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Studies on Diazepines. XIII.¹⁾ Photochemical Behavior of Pyrazine, Pyrimidine, and Pyridazine N-Imides

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Photolyses of various diazine N-ethoxycarbonylimides (3, 9, and 19), prepared from the corresponding diazines (1, 8, and 17), resulted in the formation of the pyrazole derivatives (4 and 10) from pyrazine and pyrimidine N-imides, and of the pyrrole derivatives (20) from pyridazine N-imides. These photolyses may proceed by rearrangement to diaziridine intermediates, followed by ring expansion to the corresponding 1,2,5-, 1,2,4-, or 1,2,3-triazepines (6, 12, or 22), which then undergo isomerization to the triaza[3.2.0]-bicycloheptadienes (7, 13, and 23), followed by elimination to give the products (4, 10, and 20, respectively).

Keywords—pyrazine N-imides; pyrimidine N-imides; pyridazine N-imides; pyrazoles; pyrroles; photolysis; rearrangement; triazepine intermediates

Since pyridine N-acylimides were shown to undergo photo-induced rearrangement to give 1,2-diazepines,³⁾ the photochemical behavior of aromatic amine N-imides has received much attention in connection with the photochemistry of the analogous N-oxides.⁴⁾ Investigations in the pyridine,⁵⁾ quinoline,^{6,7)} and isoquinoline⁶⁾ series have shown that the photolysis of their N-imides involves initial rearrangement to diaziridine intermediates, which then undergo either ring expansion to 1,2-diazepines or N–N bond fission to 2-aminopyridine derivatives. Very recently, we reported an additional pathway; *i.e.*, the formation of 1,3-diazepines from diaziridine intermediates by further rearrangement and ring expansion in the photolysis of isoquinoline and related fused pyridine N-imides.⁸⁾ In view of these results, diazine N-imides were expected to undergo similar photo-induced rearrangement to give the corresponding triazepines. Of the four theoretically possible monocyclic triazepines, 1,2,4-triazepines have been reported.⁹⁾ However, the fully unsaturated 1,2,3-, 1,2,5-, and 1,3,5-isomers are little known.

Therefore we examined the photochemical behavior of pyrazine,¹⁰⁾ pyrimidine, and pyridazine N-imides as part of our studies on diazepines. The results are presented here.

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Pyrazine N-Imides

The pyrazines (**1a—d**) were aminated with O-mesitylenesulfonylhydroxylamine (MSH; H_2NOMes) according to the method of Tamura *et al.*¹¹⁾ to give the corresponding N-amino-pyrazinium mesitylenesulfonates (**2**) in good yields; these were treated with ethyl chloroformate in the presence of potassium carbonate to give the pyrazine N-ethoxycarbonylimides (**3**) in 35–75% yields. Irradiation of the resulting N-imides (**3a—d**) in acetone solution for 2–4 hr gave the pyrazoles (**4**) and the parent pyrazines (**1**) in the yields shown in Chart 1. Besides these products, the formation of hydrogen cyanide (from **3a**), acetonitrile (from **3b** and **3c**), or benzonitrile (from **3d**) was also observed.

Chart 1

Although all attempts to isolate the key intermediates (**6**) and (**7**) failed, we believe that a reasonable mechanism for the formation of the pyrazoles (**4**) involves initial ring expansion to the 1,2,5-triazepines (**6**) *via* the diaziridines (**5**), by analogy with pyridine⁵⁾ and quinoline N-imides.⁷⁾ The triazepines (**6**) may then isomerize to the bicyclic valence isomers (**7**) followed by extrusion of R^3CN to produce the pyrazoles (**4**). 1,2,4-Triazepines are known to undergo similar valence bond isomerization and elimination to give pyrazoles under both thermal and photochemical conditions.^{9,12)} Such reactions are also observed in the photolysis of other heteropines such as diazepines,¹³⁾ oxazepines,¹⁴⁾ and 2,3-benzodiazepines.¹⁵⁾ This photochemical behavior of the pyrazine N-imides is somewhat different from that of the pyrazine N-oxides, which give imidazoles by ring contraction of oxadiazepine intermediates.¹⁶⁾ The 2,5-dimethylpyrazine 1-imide (**3c**) rearranges exclusively to the less hindered α -carbon; this reaction is analogous to that observed for 2-methylpyridine N-imides.¹⁷⁾

