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(28) No apparent variation in the percentage yield of formate esters was observed in separate experiments in which 1 equiv of water (relative to amine) was added to the NOCl/DMF reaction solution prior to introduction of the amine.
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Azoloquinoxaline *N*-Oxides

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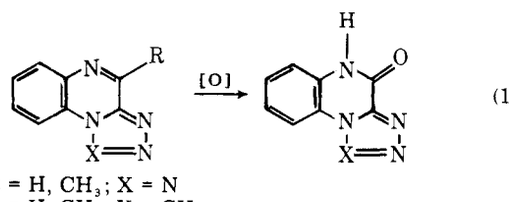
The previously inaccessible *v*-triazolo[1,5-*a*]quinoxaline 5-oxide (**3**), *s*-triazolo[4,3-*c*]quinoxaline 5-oxide (**6**), and tetrazolo[1,5-*a*]quinoxaline 5-oxide (**7**) ring systems have been prepared from *N*-oxide precursors. Previous attempts by others to prepare these compounds by N-oxidation of the appropriate azoloquinoxalines led to C-4 oxidation instead of N-oxidation. This study shows that by introducing the *N*-oxide function at an early stage in the synthetic sequence, the problem of ring carbon oxidation at C-4 is avoided.

Although the chemistry of *s*-triazolo[4,3-*c*]quinoxalines has been extensively studied[1-10] and there is one report[11] concerning the preparation of the *v*-triazolo[1,5-*a*]quinoxaline ring system, the corresponding *N*-oxides in either system have not been prepared. Similarly, tetrazolo[1,5-*a*]quinoxalines are known,[12,13] but the *N*-oxides are not. Attempts by others to prepare these *N*-oxides by oxidation of the known azoloquinoxalines with hydrogen peroxide in acetic acid, alkaline potassium permanganate, or acidic chromic anhydride resulted in oxidation at C-4 instead of N-oxidation (eq 1).[1] We reasoned that these compounds could be prepared from *N*-oxide precursors, thereby avoiding the necessity for N-oxidation at a late stage in the synthesis. Until recently, there were few methods available for the selective synthesis of suitable 3-substituted quinoxaline 1-oxide (**1**) precursors, but it has been demonstrated in these laboratories that certain quinoxaline 1,4-dioxides bearing an electron-withdrawing group in the 2 position can be selectively monodeoxygenated to afford good yields of the desired starting materials.[14] Following this concept, we have developed general procedures for the synthesis of *v*-triazolo[1,5-*a*]quinoxaline 5-oxides (**3**), *s*-triazolo[4,3-*c*]quinoxaline 5-oxides (**6**), and tetrazolo[1,5-*a*]quinoxaline 5-oxides (**7**).



(1)

R = H, CH_3; X = N
R = H, CH_3; X = CH

None of the known methods for preparing *v*-triazolopyridine and *v*-triazoloquinoline derivatives[15-17] proved to be satisfactory for the preparation of the corresponding quinoxaline analogues. Eventually, we succeeded in obtaining *v*-triazolo[1,5-*a*]quinoxaline 5-oxides (**3**) by modifying a procedure for preparing α-pyridyldiazomethane *N*-oxides.[18,19] The requisite 3-substituted quinoxaline 1-oxides (**1**) were available from the corresponding quinoxaline 1,4-dioxides by selective monodeoxygenation.[14] Treatment of **1** with *p*-toluenesulfonylhydrazine in methanol gave the tosylhydrazones

