[Chem. Pharm. Bull. 23(11)2791—2797(1975)]

UDC 547.852.2.04 : 547.583.5.04 : 547.239.2.04

Studies on Pyridazines. XXIV.[1] The Reaction of Pyridazine N-Oxides and Pyridazinium Ylides with Benzyne

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(Received April 30, 1975)

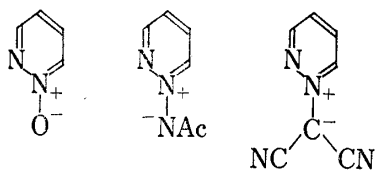
The reaction of pyridazine N-oxide (**1**) with benzyne produced 1-benzoxepine (**5**) in moderate yield, *via* the 1,3-cycloadduct (**4**). By the similar reaction, N-acetyliminopyridazinium ylide (**2**) and pyridazinium dicyanomethylide (**3**) yielded the 1,3-cycloadducts (**9** and **21**).

The adduct (**9**) was transformed into the 3-vinylindazole (**10**) and 3-(2-acetoanilino)-pyridazine (**11**) by heating or treatment with sodium methoxide. Irradiation of the adduct (**9**) resulted in the aromatization to form indazolo[2,3-*b*]pyridazine (**12**) and in the ring contraction to form indole derivatives (**13** and **14**) *via* 1-benzazepine (**19**).

The formation mechanism of these compounds is also discussed.

The 1,3-dipolar cycloaddition reactions of zwitterionic ylides of aza-aromatic heterocycles with dipolarophiles have been extensively studied.[3] As for pyridazinium ylides, the cycloaddition with acetylenedicarboxylates[4–6] and cyanoethylenes[4,7] to give the corresponding pyrazolo[1,5-*b*]pyridazines and pyrrolo[1,2-*b*]pyridazines was reported, however, the reaction with benzyne has not yet been reported.

On the other hand, although the reactions of pyridine,[8] isoquinoline,[9] and acridine N-oxides[10] with dipolarophiles have been known, the similar reactions of pyridazine N-oxides have not been known. Thus, we have examined the reactions of pyridazine N-oxides (**1**), N-acetyliminopyridazinium ylide (**2**), and pyridazinium dicyanomethylide (**3**) with benzyne as a dipolarophile.



1 **2** **3**

Chart 1

Unlike other dipolarophiles such as acetylenes and ethylenes, benzyne reacted with the N-oxides (**1**) to give 1-benzoxepines in moderate yields, eliminating molecular nitrogen. Reaction of the ylides (**2**, **3**) with benzyne afforded the 1,3-adducts, hitherto obtained for the first time in pyridazine species. The 1,3-adducts were then submitted to thermolysis and photolysis to give interesting results, on which we now report.

* Dedicated to the memory of Prof. Eiji Ochiai.

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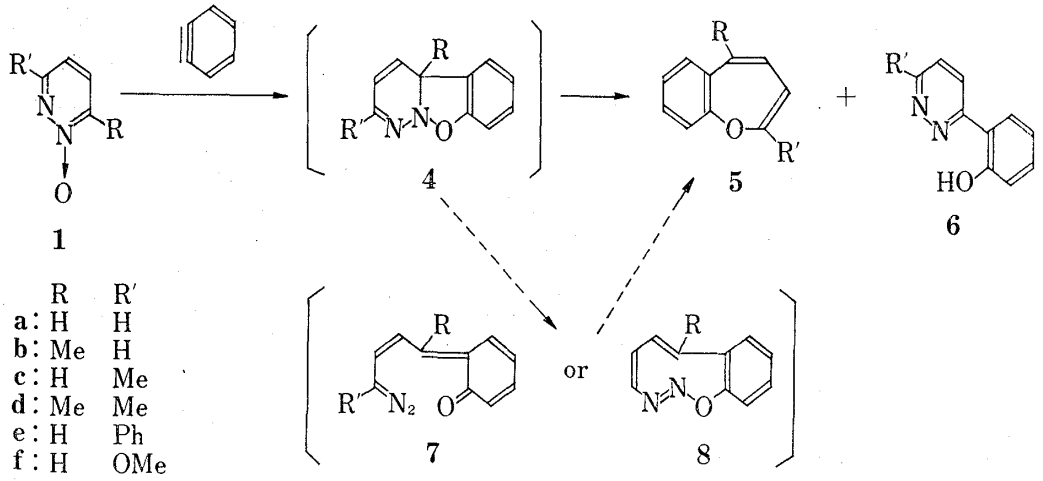
1. Reaction of Pyridazine N-oxides with Benzyne

