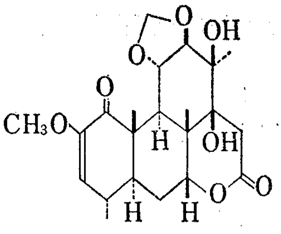
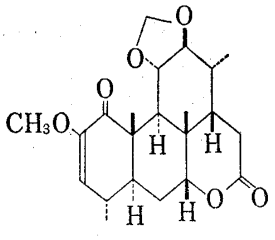
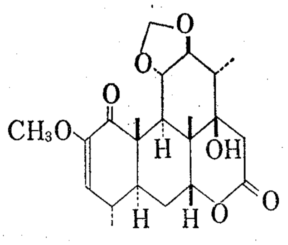

I


II


III

The partial structures thus deduced, along with the previously assigned oxygen functions, have many common features with those of picrasin D (II) and picrasin E (III),[7] indicating that picrasin F is similar in structure to picrasin D and E. In support of this supposition, the NMR parameters for certain hydrogens and optical rotatory dispersion (ORD) and circular dichroism (CD) data of picrasin F are in agreement with those of picrasin D and E.

Picrasin F differs from picrasin E in having one extra oxygen which can only be accomodated as a tertiary hydroxyl at C-13 by the following data that 1) the C-12 hydrogen signal in the NMR spectrum appears as a doublet showing coupling only with the C-11 hydrogen and 2) the C-13 methyl hydrogen signal occurs as a singlet at a deshielded position (δ 1.54 ppm). The nuclear Overhauser effect between one of the C-15 hydrogens and the C-13 methyl hydrogens indicates the α-configuration of the C-13 methyl group.

Accumulated data has led to the conclusion that picrasin F has the stereostructure I.

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Photochemistry. V.[1] Photocyclization of 3,4,6-Tri- and 3,4,5,6-Tetraphenylpyridazines. Formation of 1,2-Diazapolyarenes

In a previous paper, we have reported[2] that an irradiation of 3,4,5,6-tetraphenylpyridazine 1-oxide resulted in the rearrangement of the oxygen atom of N-oxide group, followed by elimination of the nitrogen molecule to form tetraphenylfuran, *cis*- and *trans*-dibenzoylstilbene, and $\Delta^{3,6}$-bicycloheptadienone derivative.

The present paper deals with the photolyses of polyphenylpyridazines lacking N-oxide groups. Interestingly, as the result, the oxidative cyclization among substituent phenyl groups occurred to form various kinds of 1,2-diazapolyarenes.

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1) Part IV: T. Tsuchiya, H. Arai, H. Kawamura, and H. Igeta, *Chem. Pharm. Bull.* (Tokyo), in press.
2) T. Tsuchiya, H. Arai, and H, Igeta, *Tetrahedron Letters*, **1971**, 2579.

After irradiation[3] of 3,4,5,6-tetraphenylpyridazine[4] (I) in methanol for 12 hr, the solvent was removed and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 layer was evaporated to dryness and the product was dissolved in a small amount of AcOEt, and submitted to column chromatography on Avicel.

From the eluate with AcOEt, 1,4-diphenyl-2,3-diazatriphenylene (III), cyclized between phenyl group at 4- and 5-positions, and the starting material (I) (*ca.* 20%) were obtained. The residue insoluble in CH_2Cl_2, was dissolved in benzene and was separated by column chromatography on alumina. From the eluate with benzene, 3-phenyl-1,2-diazadibenzo[fg,op]naphthacene(IV), cyclized among three phenyl groups at 3-, 4-, and 5-positions, was obtained. And then, from the eluate with methanol, 15,16-diazatribenzo[b,n,pqr]perylene[5] (V), cyclized among all four phenyl groups, was obtained. Their yields are listed in the Chart.

Next, I was irradiated in CH_2Cl_2 for 12 hr to give III and IV in 1—2% and *ca.* 20% yields, respectivley. In this case, V was not obtained, probably due to the poor solubility of IV in this solvent and as soon as IV was formed, precipitation occurred. Actually, an irradiation of IV in methanol afforded V.