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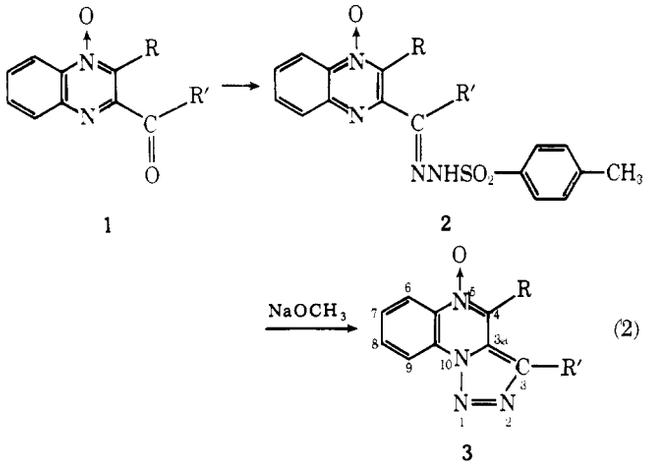
in high yield (eq 2). In most cases, stirring a methanolic solution of **2** with 1 equiv of sodium methoxide led to the formation of the ν-triazolo[1,5-*a*]quinoxalines. However, when R = R′ = CH_3, the sodium salt of the tosylhydrazone was isolated instead. Heating this salt in dimethylformamide at 100 °C led to the corresponding triazole. Conversion of the tosylhydrazones to the triazoles occurred in good yields.

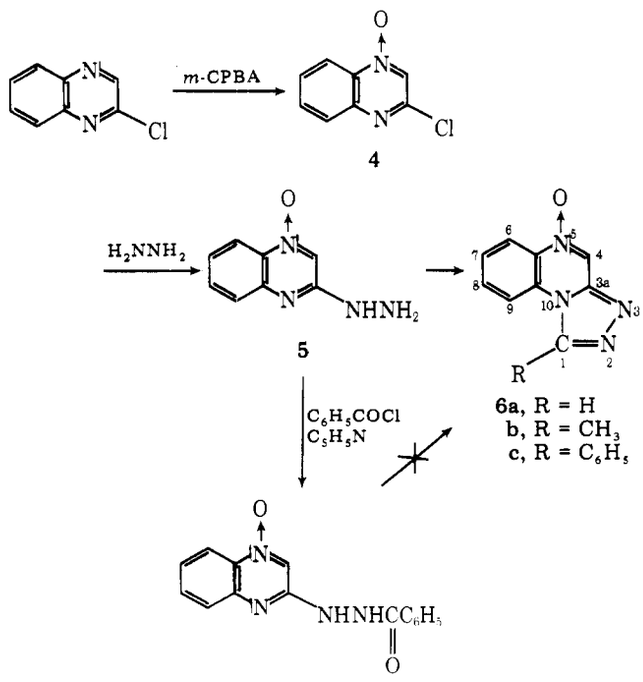


1 2 3 (2)

a, R = R′ = H; b, R = CH_3, R′ = H; c, R = R′ = CH_3

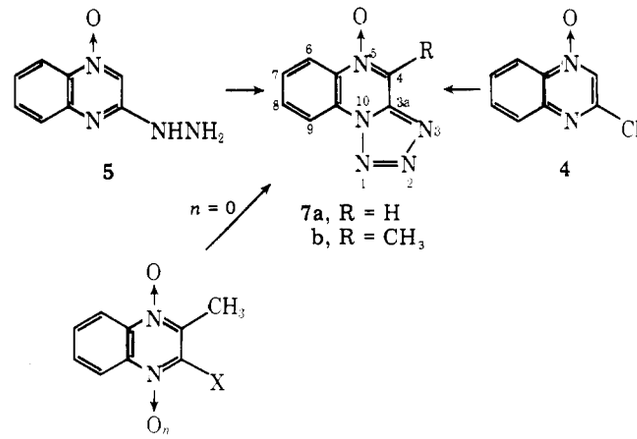
The triazoles were characterized on the basis of their spectral properties and combustion analysis. For example, the NMR spectrum of **3a** (R = R′ = H) exhibits a singlet at δ 9.20 (H-4), a multiplet at δ 8.50 (H-6 and H-9), a singlet at δ 8.37 (triazole H), and a multiplet at δ 8.00 (H-7 and H-8). By comparison, the triazole ring proton in ν-triazolo[1,5-*a*]-quinoline appears as a singlet at δ 8.04.[16] The mass spectrum of **3a** exhibits a molecular ion at *m/e* 186 with principal fragments at *m/e* 170 ($M^+ - O$) and 158 ($M^+ - N_2$). No absorption due to the diazo tautomer (ca. 2000 cm^{-1}) was detected in the infrared spectrum of **3a**. The other compounds of the type **3** exhibit similar spectral properties.