It is known that the reaction[8] of pyridine N-oxides with dipolarophiles such as hexafluoropropylene and phenylisocyanate afforded the 1,3-adduct, followed by cleavage of N–O bond to give 2-substituted pyridines. Similar reactions on pyridazines have not been carried out, so we have tried the reactions with acetylenes and ethylenes and have found that any reaction has not occurred. Then, the reaction with benzyne was examined.

Pyridazine N-oxides (**1a—f**) were reacted with benzyne, prepared from *n*-butyl nitrite and anthranilic acid by Reynolds's method,[11] followed by separation by chromatography on alumina to give the corresponding 1-benzoxepines (**5**) in 25—70% yields along with the rearranged products, *i.e.*, 3-(2-hydroxyphenyl)pyridazines (**6**) in 10—20% yields.



	R	R′
a	H	H
b	Me	H
c	H	Me
d	Me	Me
e	H	Ph
f	H	OMe

Chart 2

Unlike the case of the ylides (**2**, **3**), although the 1,3-cycloadduct (**4**) was not isolated, the adduct of the N-oxide (**1**) with benzyne must be formed initially, followed by fission of N–O bond to give the diazo-keto intermediate (**7**), which might be transformed into benzoxepine (**5**) by elimination of molecular nitrogen and ring closure.

Similar to the case of the reaction[12] of N-methoxypyridazinium salts with nucleophile, another course *via* the intermediate (**8**) by Cope-rearrangement might be taken in consideration. Of the two courses the definite rout is still subtle at present. When R represents H, fission of the O–N bond is accompanied by elimination of a proton on the 6-position to give the compound (**6**). Actually, the compounds (**1b** and **1d**) having substituents in the 6-position did not afford **6**.

Under this condition, the compounds (**1b** and **1d**) afforded the products (**5**) in moderate yields of 60—70% based on the consumed starting materials, and about halves of the starting materials were recovered unchanged, suggesting that the initial 1,3-cycloaddition might be hindered by substituent effect in the α-position.

The compound (**1f**) having methoxy group in the 3-position did not afford benzoxepine (**5**), but gave solely **6**. 1-Benzoxepine (**5a**) thus obtained was a known compound[13] and structures of the other benzoxepines were confirmed from their microanalytical and spectral data. These results may give a valuable synthetic route of 1-benzoxepines.

11) G.A. Reynolds, *J. Org. Chem.*, **29**, 3733 (1964).
12) C-S. Kaneko, T. Tsuchiya, and H. Igeta, *Tetrahedron Letters*, **1973**, 2347.
13) A. Shani and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 6310 (1967); E.E. Schweizer, M.S.El-Bakoush, K.K. Light, and K.H. Oherle, *J. Org. Chem.*, **33**, 2590 (1967).

2. Reaction of N-Acetyliminopyridazinium Ylide with Benzyne

It is well known that the reaction of N-iminopyridazinium ylides with acetylenes afford pyrazolo[1,5-*b*]pyridazines *via* 1,3-adducts as shown in Chart 3.

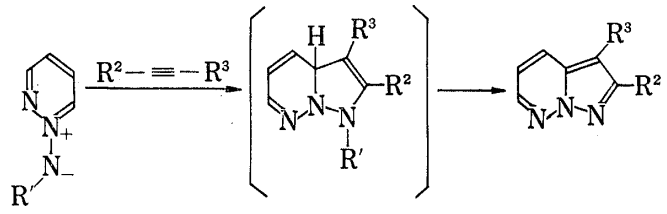


Chart 3

However, the reaction with benzyne has not yet been known. Treatment of N-aceytliminopyridazinium ylide (**2**)[14] with benzyne under similar condition to the case of the N-oxide (**1**), afforded the cycloadduct (**9**) in *ca.* 70% yield.[15] The isolation of such a cycloadduct is the first example in pyridazine species. Then, chemical behavior of the adduct (**9**) was examined.