An irradiation of I in benzene resulted in the recovery of the starting material.

In every case of the present experiment, 3,4-diphenyl-1,2-diazatriphenylene, cyclized between two pheny groups at 3- and 4-positions, was not isolated. So it is considered that the cyclization between the phenyl groups at 4- and 5-positioned took place, followed by the formation of V *via* IV.

An irradiation of I in methanol for a long time increased the yield of V, and also afforded the nitrogen free compounds in a small amount, on which further investigations are now under way.

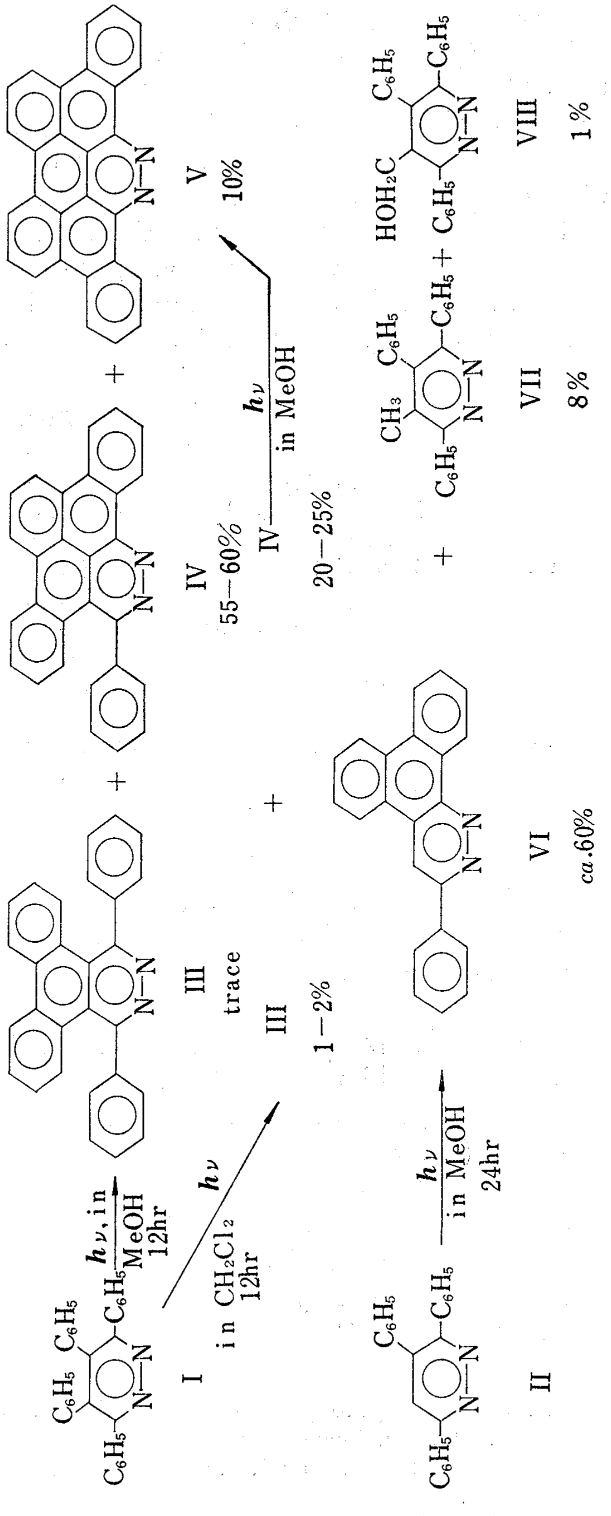

Chart 1

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3) High pressure mercury lamp (400W, Nikko Sekiei Co., Japan) was used as a light source.

4) R.A. Carboni and R.V. Rindsey, *J. Am. Chem. Soc.*, **81**, 4342 (1959).

5) A. Zinke, *Monatsh.*, **80**, 202 (1949).