From a consideration of the methods available for the preparation of *s*-triazolo[4,3-*c*]quinoxalines,[2,3] we felt that the corresponding *N*-oxides (**6**) would be accessible through similar chemistry. The requisite 3-hydrazinoquinoxaline 1-oxide (**5**) was prepared in 63% yield by the action of hydrazine hydrate on 3-chloroquinoxaline 1-oxide (**4**).[20] Heating **5** in refluxing triethyl orthoformate gave **6a** in 61% yield, while heating **5** in acetic acid gave **6b** in 30% yield. Attempts to prepare **6c** from **5** and benzoyl chloride in refluxing pyridine led only to benzoylation of the hydrazino moiety, and the resulting hydrazide resisted cyclization.



4 5 6a, R = H; b, R = CH_3; c, R = C_6H_5

We have used intermediate **5** to also prepare tetraazolo[1,5-*a*]quinoxaline 5-oxide (**7a**), in 60% yield, by diazotization in aqueous acetic acid. Alternatively, displacement of **4** by sodium azide in Me_2SO gave **7a** in 46% yield. None of the azide tautomer could be detected in the product by infrared spectroscopy. The mass spectrum of **7a** exhibits a molecular ion at *m/e* 187 with loss of nitrogen and hydrogen cyanide to give a principal fragment at *m/e* 132. In the NMR spectrum of **7a**, H-4 appears as a singlet at δ 9.50. This chemical shift compares favorably with that assigned to H-4 for the triazole **3a**.



5 4 7a, R = H; b, R = CH_3

8a, X = SO_2CH_3; *n* = 1
b, X = N_3; *n* = 1
c, X = N_3; *n* = 0
d, X = SO_2CH_3; *n* = 0

An alternate route was used for the preparation of the 4-methyl analogue **7b**. Since 3-chloro-2-substituted quinoxaline 1-oxides (**4**) were unknown at the time of this study[24] and could not be conveniently prepared from the corresponding 1,4-dioxides, we explored the use of methylsulfonylmethylquinoxaline 1,4-dioxides (e.g., **8a**), which were readily available.[25] In a related study[26] we found that 2-methyl-3-methylsulfonylquinoxaline 1,4-dioxide (**8a**) afforded 2-azido-3-methylquinoxaline 1,4-dioxide (**8b**) in high yield. We expected the corresponding mono *N*-oxide **8c**, in which N-4 is not oxidized, to exist predominantly as the tetrazole tautomer **7b**, but the thermal instability of **8b** precluded its deoxygenation. However, **8a** was selectively deoxygenated[14] with trimethyl phosphite in refluxing 1-propanol to give **8d** in 73% yield, and reaction of **8d** with sodium azide in Me_2SO gave **7b** in 89% yield.

In summary, we have shown that the previously unaccessible ν-triazolo[1,5-*a*]-, *s*-triazolo[4,3-*c*]-, and tetrazolo[1,5-*a*]quinoxaline 5-oxides can be prepared in good yield. By introducing the *N*-oxide function at an early stage in the synthetic sequence, the problem of ring carbon oxidation at C-4 is avoided.

Experimental Section

General. Melting points (uncorrected) were taken with a Thomas-Hoover capillary apparatus. NMR spectra were recorded on Varian A-60 and T-60 spectrometers with Me_4Si as an internal standard. IR spectra were determined with a Perkin-Elmer Model 21 spectrophotometer; UV spectra were recorded on a Cary Model 14 spectrophotometer; and mass spectra were obtained with a Perkin-Elmer RMU-6E mass spectrometer. Microanalyses were performed by the Pfizer Analytical Department. All evaporations were conducted in vacuo using either a water aspirator or a vacuum pump.