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Pyrimidine N-Imides

Several pyrimidine derivatives were aminated with MSH to give the corresponding N-aminopyrimidinium salts, which readily decomposed upon treatment with acylating reagents. However, treatment of 5-methylpyrimidine (**8**) with ethyl azidoformate gave the desired N-imide (**9**) in 18% yield, though the unsubstituted-, 2-methyl-, and 4-methyl- pyrimidines did not give their N-imides. Irradiation of the imide (**9**) gave 1-ethoxycarbonyl-4-methylpyrazole (**10**) and the parent amine (**8**) in 42% and 13% yields, respectively.

Chart 2

This conversion of the imide (**9**) to the pyrazole (**10**) may also involve initial formation of the 1,2,4-triazepine (**12**) *via* the diaziridine intermediate (**11**), followed by isomerization to the bicyclic compound (**13**), from which HCN would then be eliminated to give the product (**10**). Although there is another possible route *via* the different intermediates (**14**), (**15**), and (**16**), this route seems less likely in view of the results of photolysis of 5-methylpyrimidine N-oxides, in which a preference for intermediate oxaziridine formation at C-2 rather than at C-6 is observed.¹⁸⁾ However, no conclusion regarding this regioselectivity can be drawn at this time because the photolysis of 2- and 4-methylpyrimidine N-imides could not be examined, as stated above.

Pyridazine N-Imides

As in the case of pyrazines (**3**), the pyridazine N-ethoxycarbonylimides (**19a–c**) were prepared from the corresponding pyridazines (**17**) by N-amination followed by ethoxycarbonylation. The orientation of the N-imide group of **19c** is analogous to the orientation in the case of 3-methoxypyridazine N-oxide.¹⁹⁾ Irradiation of the imides (**19**) resulted in the formation of the pyrrole derivatives (**20**) and the parent pyridazines (**17**) in the yields shown in Chart 3.

This photolysis may also involve the initial formation of the 1,2,3-triazepines (**22**), which then undergo either isomerization to **23** or ring opening to **24**, followed by loss of nitrogen

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Chart 3

to give the pyrroles (20). Direct formation of 20 from the triazepines (22) by loss of nitrogen is also possible. This photochemical behavior of the pyridazine N-imides is analogous to that observed for pyridazine N-oxides, which give furans and/or pyrazoles *via* 1,2,3-oxadiazepine and diazoketone intermediates.^{20,21)}

Experimental

Melting points were measured on a Yamato MP-2 apparatus and are uncorrected. Infrared (IR) spectra were determined with a JASCO IRA-2 spectrometer and mass (MS) spectra were recorded on a JEOL-D100 instrument. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-MH100 spectrometer in CDCl₃ using tetramethylsilane as an internal standard unless otherwise stated, and spectral assignments were confirmed by spin-decoupling experiments. Microanalyses were performed in the Microanalytical Laboratory of this School by Mrs R. Igarashi. Photolyses were carried out in an immersion apparatus equipped with a 400 W high-pressure Hg lamp and a Pyrex filter, which was cooled internally with running water.

Materials—2,6-Diphenylpyrazine (1d),²²⁾ 3,6-dimethylpyridazine (18b),²³⁾ and 3-methoxypyridazine (18c)²⁴⁾ were prepared by the reported procedures. The other amines are commercially available.

N-Aminopyrazinium Mesitylenesulfonates (2a—d)—General Procedure: The salts were prepared according to the procedure of Tamura *et al.*¹¹⁾ A solution of O-mesitylenesulfonylhydroxylamine (MSH) (1.1 mol equiv.) in CH₂Cl₂ (100—150 ml) was added dropwise to a solution of the pyrazine (1: 0.05—0.1 mol) in CH₂Cl₂ (50—80 ml) with constant stirring in an ice bath. The reaction mixture was stirred at room temperature for an additional 20 min and then ether (300—400 ml) was added to the mixture. The resulting crystalline precipitates were collected by filtration and recrystallized from ethanol or ethanol-ethyl acetate to give the salts (2).