Heating of **9** in xylene for 2 days under reflux caused the ring fission to give 3-vinylindazole (**10**)[16] and 3-(2-acetoanilino)pyridazine (**11**) in *ca.* 25% and 55% yields, respectively. Reaction of **9** with sodium methoxide in methanol at 0—5° for 1 hr also gave **10** and **11** in 45% and 16% yields, respectively.

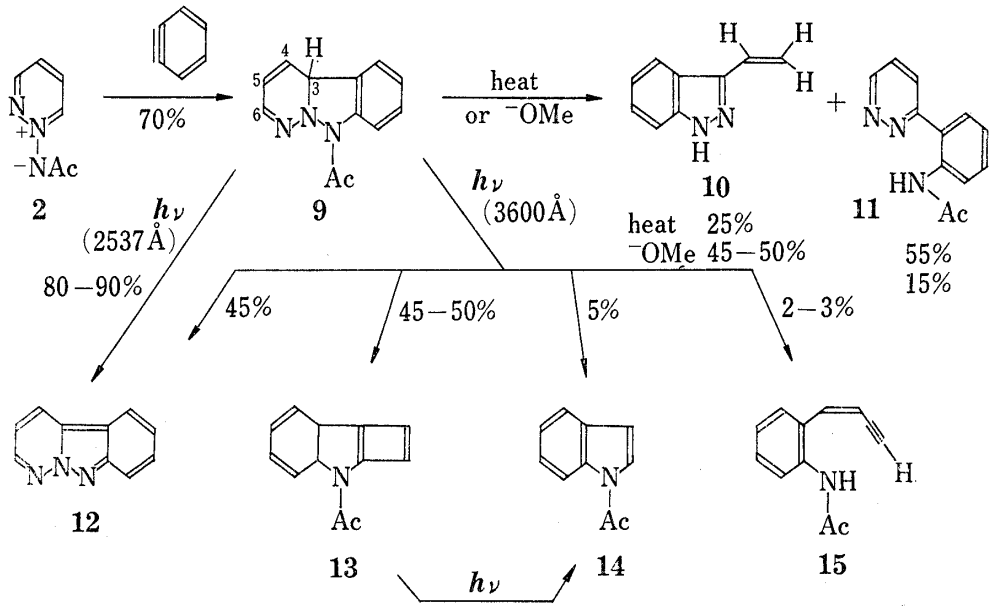


Chart 4

Irradiation (2537 Å) of **9** in dichloromethane caused aromatization to give indazolo[2,3-*b*]pyridazine (**12**) in 80—90% yield. Interestingly, the irradiation (3600 Å) afforded not only **12** in 45% yield but also indoles (**13**) in 40—50% yield and **14** in *ca.* 5% yield. Besides them, a small amount of vinylacetylene derivative (**15**) was also obtained. Irradiation of the compound (**13**) thus isolated gave **14**, indicating that acetylene was eliminated from **13** by irradiation to give **14**.

Formation mechanism of **10** and **11** by base or heat might be proceeded as shown in Chart 5. The compound (**9**) is transformed *via* path A into the intermediate (**16**) by N–N bond fission, followed by elimination of HCN to give vinylindazole (**10**). Fission *via* path B affords anilinopyridazine. Facility of bond fission of the two paths depends on the N-substituents. While, in the case of electron withdrawing group such as acetyl group the fission *via* path B

14) T. Okamoto, M. Hirobe, and A. Ohsawa, *Chem. Pharm. Bull.* (Tokyo), **14**, 518 (1966).
15) Besides, acetoanilinopyridazine (**11**) was obtained in *ca.* 10% yield.
16) J. Kurita and T. Tsuchiya, *J.C.S. Chem. Comm.*, **1974**, 936.

takes precedence, in the case of N-H, fission *via* path A occurs. This assumstion is confirmed by the fact that the reaction of **9** with methoxide anion causes easily deacetylation to give **10** in higher yield than that of the case of thermolysis.