3,4,6-Triphenylpyridazine³⁾ (II) was irradiated in methanol for 24 hr, and the solvent was removed. The residue thus obtained was separated by column chromatography on alumina. From the eluate with CH_2Cl_2, 5-methyl-3,4,6-triphenylpyridazine (VII), mp 177—178°, nuclear magnetic resonance (NMR) ($CDCl_3$) δ; 2.12 (3H, s), 6.95—7.8 (15H, m), and 5-hydroxymethyl-3,4,6-triphenylpyridazine (VIII), mp 143—145°, NMR ($CDCl_3$) δ; 2.30 (1H, broad, erased by D_2O), 4.36 (2H, broad), 7.1—7.95 (15H, m), was obtained.⁶⁾ Then, from the eluate with methanol, 3-phenyl-1,2-diazatriphenylene (VI), cyclized between phenyl groups at 3- and 4-positions was obtained. Their yields are listed in the Chart.

An irradiation of II in CH_2Cl_2 for 24 hr, afforded VI in a small amount and the starting material in a large quantity. But an irradiation for 120 hr resulted in the formation of VI in *ca.* 40% yield and of the nitrogen free compound in a small amount, similar to the case of I, on which further examinations are now being undertaken.

The values of elementary analyses, molecular weight determinations (by mass spectrometry) of these products are acceptable for their structures. The compound (V) is the known substance, whose physical data are coincidental with those given in the literature.⁵⁾

TABLE I

Compound	mp (°C) (Solv. for recrys.)	UV λ_{max}^{MeOH} mμ (log ε)	NMR ($CDCl_3$), δ
III	213—215 (AcOEt)	259 (4.45) 277 (4.77)	6.5—8.8 (18H, unassigned m.c.)
IV	310 (AcOEt–MeOH)	270 (4.25) 285 (4.22)	7.2—7.8 (8H, m), 8.2—8.6 (7H, m), 9.45 (1H, q)
V	360 (nitrobenzene)	233 (4.88) 280 (4.64)	a)
VI	161—162 (AcOEt)	263 (4.66) 277 (4.00)	7.4—7.85 (7H, m), 8.1—8.6 (5H, m) 8.53 (1H, s, H_4), 9.5 (1H, q)

a) sparingly soluble in organic solvent

The NMR spectra of III, IV ,and VI are shown in the Table. The spectral charts of IV and VI resemble each other and the quartet signals (1H) at around 9.5 δ are assigned to 14-H and 12-H, respectively, and this value is almost consistent with the value,⁷⁾ 9.45 δ, of benzo[h]quinoline.

The signals at around 8.1—8.6 δ amount to 7H in IV, due to five protons of H_4, H_7, H_8, H_{10}, H_{11}, and two *ortho* protons (H_2', H_6') of the phenyl ring. These values of chemical shifts are well agreed with those of H_1-, H_4-, H_5- *etc.* protons⁸⁾ (8.56 δ) of triphenylene, H_1 (8.55 δ)-, H_{10} (8.28 δ)-protons of benzo[f]quinaldine,⁷⁾ and *ortho* protons⁹⁾ (7.9—8.2 δ) of the phenyl group of 3-phenylpyridazines. The signals at 7.1—7.8 δ are assigned to other protons of usual aromatic ring. In a spectrum of III, lack of the signal at lower field than 9.0 δ leads to denial of the 1,2-diazatriphenylene structure.

The oxidative photocyclization are well known in the cases of the formation of phenanthrene from stilbene,¹⁰⁾ and of benzo[c]cinnoline from azobenzene.¹¹⁾ And also some re-

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6) Methylation and hydroxymethylation of the ring of the aromatic amine by irradiation in methanol are already known, including the case of pyridazines.
cf. M. Ogata and H. Kano, *Chem. Commun.*, **1967**, 1176 . T. Tsuchiya, H. Arai, and H. Igeta, unlublisshed redults.

7) E.V. Donkt, R.H. Martin, and F. Greets–Evrard, *Tetrahedron*, **20**, 1495 (1964).

