# Aziridines. XXI. The 1,4-Diazabicyclo[4.1.0]hept-4-enes and 1,1a-Dihydro-1,2-diarylazirino[1,2-*a*]quinoxalines

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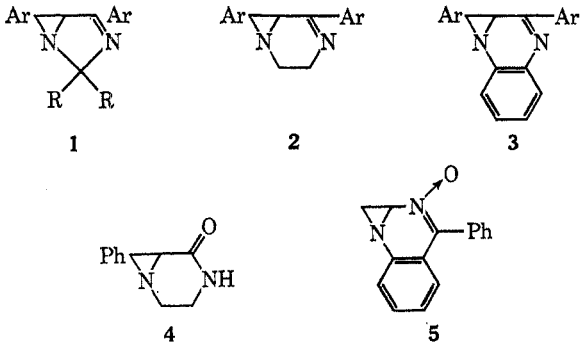
The syntheses and reactions of the 1,4-diaza[4.1.0]hept-4-enes (**2**) and the 1,1a-dihydro-1,2-diarylazirino-[1,2-*a*]quinoxalines (**3**) are described. These compounds are prepared by the reaction of 1-phenyl-2,3-dibromo-3-aryl-1-propanones with ethylenediamine and *o*-phenylenediamine, respectively. Compounds **3** undergo carbon–carbon bond fission of the aziridine ring in refluxing toluene and form adducts with diethyl azodicarboxylate, dimethylacetylene dicarboxylate, dibenzoylacetylene, aromatic aldehydes and acenaphthylene. Compounds such as **3** also react with nitrosobenzene to form nitrones and 2-phenylquinoxaline and pyrolyze to stilbenes and 2-phenylquinoxaline. Compounds **3** isomerize in the presence of acid to 2-benzyl-3-arylquinoxalines. Compounds **2** are converted in concentrated sulfuric acid into benzyl phenyl diketones.

Recently the syntheses and reactions of the 1,3-diazabicyclo[3.1.0]hex-3-enes (**1**) were described.[1,2] We have now extended our investigations to the 1,4-diazabicyclo[4.1.0]hept-4-enes (**2**) and the 1,1a-dihydro-1,2-diarylazirino[1,2-*a*]quinoxalines (**3**). The only other compounds similar to **2** and **3** recorded in the literature are 5-keto-7-phenyl-1,4-diazabicyclo[4.1.0]-heptane (**4**)[3,4] and 7-chloro-1,3-dihydro-5-phenyl-2H-azirino[1,2-*a*]quinazoline 4-oxide (**5**),[5] respectively (Chart I).

CHART I

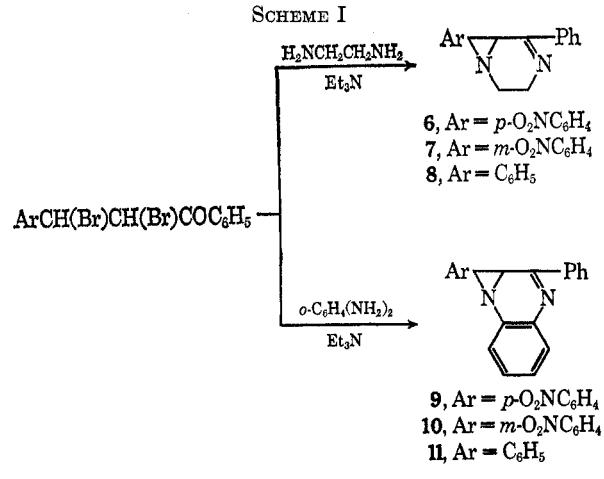



## Results

The syntheses of compounds **6**, **7**, and **8** were achieved by treating 1-phenyl-2,3-dibromo-3-aryl-1-propanones with ethylenediamine in 95% ethanol containing triethylamine (Scheme I). Replacing ethylenediamine with *o*-phenylenediamine gave rise to compounds **9**, **10**, and **11**. In one instance **9** was prepared by reacting *o*-phenylenediamine with α-bromo-4-nitrochalcone. Compound **4** had been synthesized in much the same manner by reaction of ethylenediamine and ethyl α-bromocinnamate.[3,4] Compounds **6–11** were characterized by analyses, nmr spectra and by their chemical reactions.