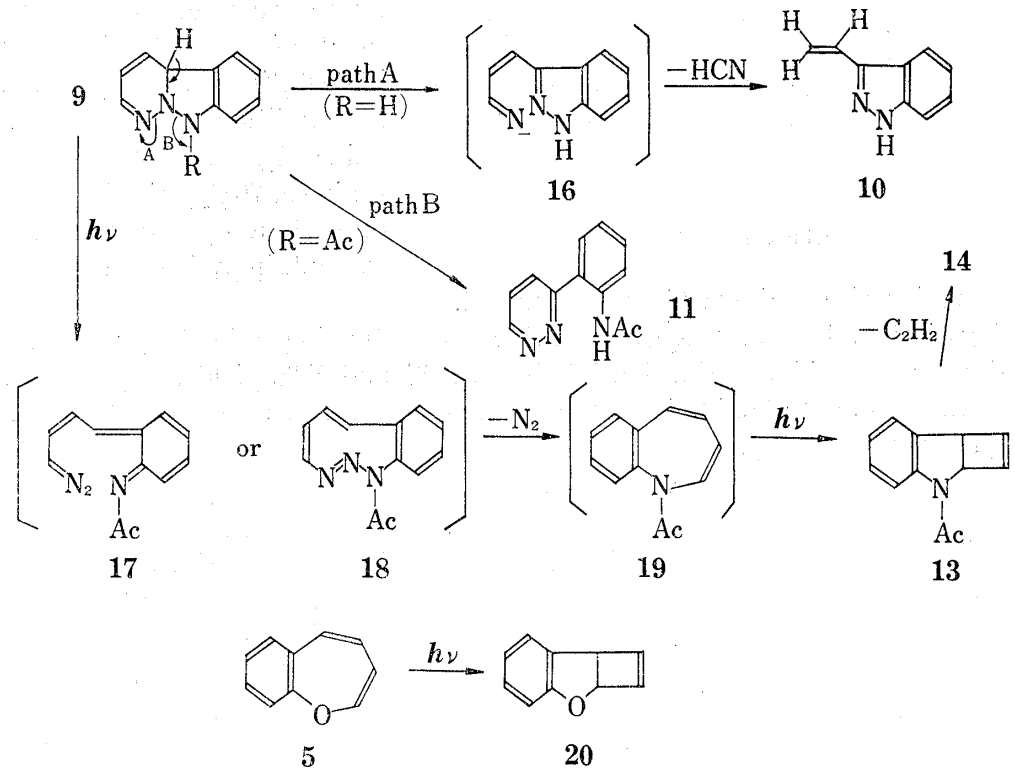


Chart 5

For formation of indoles (**13**) by irradiation, the intermediate (**17** or **18**) would eliminate molecular nitrogen to give 1-benzazepine (**19**), quite similar to the case of the formation of benzoxepine (**5**) from the N-oxides (**1**), followed by photocyclization to give **13**. The similar photocyclization was observed in the case of benzoxepines. Namely, benzoxepine (**5a**) was cyclized by irradiation (3600Å) in dichloromethane for 10 hr to give the tricyclic compound (**20**) in *ca.* 70% yield. These results may be useful for synthesizing indazolopyridazine, vinylindazoles and indoles.

3. Reaction of Pyridazinium Dicyanomethylide with Benzyne

Reaction of pyridazinium dicyanomethylide (**3**)[4,7] with benzyne similarly afforded the cycloadduct (**21**) in 70—75% yields. The adduct (**21**) was converted, by refluxing in xylene or treatment with sodium methoxide in methanol at 0—5°, to 9-cyano-isoindolino[2,3-*b*]pyridazine (**22**) in *ca.* 55% yield. In this case, any rearranged compound was not obtained.

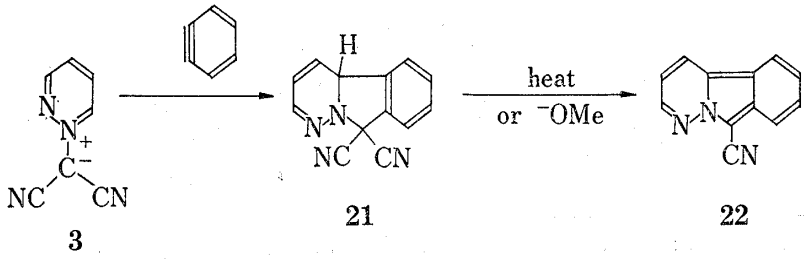


Chart 6

It is known[4,7] that the reaction of the ylide (3) with acetylene gave analogous product, *i.e.*, 7-cyanopyrrolo[1,2-*b*]pyridazine, but the intermediate cycloadduct was not isolated. The adduct (21) resisted to irradiation and even irradiation by high-pressure Hg lamp for 10 hr did not cause any reaction. The prolonged irradiation gradually caused decomposition but any characteristic product has not been obtained.