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2a: 85% yield, mp 147.5–149°, colorless prisms. *Anal.* Calcd for $C_{13}H_{17}N_3O_3S$: C, 52.87; H, 5.80; N, 14.23. Found: C, 52.59; H, 5.86; N, 14.44.

2b: 92% yield, mp 163–164.5°, colorless prisms. *Anal.* Calcd for $C_{15}H_{21}N_3O_3S$: C, 55.71; H, 6.55; N, 12.99. Found: C, 55.50; H, 6.56; N, 13.01.

2c: 89% yield, mp 122–123.5°, colorless prisms. *Anal.* Calcd for $C_{15}H_{21}N_3O_3S$: C, 55.71; H, 6.55; N, 12.99. Found: C, 55.61; H, 6.63; N, 12.78.

2d: 95% yield, mp 208–210°, colorless needles. *Anal.* Calcd for $C_{25}H_{25}N_3O_3S$: C, 67.09; H, 5.63; N, 9.39. Found: C, 66.89; H, 5.68; N, 9.22.

Pyrazine N-Ethoxycarbonylimides (3a–d)—General Procedure: Solid potassium carbonate (1.5 mol equiv.) and ethyl chloroformate (1.1 mol equiv.) were added to a solution of the salt (**2**: 0.02–0.03 mol) in ethanol (100 ml) with stirring. The mixture was stirred at room temperature for a further 15–20 hr and the resulting inorganic precipitate was filtered off. The filtrate was concentrated *in vacuo* and the residue was extracted with CH_2Cl_2 . The extract was dried over $MgSO_4$ and evaporated to dryness *in vacuo*. The resulting residue was chromatographed on silica gel, using CH_2Cl_2 –methanol (50:1) as an eluent, to give the imides (**3**).

3a: 65% yield, mp 105–106°, colorless plates (from benzene–isopropyl ether). MS *m/e*: 167 (M^+). IR ν_{max}^{KBr} cm^{-1} : 1650 (C=O). NMR δ : 8.71 (2H, m, 3- and 5-H), 9.20 (2H, m, 2- and 6-H), 1.32 and 4.18 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_7H_9N_3O_2$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.12; H, 5.43; N, 24.87.

3b: 35% yield, mp 91–93°, colorless needles (from isopropyl ether). MS *m/e*: 195 (M^+). IR ν_{max}^{KBr} cm^{-1} : 1640 (C=O). NMR δ : 2.58 (6H, s br, 3- and 5-Me), 8.83 (2H, s br, 2- and 6-H), 1.31 and 4.16 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{13}N_3O_2$: C, 55.37; H, 6.71; N, 21.53. Found: C, 55.27; H, 6.82; N, 21.41.

3c: 30% yield, mp 78–79°, colorless needles (from isopropyl ether). MS *m/e*: 195 (M^+). IR ν_{max}^{KBr} cm^{-1} : 1630 (C=O). NMR δ : 2.58 (6H, s br, 2- and 5-Me), 8.60 (1H, s br, 3-H), 9.42 (1H, s br, 6-H), 1.32 and 4.16 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{13}N_3O_2$: C, 55.37; H, 6.71; N, 21.53. Found: C, 55.17; H, 6.66; N, 21.36.

3d: 35% yield, mp 156–158°, colorless needles (from benzene). MS *m/e*: 319 (M^+). IR ν_{max}^{KBr} cm^{-1} : 1640 (C=O). NMR δ : 7.3–8.1 (10H, m, Ph-H), 9.30 (2H, s, 2- and 6-H), 1.37 and 4.16 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{19}H_{17}N_3O_2$: C, 71.45; H, 5.37; N, 13.16. Found: C, 71.35; H, 5.51; N, 13.03.