The nmr spectra of compounds **9–11** in $CDCl_3$ showed two doublets centered at approximately δ 3.0 (1 H) and 3.5 (1 H) and a complex multiplet of aromatic protons from 7.0 to 8.3, all downfield from tetramethylsilane. For compounds **6–8** the peaks of the two methylene groups overlap somewhat with the methine protons of the aziridine ring although two doublets can be discerned at about δ 3.0 (1 H) and 3.6 (1 H). The aromatic region is a complex absorption pattern extending from δ 7.2 to 8.3 (with the appropriate number of protons).

SCHEME I




Compound **9** was observed to undergo reactions in which carbon–nitrogen bond fission and carbon–carbon bond fission of the aziridine ring occurred. In aqueous acetone containing hydrochloric acid **9** isomerized into the known quinoxaline **12** (Scheme II). Heating of **9** under reduced pressure leads to *trans-p,p'*-dinitrostilbene and 2-phenylquinoxaline. Compound **11** behaved analogously when heated under reduced pressures. Nitrosobenzene and **9** in refluxing toluene formed α-*p*-nitrophenyl-N-phenylnitrone (**13**) and 2-phenylquinoxaline. The adduct **14** was obtained by heating **9** with diethyl azodicarboxylate. Compound **14** was characterized by elemental analyses and its conversion into the known 1-*p*-nitrophenyl-4-phenyl-*s*-[triazolo][4,3-*a*]quinoxaline (**15**). Reaction of **9** with dimethylacetylene dicarboxylate in refluxing toluene gave dimethyl 1-*p*-nitrophenyl-4-phenylpyrrolo[1,2-*a*]-quinoxaline-2,3-dicarboxylate (**16**). Saponification of **16** followed by decarboxylation with quinoline formed 1-*p*-nitrophenyl-4-phenylpyrrolo[1,2-*a*]quinoxaline (**17**). An analogous reaction of **9** with dibenzoylacetylene in refluxing toluene produced **18**. Heating of **9** with benzaldehyde or *p*-nitrobenzaldehyde in toluene gave the oxazolo[3,2-*a*]quinoxaline derivatives **20**. Acenaphthylene and **9** in refluxing toluene formed

(1) H. W. Heine, R. H. Weese, R. A. Cooper, and A. J. Durbetaki, *J. Org. Chem.*, **32**, 2708 (1967).