Experimental

IR spectra were determined with a JASCO IR-1 spectrometer and mass spectra were recorded on a Hitachi RMS-4 instrument. NMR spectra were recorded on Hitachi R-20 and R-22 spectrometers in CCl_4 or $CDCl_3$ solution using tetramethylsilane (TMS) as internal standard. NMR spectra assignment were confirmed by spin-decoupling experiments. Melting points were measured on a Yamato MP-1 apparatus and are uncorrected. Microanalyses were performed in the analytical laboratory, Showa University. Photolyses were carried out in a photochemical reactor (Nikko Sekiei Co., Japan) equipped with six 3600 Å or 2537 Å lamps using a quartz vessel.

Reaction of Pyridazine N-Oxides (1a—f) with Benzene——General Procedure: To a solution of the N-oxide (**1**, 1 g) and *n*-butyl nitrilte (1.5 equiv.) dissolved in CH_2Cl_2 (30 ml), a solution of anthranilic acid (1.5 equiv.) in acetone (20 ml) was added over a 30 min period under stirring at 40—50°. The reaction mixture was stirred for an additional 2 hr at the same temperature and then was evaporated *in vacuo*. The residue was extracted with benzene and the extract was chromatographed over alumina.

From the eluate with benzene–CH_2Cl_2 (1: 1), 1-benzoxepine (**5**) and 3-(2-hydroxyphenyl)pyridazine (**6**) were obtained. From the eluate with CH_2Cl_2, unchanged starting N-oxide (**1**) was recovered. (**1a**: 0.8%, **1b**: 45%, **1c**: 0.7%, **1d**: 40%, **1e**: 9%, **1f**: —0%). In the case of **1f**, **5** was not obtained, and 3-substituted N-oxides (**1b** and **1d**) did not afford **6**. The yields as well as analytical, physical, and NMR spectral data for compounds (**5** and **6**) are collected in Table I and II.

Table I

Compound	bp °C/mmHg (bath temp) or mp °C (solvent)	Formula (*m/e* M+)	Analyses (%) Calcd. C	H	N	Found C	H	N
5a	50/0.5	$C_{10}H_8O$ (144)	83.31	5.59	—	83.24	5.49	—
5b	68/0.5	$C_{11}H_{10}O$ (158)	83.51	6.37	—	83.11	6.28	—
5c	65/0.5	$C_{11}H_{10}O$ (158)	83.51	6.37	—	83.80	6.51	—
5d	98/0.5	$C_{12}H_{12}O$ (172)	83.69	7.02	—	83.47	6.98	—
5e	52—53 (MeOH)	$C_{16}H_{12}O$ (220)	87.24	5.49	—	87.16	5.44	—
6a	118—120 (iso-PrOH)	$C_{10}H_8ON_2$ (172)	69.75	4.68	16.27	69.58	4.71	16.07
6c	128—129 (iso-PrOH)	$C_{11}H_{10}ON_2$ (186)	70.95	5.41	15.05	71.14	5.53	14.89
6e	168—170 (AcOEt)	$C_{16}H_{12}ON_2$ (248)	77.40	4.87	11.28	77.68	4.71	11.51
6f	117—119 (MeOH)	$C_{11}H_{10}ON_2$ (202)	65.33	4.98	13.86	65.14	5.08	14.03

Reaction of N-Acetyliminopyridazinium Ylide (2) with Benzyne——To a solution of **2** (1 g) and *n*-butyl nitrite (1.4 g) dissolved in CH_2Cl_2 (30 ml), a solution of anthranilic acid (1.5 g) in acetone (20 ml) was added and worked up according to the general procedure for the N-oxide (**1**).