Photolysis of the Pyrazine N-Imides (3)—General Procedure: A solution of the imide (**3**: 0.3–0.5 g) in acetone or benzene (200–300 ml) was irradiated for 2–4 hr. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using *n*-hexane– CH_2Cl_2 as an eluent to give the pyrazoles (**4**) and the parent pyrazines (**1**) successively, in the yields shown in Chart 1. The N-ethoxycarbonylpyrazoles (**4a–c**) were identical with authentic samples prepared from the corresponding N-unsubstituted pyrazoles by treatment with ethyl chloroformate according to the reported method.²⁵ The compound (**4d**) was characterized by spectral comparison with **4a–c** and reported analogs.²⁶

4a: oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1760 (C=O). NMR δ : 6.42 (1H, dd, 4-H), 7.76 (1H, d, 3-H), 8.17 (1H, d, 5-H), $J_{3,4}=2$, $J_{4,5}=4$ Hz, 1.38 and 4.46 (3H, t, and 2H, q, CO_2Et).

4b: oil. NMR δ : 2.18 (3H, s br, 4-Me), 7.55 (1H, s br, 3-H), 7.98 (1H, m, 5-H), 1.43 and 4.46 (3H, t, and 2H, q, CO_2Et).

4c: oil. NMR δ : 2.32 (3H, s br, 3-Me), 6.22 (1H, d, 4-H), 8.03 (1H, d, 5-H), 1.43 and 4.48 (3H, t, and 2H, q, CO_2Et), $J_{4,5}=4$ Hz.

4d: mp 139–141°, colorless prisms (from isopropyl ether). MS *m/e*: 216 (M^+). IR ν_{max}^{KBr} cm^{-1} : 1760 (C=O). NMR δ : 7.1–7.5 (5H, m, Ph-H), 7.95 (1H, s br, 3-H), 8.29 (1H, s br, 5-H), 1.42 and 4.43 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.57; H, 5.60; N, 12.78.

5-Methylpyrimidine 1-Ethoxycarbonylimide (9)—A mixture of 5-methylpyrimidine (10 g) and ethyl azidoformate (6 g) was heated at 90° for 60 hr with stirring and then evaporated to dryness *in vacuo*. The resulting solid was recrystallized from benzene to give the imide (**9**): 3.48 g, 18% yield, mp 143–145°, colorless needles. MS *m/e*: 181 (M^+). IR ν_{max}^{KBr} cm^{-1} : 1730 (C=O). NMR δ : 2.46 (3H, s br, 5-Me), 8.47 (1H, m, 4-H), 9.18 (1H, s br, 6-H), 9.34 (1H, s, br, 2-H), 1.32 and 4.16 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_8H_{11}N_3O_2$: C, 53.03; H, 6.12; N, 23.19. Found: C, 52.78; H, 6.15; N, 23.44.

Photolysis of the Imide (9)—A solution of **9** (0.5 g) in benzene (300 ml) was irradiated for 3 hr and then the solvent was removed *in vacuo*. The residue was chromatographed on silica gel using *n*-hexane– CH_2Cl_2 (1:1) as an eluent to give 1-ethoxycarbonyl-4-methylpyrazole (**10=4b**: 260 mg, 42% yield) and the parent pyrimidine (**8**: 60 mg, 13% yield).

N-Aminopyridazinium Mesitylenesulfonates (18a–c)—General Procedure: The pyridazines (**17**:

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10—15 g) were treated with MSH and worked up as described for **1** to give the salts (**18**), which were purified by recrystallization from ethanol–isopropyl ether.

18a: 76% yield, mp 156—157° (lit.²⁷) mp 154—155°).

18b: 93% yield, mp 161—162°, colorless prisms. *Anal.* Calcd for $C_{15}H_{21}N_3O_3S$: C, 55.71; H, 6.55; N, 12.99. Found: C, 55.50; H, 6.60; N, 12.76.

18c: 85% yield, mp 138—140°, colorless prisms. *Anal.* Calcd for $C_{14}H_{19}N_3O_4S$: C, 51.68; H, 5.89; N, 12.91. Found: C, 51.47; H, 5.99; N, 12.68.