2-Methylquinoxaline-3-carboxaldehyde 1-Oxide (1b). 2-Hydroxymethyl-3-methylquinoxaline 1,4-dioxide[27] (4.29 g, 20.8 mmol) was added cautiously in several portions with stirring to concentrated sulfuric acid (10 mL) at room temperature (the addition is exothermic). The dark reaction mixture was stirred at room temperature for 3 h, and then it was heated to 70 °C for 30 min. After the reaction mixture had cooled to room temperature, it was poured onto crushed ice. Insoluble material was removed by filtration and the filtrate extracted with several portions of chloroform. The combined chloroform layers were dried ($MgSO_4$) and evaporated to give a residue which was purified by column chromatography on silica gel. Elution of the column with benzene gave 200 mg of an unidentified solid. Further elution with chloroform gave 1.40 g (36%) of **1b** after recrystallization from acetone: mp 167–169 °C; NMR ($CDCl_3$) δ 3.00 (3, s, CH_3), 7.90 (2, m, H-6, H-7), 8.30 (1, m, H-8), 8.65 (1, m, H-5), 10.2 (1, s, CHO); IR (KBr) 2740, 1725 cm^{-1}; mass spectrum, *m/e* 188 (M^+). Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.25; N, 14.89. Found: C, 63.57; H, 4.45; N, 14.63.

Quinoxaline-3-carboxaldehyde 1-Oxide *p*-Toluenesulfonylhydrazone (2a). A solution of quinoxaline-3-carboxaldehyde 1-oxide[14] (0.95 g, 5.4 mmol) and *p*-toluenesulfonylhydrazine (2.10 g, 11.2 mmol) in methanol (100 mL) was heated on a steam bath for 30 min and cooled, and the precipitate was filtered and washed with ether to give 1.82 g (98%) of **2a:** mp 160 °C dec; NMR (CF_3COOH) δ 2.43 (3, s, CH_3), 7.57 (4, q, aromatic H's), 8.10 (3, m, H-5, H-6, H-7), 8.13 (1, s, CH), 8.57 (1, m, H-8), 9.06 (1, s, H-2); mass spectrum, *m/e* 342 (M^+). Anal. Calcd for $C_{16}H_{14}N_4O_3S$: C, 56.13; H, 4.12; N, 16.36. Found: C, 55.84; H, 4.35; N, 15.94.

2-Methylquinoxaline-3-carboxaldehyde 1-Oxide *p*-Toluenesulfonylhydrazone (2b). A solution of 2-methylquinoxaline-3-carboxaldehyde 1-oxide (0.64 g, 3.38 mmol) and *p*-toluenesulfonylhydrazine (0.66 g, 3.38 mmol) in absolute methanol (50 mL) was warmed on a steam bath for 1 h and cooled, and the precipitate was filtered to give 0.94 g (78%) of **2b:** mp 142–143 °C dec; NMR (CF_3COOH) δ 2.02 (3, s, CH_3), 2.37 (3, s, CH_3), 7.27 (4, q, aromatic H's), 7.50–8.00 (3, m, H-5, H-6, H-7), 8.00 (1, s, CH), 8.25 (1, m, H-8); IR (KBr) 1333, 1163 cm^{-1}; mass spectrum, *m/e* 356 (M^+). Anal. Calcd for $C_{17}H_{16}N_4O_3S$: C, 57.29; H, 4.52; N, 15.72. Found: C, 57.48; H, 4.62; N, 15.92.

3-Acetyl-2-methylquinoxaline 1-Oxide *p*-Toluenesulfonylhydrazone (2c). A solution of 3-acetyl-2-methylquinoxaline 1-oxide[14] (1.70 g, 8.4 mmol) and *p*-toluenesulfonylhydrazine (1.55 g, 8.4 mmol) in methanol (25 mL) was heated under reflux for 1 h and then cooled, and the precipitate was filtered to give 2.53 g (80%) of **2c:** mp 190–193 °C dec; NMR (Me_2SO-d_6) δ 2.37 (3, s, CH_3), 2.40 (3, s, CH_3), 2.70 (3, s, $COCH_3$), 7.60 (4, q, aromatic H's), 7.80 (3, m, H-5, H-6, H-7), 8.40 (2, m, H-8, HN); IR (KBr) 2985, 1333, 1162, 917, 772 cm^{-1}; mass spectrum, *m/e* 370 (M^+). Anal. Calcd for $C_{18}H_{18}N_4O_3S$: C, 58.31; H, 4.86; N, 15.12. Found: C, 58.00; H, 4.80; N, 15.10.