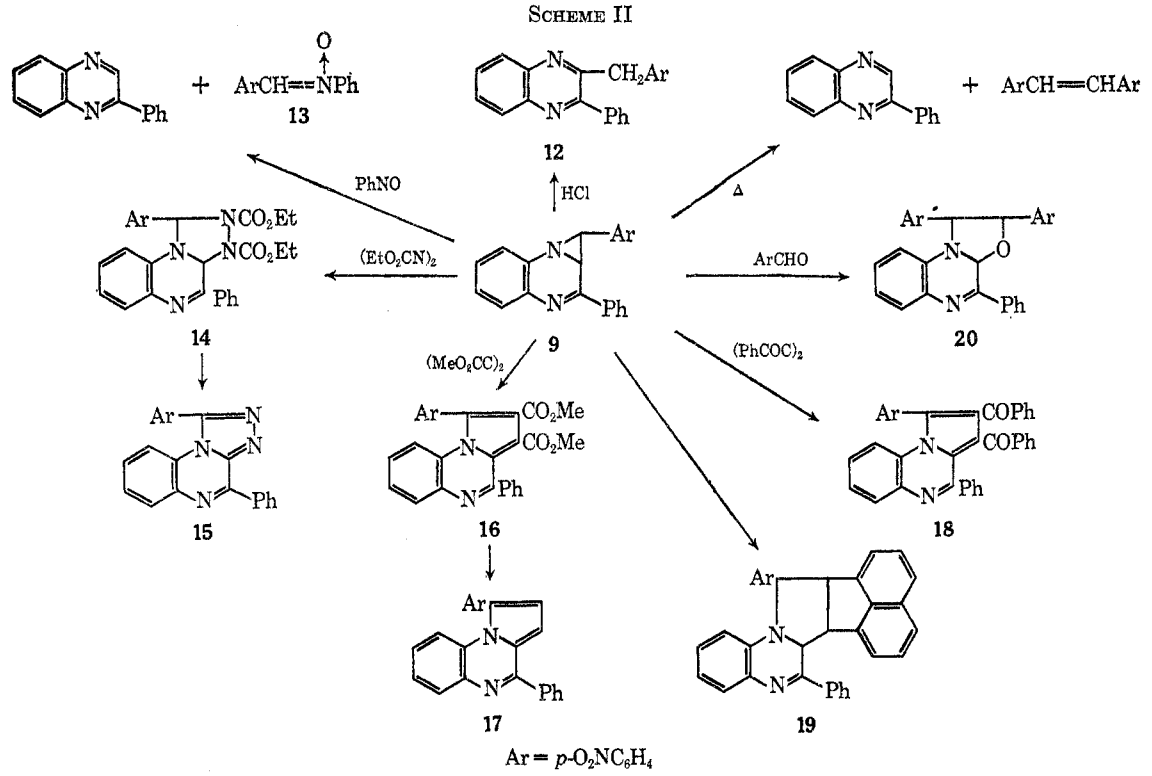
(2) H. W. Heine, A. B. Smith, and D. Bower, *ibid.*, **33**, 1097 (1968).

(3) H. Moureu, P. Chovin, and L. Petit, *C. R. Acad. Sci., Paris*, **243**, 910 (1956).

(4) H. Moureu, P. Chovin, and L. Petit, *Bull. Soc. Chim. Fr.*, 1785 (1956).

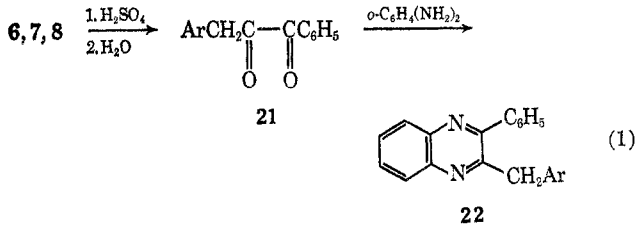
(5) G. F. Field, W. J. Zally, and L. H. Sternbach, *J. Amer. Chem. Soc.*, **89**, 332 (1967).

SCHEME II




6a,6b,12b,13-tetrahydro-13-*p*-nitrophenyl-6-phenylacenaphtho[1′,2′:3,4]pyrrolo[1,2-*a*]quinoxaline (**19**). All these reactions are summarized in Scheme II.

Dissolution of compound **6** in concentrated sulfuric acid followed by pouring the reaction mixture on ice gave the known α diketone **21**. Compounds **7** and **8** also formed the corresponding α diketones. The structure of all of the α diketones isolated were confirmed by converting them into the known quinoxalines (**22**) (eq 1). Significantly, 2-*p*-nitrophenyl-3-benzoylaziridine (**23**) in sulfuric acid also forms **21**.

