienone, is already known.[15] Examples of the rearrangement of the oxygen atom of **2** to the substituent, are scarcely known in other aromatic amine N-oxides.

Thus, it is interesting that triphenylpyridazine N-oxide (VIII) does not afford $\Delta^{3,6}$-bicycloheptadienone (**13**), and in turn, tetraphenylpyridazine N-oxide (II) does not give benzoylcyclopropene.

The detailed mechanism of the rearrangement reaction is now under way.

Experimental

Preparation of 3,4,5,6-Tetraphenylpyridazine 1-Oxide (II)——To a solution of I[7] (3g) dissolved in 150 ml of AcOH, 15 ml of H_2O (30%) was added and was kept at 70° for 6 hr. To the reaction mixture, water was added and condensed *in vacuo*, and this procedure was repeated three times. The residue was neutrallized with Na_2CO_3 solution, followed by extraction with CH_2Cl_2. The CH_2Cl_2 layer was dried on Na_2SO_4, and evaporated. The residue thus obtained was recrystallized from benzene to crystals, mp 185—186°, M^+ *m/e* 400, 2.4g. *Anal.* Calcd. for $C_{28}H_{20}ON_2$: C, 83.97; H, 5.03; N, 7.00. Found: C, 83.91; H, 4.99; N, 7.23.

Preparation of 3,4,6-Triphenylpyridazine 1-Oxide (VIII)——The compound[7] (VII, 3 g) was treated and worked up in the same manner as described for II, affording crystals (from benzene), mp 170—171°, M^+ *m/e* 324, 2.2 g. *Anal.* Calcd. for $C_{22}H_{16}ON_2$: C, 81.46; H, 4.97; N 8.64. Found: C, 81.50; H, 5.01; N, 8.54.

Irradiation of 3,4,5,6-Tetraphenylpyridazine 1-Oxide (II)——A solution of II (1 g) dissolved in 300 ml of CH_3COCH_3 or CH_2Cl_2 was irradiated with high pressure mercury lamp (200W) with pyrex filter for 3 hr. The reaction mixture was evaporated *in vacuo* and the residue was separated by column chromatography on silica gel. From the eluates with benzene, the following four kinds of compounds were obtained successively.

Tetraphenylfuran (III): 90 mg, mp 172—173° (from gla. AcOH). *Anal.* Calcd. for $C_{28}H_{20}O$: C, 90.29; H, 5.41. Found: C, 90.04; H, 5.30. This compound was also confirmed by the direct comparison of the authentic sample prepared by alternative route given in the literature.[9]

cis-Didenzoylstilbene (IV): 96 mg, mp 211—212° (from AcOEt), $\nu_{C=O}$ (KBr); 1670 cm^{-1}. *Anal.* Calcd. for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.35; H, 5.14. This compound was also confirmed by the direct comparison of the authentic sample prepared by alternative route given in the literature.[9]

trans-Dibenzoylstilbene (V): 92 mg, mp 250—251° (from AcOEt), $\nu_{C=O}$ (KBr); 1670 cm^{-1}. *Anal.* Calcd. for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.24; H, 5.35. This compound was also confirmed by the direct comparison of the authentic sample prepared by alternative route given in the literature.[10]

1-(1,2,3-Triphenylcyclopropenyl)-$\Delta^{3,6}$-bicyclo[3,2,0]heptadien-2-one (VI): 220 mg, mp 155—156° (from MeOH). *Anal.* Calcd. for $C_{28}H_{20}O$: C, 90.29; H, 5.41. Found: C, 90.10; H, 5.30. Then, from the eluate with CH_2Cl_2, 3,4,5,6-tetraphenylpyridazine (I), mp 193—194°, 150 mg, was obtained.

Irradiation of II for 6 hr——The compound (II, 1 g) was treated and worked up in the same manner as described above, giving III, 7—8 mg, IV, 190 mg, V, 140 mg, VI, 265 mg, and I, 205 mg.

Irradiation of 3,4,6-Triphenylpyridazine 1-Oxide (VIII)——A solution of VIII (2 g) dissolved in 350 ml of CH_3COCH_3 was irradiated for 3 hr in the same condition as descrived for II. The reaction mixture was evaporated *in vacuo* and the residue was separated by column chromatography on silica gel. From the eluates with benzene, the following three kinds of compounds were obtained successively.

2,3,5-Triphenylfuran (IX): 240 mg, mp 92—93° (from MeOH–AcOEt), M^+ *m/e* 296, NMR ($CDCl_3$) δ; 6.77 (1H, s, 4-H). *Anal.* Calcd. for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.41; H, 5.45. This compound was also confirmed by the direct comparison of the authentic sample prepared by alternative route given in the literature.[12]

3-Benzoyl-1,2-diphenyl-1-cyclopropene (XI): 190 mg, mp 152—153° (from MeOH), M^+ *m/e* 296. *Anal.* Calcd. for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.00; H, 5.45.

cis-Dibenzoylstyrene (X): 235 mg, mp 124—125° (from MeOH), M^+ *m/e* 312. *Anal.* Calcd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.28; H, 5.15. This compound was confirmed by the direct comparison of the authentic sample prepared by alternative route given in the literature.[13] Then, from the eluate with CH_2Cl_2, 3,4,6-triphenylpyridazine (VII), mp 172° (from MeOH), *ca.* 100 mg, was obtained.

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15) W.G. Dauben, K. Kch, S.L. Smith, and O.L. Chapmann, *J. Am. Chem. Soc.*, **85**, 2616 (1963); T. Miyashi, M. Nitta, and T. Mukai, *Tetrahedron Letters*, **1967**, 3433; T. Mukai and T. Miyashi, *Tetrahedron*, **23**, 1613 (1967).