8) R.H. Martin, N. Defay, F. Greets–Evrard, and S. Delavarenne, *Tetrahedron*, **20**, 1073 (1964).

9) I. Crossland, *Acta Chem. Scand.*, **20**, 258 (1966).

10) W.M. Moore, D.D. Morgan, and F.R. Stermitz, *J. Am. Chem. Soc.*, **85**, 892 (1963).

11) G.E. Lewis, *J. Org. Chem.*, **25**, 2198 (1960).

ports[12] on the cyclization among substituent phenyl groups of the aromatic ring are published.

But it is interesting that the photocyclization among phenyl groups on the ring of N-heterocycles, as in the case of the present experiment, are scarcely known. So the present work must be very useful for the application of the syntheses of azaarens. Further investigations are now under way.

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[12] N. Toshima and I. Moritani, *Tetrahedron Letters*, **1967**, 357, 462.

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UDC 547.279.52.04 : 547.556.7.04

Reactions of β-Keto Sulfide and Sulfoxide with Nitrene and Diazonium Salt

The introduction of nitrogen function to the α-carbon of sulfide *via* ylide intermediate is a versatile synthetic method. In the total synthesis of cephalosporin-C, Woodward *et al.*[1] have reported the reaction of dimethyl azodicarboxylate with (L)-(—)methyl N-*tert*-butyloxycarbonyl-2,2-dimethyl-thiazolidine-4-carboxylate to give hydrazodiester in high yield.

From this point of view, we investigated the reactivity of nitrene and diazonium compound to sulfide and sulfoxide. Here we wish to report our results of the reactions of ω-(methylmercapto)acetophenone (I) and ω-(methylsulfinyl)acetophenone (VII) with carboethoxynitrene and *p*-nitrobenzenediazonium fluoroborate.

Irradiation of I in the presence of one equivalent of ethyl azidoformate[2] in methylene chloride with a low-pressure mercury lamp for 4 hr afforded acetophenone as a sole product.[3]

On the other hand, heating of a solution of I and ethyl azidoformate in methylene bromide at 110° for 45 hr afforded 2,5-diphenyl-3,4-dimercaptomethylfurane (III) in 20% yield. mp 87°. IR $^{\text{Nujol}}_{\text{max}}$ cm^{-1}: 1602. UV $\lambda^{\text{ethanol}}_{\text{max}}$ nm (ε): 229 (18800), 278 (13700), 320 (20800). NMR[4] δ: *ca.* 7.40 (6H, m), *ca.* 8.20 (4H, m), 2.43 (6H, s, CH_3S-). M$^+$ 330 ($C_{18}H_{16}S_2O$).[5]

However, when the reaction was run without the solvent, 1,4-diketone (IV) was obtained. mp 207°. IR $\nu^{\text{Nujol}}_{\text{max}}$ cm^{-1}: 1666 (C=O). UV $\lambda^{\text{ethanol}}_{\text{max}}$ nm: 246. NMR δ: *ca.* 7.60 (6H, m), *ca.* 8.10 (4H, m) 4.97 (2H, s), 2.03 (6H, s, CH_3S-). M$^+$ 330 ($C_{18}H_{18}S_2O_2$). Diketone (IV) was converted to the furane (III) on treatment with BF_3-etherate in low yield.

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[1] *a*) R.B. Woodward, K. Heusler, J. Gosteli, P. Naegeli, W. Oppolzer, R. Ramage, S. Ranganathan and H. Vorbruggen, *J. Am. Chem. Soc.*, **88** 852 (1966); *b*) R.B. Woodward, *Science*, **153**, 487 (1966).

[2] J.S. McConaglay and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 4450 (1967).

[3] Hogeveen, H. and Smit, J., *Rec. Trav. Chim. Pays-Bas*, **85**, 489 (1966).

[4] The NMR spectra were taken in $CDCl_3$ solution and calibrated to internal standard of tetramethylsilane. Chemical shifts are expressed in ppm (δ): s: singlet; d: doublet; q: quartet; sept: septet; m: multiplet.

[5] Satisfactory analyses were obtained on all compounds obtained.