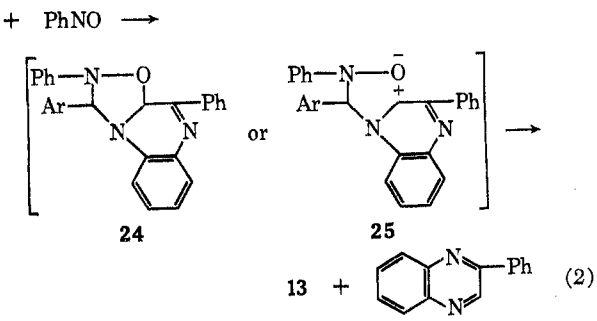



(1)

## Discussion

The reactions of **9** to form **13**, **14**, **16**, **18**, **19**, and **20** as well as the pyrolysis of **9** to form *p*,*p*′-dinitrostilbene and 2-phenylquinoxaline can be envisaged as occurring by an initial cleavage of the carbon–carbon bond of the aziridine ring to form a 1,3-dipole intermediate. The 1,3-dipolar species subsequently undergoes (in most cases) a cycloaddition to an unsaturated substrate to give the depicted polycyclic systems. The related 1,3-diazabicyclo[3.1.0]hex-3-enes (**1**) have also been shown to undergo 1,3 cycloadditions to various alkenes and alkynes.[2] Other aziridines that behave similarly are 1,2,3-triarylaziridines,[6] 2-aroylaziridines,[7] 2,3-diaroylaziridines,[8] and 2,3-dicarbethoxyaziridines.

The formation of the nitrone **13** and 2-phenylquinoxaline from the reaction of **9** with nitrosobenzene may result from a 1,3 elimination of an intermediate cyclic adduct such as **24**. However, there is no evidence to preclude the possibility that the nitrone **13** is derived from dipolar intermediate **25** (eq 2). Huisgen and co-




(2)

workers[10] also obtained a nitrone by treating the nitrile ylide $C_6H_5C{\equiv}N^+C^-HC_6H_4NO_2$-*p* with nitrosobenzene.

Another dipolar species **26** somewhat similar to **25** may be responsible for the formation of *p*,*p*′-dinitrostilbene and 2-phenylquinoxaline when **9** is pyrolyzed (eq 3). A related reaction, the cyclodimerization of 1-*p*-methoxyphenyl-2,3-dicarbomethoxyaziridine to 1,4-di(*p*-methoxyphenyl)-2,3,5,6-tetracarbomethoxypiperazine, has been reported.[8]

On the basis of the direction of the addition of **9** to nitrosobenzene it was surmised that the adduct of **9** with *p*-nitrobenzaldehyde would be 1,2-dihydro-1,2-di(*p*-nitrophenyl)-4-phenyl-3aH-oxazolo[3,2-*a*]quinoxaline (**27a**) rather than **27b**. This point was resolved

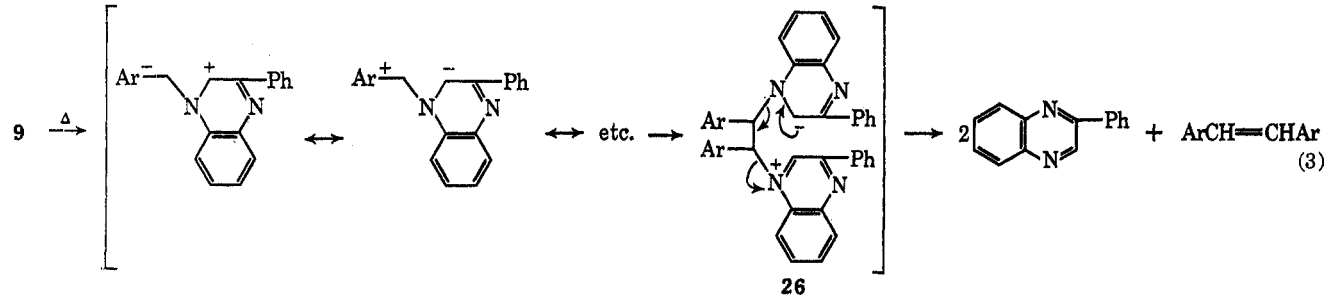
(6) H. W. Heine and R. E. Peavy, *Tetrahedron Lett.*, 3123 (1965); H. W. Heine, R. E. Peavy, and A. J. Durbetaki, *J. Org. Chem.*, **31**, 3924 (1966).