***v*-Triazolo[1,5-*a*]quinoxaline 5-Oxide (3a).** To a stirred solution of sodium methoxide (180 mg, 3.36 mmol) in methanol (50 mL) at room temperature was added portionwise quinoxaline-3-carboxaldehyde 1-oxide *p*-toluenesulfonylhydrazone (1.15 g, 3.36 mmol). During the addition the solution took on a deep red color. After stirring for 1 h, the precipitate which formed was collected by filtration and recrystallized from methanol to give 425 mg (70%) of **3a:** mp 202–204 °C dec; NMR (Me_2SO-d_6) δ 8.00 (2, m, H-7, H-8), 8.37 (1, s, H-3), 8.50 (2, m, H-6, H-9), 9.20 (1, s, H-4); mass spectrum, *m/e* 186 (M^+). Anal. Calcd for $C_9H_6N_4O$: C, 58.06; H, 3.25; N, 30.09. Found: C, 57.75; H, 3.28; N, 30.25.

4-Methyl-*v*-triazolo[1,5-*a*]quinoxaline 5-Oxide (3b). A stirred suspension of 2-methylquinoxaline-3-carboxaldehyde 1-oxide *p*-toluenesulfonylhydrazone (773 mg, 2.17 mmol) in methanol (25 mL) was treated portionwise with a solution of sodium methoxide (117 mg, 2.17 mmol) in methanol (5 mL). After stirring at room temperature for 2 h, the precipitate was collected by filtration and recrystallized from ethyl acetate to give 225 mg (52%) of **3b:** mp 219–220 °C dec; NMR (Me_2SO-d_6) δ 2.83 (3, s, CH_3), 7.80 (2, m, H-7, H-8), 8.45 (1, s, H-3), 8.60 (2, m, H-6, H-9); IR (KBr) 1740, 1280, 1110 cm^{-1}; mass spectrum, *m/e* 200 (M^+). Anal. Calcd for $C_{10}H_8N_4O$: C, 59.99; H, 4.03; N, 27.99. Found: C, 59.36; H, 3.99; N, 27.95.

3,4-Dimethyl-*v*-triazolo[1,5-*a*]quinoxaline 5-Oxide (3c). A stirred suspension of 3-acetyl-2-methylquinoxaline 1-oxide *p*-toluenesulfonylhydrazone (2.50 g, 6.75 mmol) in methanol (30 mL) was treated dropwise with a solution of sodium methoxide (356 mg, 6.75 mmol) in methanol (5 mL) at room temperature. After the mixture was stirred for 1 h with no precipitate formation, the solvent was evaporated in vacuo to give a yellow solid which was heated in dry dimethylformamide (80 mL) at 100 °C for 1 hr. The colorless solution then was poured into water (200 mL) and extracted with two 100-mL portions of ethyl acetate. Evaporation of the dried ($MgSO_4$) ethyl acetate solution gave 670 mg (53%) of **3c:** mp 199–202 °C dec (recrystallization from methanol); NMR ($CDCl_3$) δ 2.83 (3, s, CH_3), 2.92 (3, s, CH_3), 7.78 (2, m, H-7, H-8), 8.55 (2, m, H-6, H-9); mass spectrum, *m/e* 214 (M^+). Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.70; N, 26.16. Found: C, 61.42; H, 4.67; N, 26.43.