Pyridazine N-Ethoxycarbonylimides (19a—c)—Method A: The salt (**18**: 10—20 g) was treated with ethyl chloroformate and worked up as described for **2** to give the imide (**19**). Method B: A mixture of the salt (**18**: 10—20 g) and ethyl chloroformate (150 ml) was heated at 105° with stirring for 5 hr. After removal of the excess reagent *in vacuo*, the resulting residue was dissolved in CH_2Cl_2 (300—500 ml), dried over $MgSO_4$, and then concentrated *in vacuo*. The residue was chromatographed on silica gel using CH_2Cl_2 –methanol as an eluent to give the imide (**19**).

19a: 25% yield (Method B); ca. 5% yield (Method A), yellow oil (picrate: mp 144—145.5°, yellow plates from ethanol). MS *m/e*: 167 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1640 (C=O). NMR δ : 7.63 (1H, dd, 4-H), 8.10 (1H, m, 5-H), 8.95 (1H, m, 3-H), 9.82 (1H, d, 6-H), $J_{3,4}=4$, $J_{4,5}=8$, $J_{5,6}=5$ Hz, 1.35 and 4.26 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{13}H_{12}N_6O_9$ (picrate): C, 39.40; H, 3.05; N, 21.21. Found: C, 39.56; H, 3.01; N, 20.97.

19b: 15% yield (Method A), mp 117—120°, yellow needles (from ethyl acetate). MS *m/e*: 197 (M^+). IR ν_{max}^{KBr} cm^{-1} : 1640 (C=O). NMR δ : 2.65 (3H, s br, 3-Me), 2.70 (3H, s br, 6-Me), 7.51 (1H, d, 4-H), 7.89 (1H, d, 5-H), 1.32 and 4.19 (3H, t, and 2H, q, CO_2Et), $J_{4,5}=8$ Hz. *Anal.* Calcd for $C_9H_{13}N_3O_2$: C, 55.37; H, 6.71; N, 21.53. Found: C, 55.09; H, 6.88; N, 21.36.

19c: 80% yield (Method A), mp 147—149°, yellow needles (from benzene). MS *m/e*: 207 (M^+). IR ν_{max}^{KBr} cm^{-1} : 1640 (C=O). NMR δ : 4.16 (3H, s, OMe), 7.07 (1H, d, 4-H), 7.84 (1H, dd, 5-H), 9.88 (1H, d, 6-H), 1.37 and 4.25 (3H, t, and 2H, q, CO_2Et), $J_{4,5}=8$, $J_{5,6}=5$ Hz. *Anal.* Calcd for $C_8H_{11}N_3O_3$: C, 48.72; H, 5.62; N, 21.31. Found: C, 48.78; H, 5.66; N, 21.21.

Photolysis of the Pyridazine N-Imides (19a—c)—A solution of the imide (**19**: 0.5 g) in benzene (300 ml) was irradiated and worked up as described for **3** to give the pyrrole derivatives (**20**) and the parent pyridazines (**17**) successively, in the yields shown in Chart 3. Irradiation times were as follows: **19a**; 12 hr, **19b**; 22 hr, and **19c**; 1.5 hr. The compound (**20a**) was identical with an authentic sample prepared from pyrrole by the reported procedure²⁸) and **20b** was characterized by spectral comparison with reported data.²⁹)

20a: colorless oil. MS *m/e*: 139 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1740 (C=O). NMR δ : 6.13 (2H, m, 3- and 4-H), 7.15 (2H, m, 2- and 5-H), 1.39 and 4.34 (3H, t, and 2H, q, CO_2Et).

20b: colorless oil. MS *m/e*: 167 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1740 (C=O). NMR δ : 2.13 (6H, s, 2- and 5-Me), 6.60 (2H, s, 3- and 5-H), 1.35 and 4.31 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.51; H, 7.88; N, 8.27.

20c: colorless oil. MS *m/e*: 169 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1740 (C=O). NMR δ : 3.92 (3H, s, OMe), 5.36 (1H, dd, 3-H), 6.07 (1H, dd, 4-H), 6.88 (1H, dd, 5-H), $J_{3,4}=4$, $J_{3,5}=2$, $J_{4,5}=4$ Hz, 1.40 and 4.43 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{11}NO_3$: C, 56.79; H, 6.55; N, 8.28. Found: C, 56.63; H, 6.51; N, 8.21.

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