(7) A. Padwa and L. Hamilton, *Tetrahedron Lett.*, 4363 (1965); A. Padwa and L. Hamilton, *J. Heterocycl. Chem.*, **4**, 118 (1967).

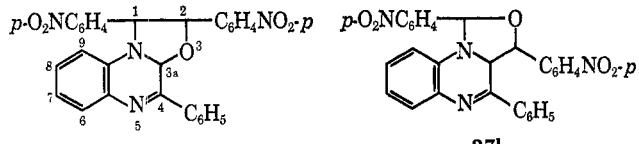
(8) R. Huisgen, W. Scheer, G. Szemies, and H. Huber, *Tetrahedron Lett.*, 397 (1966).

(9) R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967).

(10) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhoffer, *Angew. Chem. Intern. Ed. Engl.*, **1**, 50 (1962).

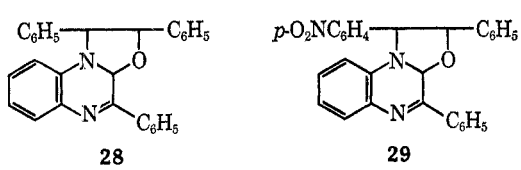


by nmr studies. The aliphatic region of the nmr spectrum shows a singlet at $\delta$ 6.32 (1 H) and a singlet at $\delta$ 4.95 (2 H). The fact that two of the methine protons absorb at $\delta$ 4.95 argues for structure **27a**. It seems likely that the two methine protons on carbons 1 and 2 of structure **27a** would be equivalent since the protons are attached to carbon atoms having identical substituents (*p*-nitrophenyl groups) and similar adjacent atoms (nitrogen and oxygen). If the adduct had structure **27b** the methine protons on adjacent carbon atoms would not be equivalent and two doublets should be observed. The other signal at $\delta$ 6.32 is assigned to the methine proton at **3a**.



**27a** **27b**

The nmr spectrum of the adduct of **11** and benzaldehyde was quite similar to **27a**. Two singlets at $\delta$ 4.48 (2 H) and at 6.25 (1 H) were observed. The most reasonable interpretation of the spectrum is that the singlet representing the two protons is due to the two adjacent methine protons at C-1 and C-2 of **28** having the same chemical shifts because of their similar environments. On the other hand, the adduct **29** derived from the cycloaddition of **9** to benzaldehyde shows two doublets centered at $\delta$ 4.90 (2 H) and a singlet at $\delta$ 6.28 (1 H). Since the methine protons at C-1 and C-2 are no longer equivalent because of a *p*-nitrophenyl group at C-1 and a phenyl group at C-2 a splitting pattern will result.

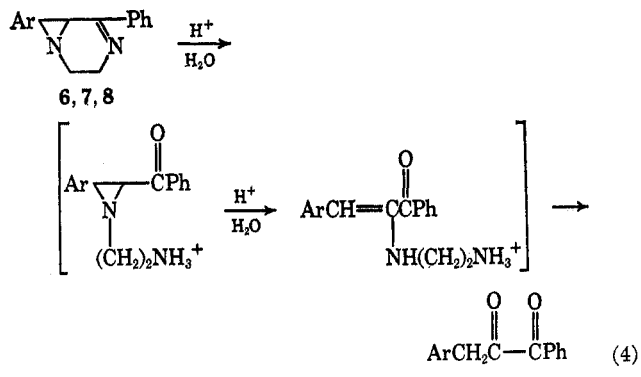


**28** **29**

The structure of the adduct **14** resulting from the cycloaddition of **9** to diethyl azodicarboxylate was adequately confirmed by elemental analyses and by its degradation to the known compound **15**.

The acid hydrolysis of **6**, **7**, and **8** as well as 2-*p*-nitrophenyl-3-benzoylaziridine to $\alpha$ diketones can be rationalized by reaction 4. The conversion of 2-aroylaziridines to $\alpha$-aminochalcones under acid conditions has been demonstrated. Thus, 1-alkyl-2,3-dibenzoylaziridines isomerize into 1-alkylamino-1,2-dibenzoylethenes in moist acetic acid.[11] The hydrolysis of 1-amino-1-aroylethenes to $\alpha$-diketones is a well-known reaction.