The resulting residue was chromatographed over alumina, eluting with benzene–CH_2Cl_2 (1: 1), to afford the cycloadduct (**9**) and 3-(2-acetoanilino)pyridazine (**11**), successively. **9**: yield 70—75%, mp 154—155° (from MeOH), IR: 1690 (C=O) cm^{-1}, Mass Spectrum *m/e*: 213 (M^+), NMR (δ); 2.44 (3H, s., $COCH_3$), 5.03 (1H, d, 3–H), 5.90 (1H, dd, 5–H), 6.55 (1H, m, 4–H), 6.90 (1H, m, 6–H), 7.05—8.05 (4H, m, Ar–H), $J_{3,4}$= 6.0, $J_{4,5}$=10.5, $J_{4,6}$=1.2, $J_{5,6}$=3.0 Hz, *Anal.* Calcd. for $C_{12}H_{11}ON_3$: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.71; H, 5.08; N, 19.65. **11**: yield, 8—10%, mp 110—111° (from AcOEt), IR; 3200 (NH), 1680 (C=O) cm^{-1}: Mass Spectrum *m/e*: 213 (M^+), NMR (δ); 2.10 (3H, s, $COCH_3$), 7.72 (1H, dd, 5–H), 7.98 (1H, dd, 4–H), 9.30 (1H, dd, 6–H), 11.75 br, (1H, NH), 7.2—8.7 (4H, m, Ar–H). *Anal.* Calcd. for $C_{12}H_{11}ON_3$: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.78; H, 5.14; N, 19.60.

Thermolysis of the Cycloadduct (9) in Xylene——A solution of **9** (0.2 g) in xylene (10 ml) was refluxed for 2 days and the solvent was evaporated *in vacuo*. The residue was chromatographed over alumina and elution with benzene–CH_2Cl_2 (2: 1) gave 3-vinylindazole (**10**) and 3-(2-acetoanilino)pyridazine (**11**), successively. **10**: yield 20—25%, mp 117—118° (from iso-Pr_2O), Mass Spectrum *m/e*: 144 (M^+), NMR (δ); 5.60 (1H, dd, J=12 and 1.2 Hz), 6.18 (1H, dd, J=17 and 1.2 Hz), 7.33 (1H, dd, J=12 and 17 Hz), 7.0—7.95 (4H,

Table II

Compound	Yield (%)	NMR spectral data δ (in $CDCl_3$) J=Hz
5a	60—65	5.35 (t, 3-H), 5.93 (dd, 4-H), 6.14 (d, 2-H), 6.54 (d, 5-H), 6.73—7.3 (4H, m, Ar-H), $J_{2,3}=J_{3,4}=5.8$, $J_{4,5}=10.4$
5b	25—30	2.19 br (s, 5-Me), 5.38 (t, 3-H), 5.95 br (d, 4-H), 6.23 (d, 2-H), 6.82—7.4 (4H, m, Ar-H), $J_{2,3}=J_{3,4}=5.6$
5c	63—65	1.89 br (s, 2-Me), 5.16 br (d,3-H), 5.79 (dd, 4-H), 6.42 (d, 5-H), 6.26—7.25 (4H, m, Ar-H), $J_{3,4}=5.6$, $J_{4,5}=10.7$
5d	39—40	1.93 br (s, 2-Me), 2.15 br (s, 5-Me), 5.18 br (d, 3-H), 5.85 br (d, 4-H), 6.7—7.4 (4H, m, Ar-H), $J_{3,4}=5.9$
5e	40—43	6.18 (d, 3- or 4-H), 6.19 (d, 3- or 4-H), 6.71 (dd, 4-H), 6.95—7.90 (9H, m, Ar-H)
6a	10—13	7.63 (dd, 5-H), 8.11 (dd, 4-H), 9.06 (dd, 6-H), 6.83—7.78 (4H, m, Ph-H), 13.45 br (OH), $J_{4,5}=9.0$, $J_{4,6}=1.8$, $J_{5,6}=5.0$
6c	18	2.68 (s, 6-Me), 4.42 (d, 4-H), 7.91 (d, 5-H), 6.70—7.75 (4H, m, Ph-H), 13.61 br (OH), $J_{4,5}=8.0$
6e	15—18	8.02 (d, 4- or 5-H), 8.06 (d, 4- or 5-H), 6.7—7.95 (9H, m, Ph-H), $J_{4,5}=2.0$
6f	85	4.09 (s, OMe), 6.99 (d, 4-H), 7.84 (d, 5-H), 6.6—7.55 (4H, m, Ph-H), 13.05 br (OH), $J_{4,5}=8.4$

m), 11.0 br (1H, NH). *Anal.* Calcd. for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.43. Found: C, 74.91; H, 5.48; N, 19.14. This compound (**10**) was also confirmed in comparison with the sample.[16] **11**: yield 55%, mp 110—111° (from AcOEt). This compound was found to be identical with the sample obtained by the reaction of **2** with benzyne above.