3-Chloroquinoxaline 1-Oxide (4). 2-Chloroquinoxaline (98.8 g, 0.60 mmol) was suspended in methylene chloride (1 L) that was cooled with an icebath, and 85% *m*-chloroperbenzoic acid (122 g, 0.60 mmol) was added to the suspension in ca. 10-g portions over a period of 40 min. After the reaction mixture was stirred at room temperature for 72 h, the resulting precipitate was collected by filtration and washed with methylene chloride. The mother liquor and the methylene chloride washings were combined and washed with a solution of 5% sodium bicarbonate. The organic layer was then dried over anhydrous magnesium sulfate and evaporated to afford a solid product. The crude product was recrystallized from methanol to give 6.89 g (63%) of **4** as colorless needles: mp 150–152 °C (lit.[21] mp 150–152 °C); NMR ($CDCl_3$) δ 6.65–7.35 (3, m, H-5, H-6, H-7), 7.55 (1, s, H-2), 7.55–7.80 (1, m, H-8); UV λ_{max} (MeOH) 243 nm (ϵ 40 900), 320 (8510); mass spectrum, *m/e* 182 ($M^+ + 2$), 180 (M^+). Anal. Calcd for $C_8H_5N_2OCl$: C, 53.20; H, 2.79; N, 15.51. Found: C, 53.10; H, 2.80; N, 15.09.

3-Hydrazinoquinoxaline 1-Oxide (5). To a suspension of 3-chloroquinoxaline 1-oxide (1.50 g, 8.3 mmol) in ethanol (15 mL) was added hydrazine hydrate (80%, 1.5 mL), and the mixture was heated under reflux for 40 min. The solid that separated on cooling the mixture was recrystallized from water to give 0.92 g (63%) of **5** as bright yellow crystals: mp 199–200 °C dec; mass spectrum, *m/e* 176 (M^+). Anal. Calcd for $C_8H_8N_4O$: C, 54.60; H, 4.58; N, 31.83. Found: C, 54.57; H, 4.59; N, 31.81.

***s*-Triazolo[4,3-*a*]quinoxaline 5-Oxide (6a).** 3-Hydrazinoquinoxaline 1-oxide (0.60 g, 3.4 mmol) was added to triethyl orthoformate (7 mL) and the mixture heated under reflux for 3 h. Upon cooling the resulting solution, almost pure product separated. This was washed with cold methanol and then recrystallized from methanol to yield 0.39 g (61%) of **6a** as pink needles: mp 272–273 °C dec; NMR (Me_2SO-d_6) δ 7.59 (2, m, H-7, H-8), 8.21 (2, m, H-6, H-9), 8.93 (s, 1, H-1), 9.70 (1, s, H-4); UV λ_{max} (MeOH) 228 nm (shoulder), 263 (ϵ 7400), 322 (10 900); mass spectrum, *m/e* 186. Anal. Calcd for $C_9H_6N_4O$: C, 58.12; H, 3.25; N, 30.12. Found: C, 58.31; H, 3.43; N, 29.56.

1-Methyl-*s*-triazolo[4,3-*a*]quinoxaline 5-Oxide (6b). A mixture of 3-hydrazinoquinoxaline 1-oxide (**5**) (4.00 g, 22.7 mmol) and glacial acetic acid (30 mL) was heated under reflux for 2 h and cooled, and the solvent was removed in vacuo. The brick-red residue was dissolved in 250 mL of boiling water, the resulting solution was treated with activated carbon and filtered through a pad of Super Cel, and the filtrate was kept in the refrigerator overnight to give 1.35 g (30%) of **6b:** mp 238–242 °C dec (recrystallization from methanol); NMR (Me_2SO-d_6) δ 2.63 (3, s, CH_3), 7.56 (2, m, H-7, H-8), 8.10 (2, m, H-6, H-9), 8.83 (1, s, H-4); mass spectrum, *m/e* 200 (M^+). Anal. Calcd for $C_{10}H_8N_4O$: C, 59.99; H, 4.03; N, 27.99. Found: C, 59.88; H, 3.95; N, 28.42.