Treatment of the Cycloadduct (9) with Sodium Methoxide——To a solution of **9** (0.3 g) dissolved in abs. MeOH (25 ml) was added sodium methoxide powder (0.3 g) and the mixture was stirred for 50 min at 0—5°. The reaction solution was passed through a column of silica gel for removing excess reagent and then evaporated to dryness *in vacuo*. The residue was chromatographed over alumina and elution with benzene–CH_2Cl_2 (3: 1) afforded 3-vinylindazole (**10**) and pyridazine derivative (**11**) in 49% and 16% yields, respectively, which were found to be identical with the samples obtained by photolysis of **9**.

Photolysis of the Cycloadduct (9)——(i) Irradiation with 2537 Å Lamps: A solution of **9** (1 g) in CH_2Cl_2 (200 ml) was irradiated with low-pressure Hg lamps (2537 Å) for 3 hr under nitrogen atmosphere at room temperature and then the solvent was evaporated *in vacuo*. The residue was chromatographed over alumina and elution with benzene–CH_2Cl_2 (1: 1) gave indazolo[2,3-*b*]pyridazine (**12**): yield 80—90%, mp 115—116° (from iso-Pr_2O), UV λ_{max}^{EtOH} nm (ε): 223.5 (39000), 273 (23000), 319 (9000), Mass Spectrum *m/e*: 169 (M^+), NMR (δ): 7.10 (1H, dd, 4-H), 7.28 (1H, dd, 6-H), 7.57 (1H, dd, 7-H), 7.94 (1H, d, 8-H), 8.02 (1H, d, 5-H), 8.37 (1H, dd, 3-H), 8.55 (1H, dd, 2-H), $J_{2,3}=4.6$, $J_{3,4}=8.0$, $J_{2,4}=2.0$, $J_{5,6}=J_{6,7}=J_{7,8}=8.0$. *Anal.* Calcd. for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.84. Found: C, 71.06; H, 4.21; N, 24.67.

(ii) Irradiation with 3600 Å lamps: A solution of **9** (1.2 g) in CH_2Cl_2 (200 ml) was irradiated with medium-pressure Hg lamps (3600 Å) for 10 hr under nitrogen atmosphere at room temperature and then the solvent was evaporated *in vacuo*. The residue was chromatographed over alumina, eluting with benzene–CH_2Cl_2 (3: 1), to give N-acetylindol (**14**, 5%), cyclobutene compound (**13**, 45—50%), indazolo[2,3-*b*]pyridazine (**12**, 45%), and vinylacetylene compound (**15**, 3—4%), successively. **12**: mp 115—116°. This compound was identical with the authentic sample obtained by the photolysis (i), by mixed melting point determination. **13**: mp 94—95° (from *n*-hexane), IR; 1670 (C=O) cm^{-1}, Mass Spectrum *m/e*: 185 (M^+), NMR (δ); 2.22 (3H, s, $COCH_3$), 4.41 (1H, b, 3-H), 5.05 (1H, dd, 2-H), 6.15 (1H, d, 4-H), 6.43 (1H, b, 3-H), 6.8—8.2 (4H, m, Ar-H), $J_{2,3}=4.0$, $J_{3,4}=2.2$, $J_{2,5}=4.0$ Hz. *Anal.* Calcd. for $C_{12}H_{11}ON$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.63; H, 5.88; N, 7.68. **14**: pale yellow oil, IR; 1710 (C=O) cm^{-1}, Mass Spectrorum *m/e*: 159 (M^+), NMR (δ): 2.55 (3H, s, $COCH_3$), 6.69 (1H, d, 3-H), 7.48 (1H, d, 2-H), 7.28—7.75 (3H, m, 5, 6, and 7-H), 8.65 (1H, dd, 4-H), $J_{2,3}=4.4$. *Anal.* Calcd. for $C_{10}H_9ON$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.61; H, 5.77; N, 8.65. This compound (**14**) is known to be rearranged to 3-acetylindole by heating. Therefore, **14** was purified by rechromatography over silica gel and was confirmed in comparison with spectral data of the authentic sample prepared by the reaction of indole with acetyl chloride in the presence of sodium hydride in tetrahydrofuran. **15**: mp 104—105° (from iso-Pr_2O–benzene), IR; 3240, 3280 (NH), 1665 (C=O) cm^{-1}, Mass Spectrum *m/e*: 185 (M^+), NMR (δ); 2.18 (3H, s, $COCH_3$), 3.23 (1H, d, J=2.4 Hz), 5.84 (1H, dd, J= 2.4 and 12.0 Hz), 6.87 (1H, d, J=12.0 Hz), 7.0—7.5 (4H, m). *Anal.* Calcd. for $C_{12}H_{11}ON$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.96; H, 5.90; N, 7.78.