Tetrazolo[1,5-*a*]quinoxaline 5-Oxide (7a). A. To an ice-cooled solution of 3-hydrazinoquinoxaline 1-oxide (1.00 g, 5.7 mmol) in acetic acid (12%, 35 mL) was added dropwise a solution of $NaNO_2$ (0.44 g, 6.4 mmol) in water (4 mL), and the mixture was kept at room temperature for 3 h. The resulting tan precipitate was collected by filtration and washed with methanol to afford 0.60 g (60%) of **7a:** mp 179–180 °C dec; NMR (Me_2SO-d_6) δ 7.70–8.25 (2, m, H-7, H-8), 8.40–8.70 (2, m, H-6, H-9), 9.50 (1, s, H-4); IR (KBr), no absorption in the $-N_3$ region (ca. 2150 cm^{-1}) was detected; UV λ_{max} (MeOH) 230 nm (ϵ 19 850), 262 (shoulder), 317 (9350); mass spectrum, *m/e* 187 (M^+). An analytical sample of **7a** was obtained by recrystallization from methanol, mp 189–190 °C dec. Anal. Calcd for $C_8H_5N_5O$: C, 51.38; H, 2.70; N, 37.43. Found: C, 51.00; H, 2.91; N, 37.04.

B. To a solution of 3-chloroquinoxaline 1-oxide (1.00 g, 5.5 mmol) in Me_2SO (15 mL) was added sodium azide (0.36 g, 5.5 mmol). After stirring the solution for 72 h at room temperature, it was diluted with water (100 mL) and a precipitate formed that was collected by filtration to afford 0.47 g (46%) of **7a,** mp 178–180 °C dec. Similar results were found when the above reaction was heated under reflux overnight in ethanol–water (1:1 v/v), and crude product **7a** was obtained in 52% yield.

2-Methyl-3-methylsulfonylquinoxaline 1-Oxide (8d). 2-Methyl-3-methylsulfonylquinoxaline 1,4-dioxide[25] (7.60 g, 30 mmol) was added to 1-propanol (75 mL) containing trimethyl phosphite (4.09 g, 33 mmol). The reaction mixture was heated under reflux for 3 h and then cooled to room temperature to afford a crystalline precipitate. The solid was collected by suction filtration and washed with 1-pro-

panol to give 5.24 g (73%) of **8d**: mp 185–187 °C dec; NMR (Me_2SO-d_6) δ 2.80 (3, s, CH_3), 3.65 (3, s, CH_3SO_2), 7.90–8.20 (3, m, H-5, H-6, H-7), 8.30–8.60 (1, m, H-8); UV λ_{max} (MeOH) 274 nm (ε 39 590), 330 (8120); mass spectrum, *m/e* 238 (M^+). Anal. Calcd for $C_{10}H_{10}N_2O_3S$: C, 50.47; H, 4.24; N, 11.77. Found: C, 50.51; H, 4.24; N, 11.57.

4-Methyltetrazolo[1,5-*a*]quinoxaline 5-Oxide (7b). To a solution of 2-methyl-3-methylsulfonylquinoxaline 1-oxide (4.00 g, 16.8 mmol) in Me_2SO (90 mL) was added sodium azide (1.10 g, 16.8 mmol). After the solution was stirred overnight at room temperature, it was diluted with water (300 mL) and a precipitate formed that was collected by suction filtration to afford 3.02 g (89%) of **7b**: mp 205–206 °C; NMR (Me_2SO-d_6) δ 2.80 (3, s, CH_3), 7.80–8.25 (2, m, H-7, H-8), 8.40–8.70 (2, m, H-6, H-9); UV λ_{max} (MeOH) 232 nm (ε 22 200), 262 (shoulder), 317 (11 000); mass spectrum, *m/e* 201 (M^+). Anal. Calcd for $C_9H_7N_5O$: C, 53.78; H, 3.51; N, 34.84. Found: C, 53.66; H, 3.62; N, 34.62.

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Registry No.—**1a**, 61522-60-9; **1b**, 67452-55-5; **1c**, 61522-56-3; **2a**, 67452-56-6; **2b**, 67452-57-7; **2c**, 67452-58-8; **3a**, 67452-59-9; **3b**, 67452-60-2; **3c**, 67452-61-3; **4**, 5227-59-8; **5**, 67452-62-4; **6a**, 67452-63-5; **6b**, 67452-64-6; **7a**, 61148-19-4; **7b**, 67452-65-7; **8a**, 39576-77-7; **8d**, 67464-71-5; 2-hydroxymethyl-3-methylquinoxaline 1,4-dioxide, 16915-79-0; *p*-toluenesulfonylhydrazine, 1576-35-8; 2-chloroquinoxaline, 1448-87-9.

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1,2-Diphenyl-3-azanaphtho[*b*]cyclobutadiene

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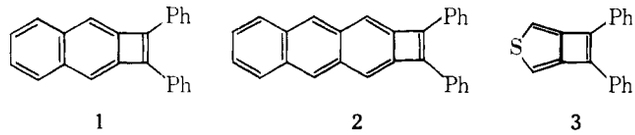
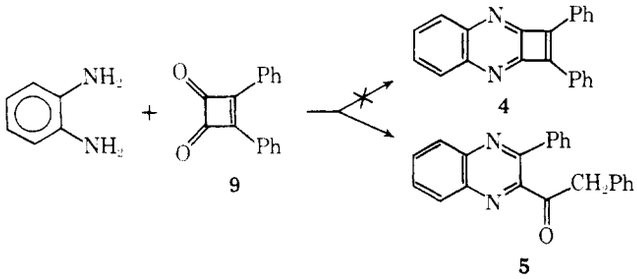
1,2-Diphenyl-3-azanaphtho[*b*]cyclobutadiene (**12**) has been synthesized. The cyclopentadienone derivative **13** and its iron tricarbonyl complex **14** were also formed during the final reduction step. The title compound, obtained as red crystals, undergoes addition reactions (reduction, oxidation) at the 1,2-double bond; it also undergoes a Diels–Alder reaction with 1,3-diphenylisobenzofuran and on heating with triiron dodecacarbonyl it is converted to a mixture of **13** and **14**. The iron tricarbonyl complex **14** is easily oxidized with Ce^{4+} to give **13**.

The synthesis of the first stable aromatic-fused cyclobutadiene, namely 1,2-diphenylnaphtho[*b*]cyclobutadiene (**1**), was reported by Cava[1] in 1963. Since then, 1,2-diphenylanthra[*b*]cyclobutadiene (**2**),[2] 6,7-diphenyl-3-thiabicyclo[3.2.0]heptatriene (**3**),[3] and a few other aromatic-fused cyclobutadienes[4,5] have been synthesized. Compound **3** represents the first known heteroaromatic-fused cyclobutadiene.



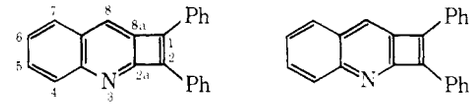
1 **2** **3**



9 **4** **5**

In 1961, Blomquist and Lalancette[6] attempted the synthesis of the diaza analogue **4** of the hydrocarbon **1** by condensation of the dione **9** with *o*-phenylenediamine; they isolated the ring cleavage product **5** rather than the desired cyclobutadiene derivative **4**.

In this paper we report the synthesis and some chemical properties of 1,2-diphenyl-3-azanaphtho[*b*]cyclobutadiene



12a **12b**

(**12**), the first example of a heteroaromatic-fused cyclobutadiene with nitrogen as the heteroatom.

Results and Discussion

o-Nitrobenzyl bromide (**6**) was converted to *o*-nitrobenzyltriphenylphosphonium bromide (**7**) in excellent yield. Wittig condensation of dione **9** with the ylide **8**, derived from the phosphonium salt **7**, afforded a mixture of *cis*- and *trans*-nitroaryls **10a** and **10b** in 85% yield. These isomers, found in the ratio of 87:13, respectively, were separated by

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