Photocyclization of 1-Benzoxepine (5a)——A solution of **5a** (0.7 g) in CH_2Cl_2 (200 ml) was irradiated with medium-pressure Hg lamps (3600Å) for 10 hr under nitrogen atmosphere at room temperature and then the solvent was evaporated *in vacuo*. The residue was chromatographed over alumina and elution with

benzene gave the cyclic compound (**20**), yield 69—70%, bp 70°/2.5 mmHg (bath temp.), Mass Spectrum *m/e*: 144 (M^+), NMR (δ); 4.28 br (1H, d, J=3.1 Hz), 5.41 (1H, dd, J=3.0 and 3.1 Hz), 6.07 (br 1H, d, J=1.5 Hz), 6.57 (1H, dd, J=3.0 and 1.5 Hz), 6.65—7.30 (4H, m). *Anal.* Calcd. for $C_{10}H_8O$: C, 83.11; H, 5.59. Found: C, 83.02; H, 5.50.

Reaction of Pyridazinium Dicyanomethylide (3) with Benzyne. Formation of the Cycloadduct (21)—— A solution of **3** (1 g) and *n*-butyl nitrite (1.2 g) in CH_2Cl_2 (30 ml) and a solution of anthranilic acid (1.45 g) in acetone (20 ml) were worked up as described for the N-oxide (**1**). After addition of ice-cold MeOH to the resulting residue, the precipitated crystals were collected by filtration and recrystallized from MeOH to give **21**, yield *ca.* 70%, mp 124—125°, IR; 2200 (CN) cm^{-1}, Mass Spectrum *m/e*: 232 (M^+), NMR (δ): 5.17 (1H, t, 5–H), 6.08 (1H, dt, 3–H), 6.39 (1H, dt, 4–H), 7.38 (1H, m, 2–H), 7.45—7.85 (4H, m, Ar–H), $J_{2,3}$=3.0, $J_{2,4}$=1.8, $J_{3,4}$=9.8, $J_{3,5}$=2.2, $J_{4,5}$=2.6 Hz. *Anal.* Calcd. for $C_{13}H_9N_4$: C, 72.40; H, 3.47; N, 24.13. Found: C, 72.66; H, 3.41; N, 24.23.

Formation of 9-Cyano-isoindolino[2,3-*b*]pyridazine (22)——(i) Thermolysis of the Adduct (21) in Xylene: A solution of **21** (0.2 g) in xylene (10 ml) was refluxed for 3 hr and the reaction mixture was evaporated to dryness *in vacuo*. The residue was purified by chromatography over alumina and elution with benzene gave **22**, yield *ca.* 55%, mp 155—156° (from MeOH), IR; 2200 (CN) cm^{-1}, UV λ_{max}^{EtOH} nm (ε); 241 (57,000), 280 (9,000), 351 (15,000), Mass Spectrum *m/e*: 193 (M^+), NMR (δ); 6.96 (1H, dd, 4–H), 8.27 (1H, dd, 3–H), 8.47 (1H, dd, 5–H), 7.1—8.05 (4H, m), $J_{2,3}$=4.8, $J_{2,4}$=1.8, $J_{3,4}$=9.0 Hz. *Anal.* Calcd. for $C_{12}H_7N_3$: C, 74.60; H, 3.65; N, 21.75. Found: C, 74.91; H, 3.55; N, 22.03.

(ii) Treatment of **21** with Sodium Methoxide: To a solution of **21** (0.3 g) dissolved in abs. MeOH (30 ml) was added sodium methoxide (0.3 g) and the mixture was worked up as described for **9**. The resulting residue was chromatographed over alumina to give **22** in 55—60% yield.