(11) A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, Jr., *J. Amer. Chem. Soc.*, **87**, 1050 (1965).



## Experimental Section

**5-Phenyl-7-(*p*-nitrophenyl)-1,4-diazabicyclo[4.1.0]hept-4-ene (6).**—To a suspension of 12.4 g of 1-phenyl-2,3-dibromo-3-(*p*-nitrophenyl)-1-propanone[12] in 1 l. of 95% EtOH was added 1.80 g of ethylenediamine and 6.06 g of triethylamine. The mixture was stirred and heated to boiling. After the dibromide had dissolved, the reaction mixture was allowed to stand overnight at room temperature. Evaporation of most of the solvent precipitated crude **6**. The crude **6** was filtered and washed with 95% EtOH and with water. A yield of 7.05 g (80%) was obtained. An analytical sample, which melted at 137–140° with decomposition, was prepared by recrystallizing from 95% EtOH. The compound is initially yellow but rapidly turns green and then blue upon exposure to light.

*Anal.* Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.85; H, 5.16; N, 14.12.

**5-Phenyl-7-(*m*-nitrophenyl)-1,4-diazabicyclo[4.1.0]hept-4-ene (7).**—To a suspension of 10.00 g of 1-phenyl-2,3-dibromo-3-(*m*-nitrophenyl)-1-propanone[13] in 1 l. of 95% EtOH was added 2.00 g of ethylenediamine and 4.89 g of triethylamine. The mixture was stirred and heated to boiling. The reaction mixture was permitted to stand overnight at room temperature. Evaporation of most of the solvent at reduced pressure left a viscous oil that slowly crystallized after several days. Filtration of the mixture gave 4.05 g of **7**. An additional 1.86 g of **7** precipitated from the filtrate the following day. The crude **7** was washed with 95% EtOH and then with water. Recrystallization from 95% EtOH gave **7** melting at 81–83°.

*Anal.* Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.75; H, 5.62; N, 14.05.

**Compound 8** was prepared by adding 5.40 g of ethylenediamine and 6.06 g of triethylamine to a suspension of 11.04 g of commercial 1,3-diphenyl-2,3-dibromo-1-propanone in 900 ml of 95% ethanol. The mixture was stirred and heated to boiling and then allowed to stand for 2 days at room temperature. The solvent was evaporated and the oily residue was dissolved in methylene chloride. The methylene chloride extract was washed with water and then evaporated. The residue was dissolved in 95% EtOH and the solution was kept in the refrigerator for several days. Gradually 3.95 g of crude **8** precipitated. Recrystallization from 95% EtOH gave **8** melting at 71–73°.

*Anal.* Calcd for $C_{17}H_{16}N_2$: C, 82.21; H, 6.50; N, 11.29. Found: C, 81.97; H, 6.61; N, 11.40.

**1,1a-Dihydro-1-(*p*-nitrophenyl)-2-phenylazirino[1,2-*a*]quinoxaline (9)** was synthesized in 60% yield by reacting 12.39 g of 1-phenyl-2,3-dibromo-3-(*p*-nitrophenyl)-1-propanone, 3.24 g of

(12) C. Weygand, E. Bauer, H. Gunther, and W. Heynemann, *Ann.*, **459**, 99 (1927).

(13) N. H. Cromwell, *J. Amer. Chem. Soc.*, **69**, 258 (1947).

*o*-phenylenediamine and 6.06 g of triethylamine according to the procedure described for the preparation of **6**. The crude **9** was recrystallized from 1-propanol and melted with decomposition at 135–137°. Compound **9** is initially yellow but turns green and then blue upon exposure to light.

*Anal.* Calcd for $C_{21}H_{15}N_3O_2$: C, 73.90; H, 4.42; N, 12.30. Found: C, 74.29; H, 4.48; N, 12.41.

**Alternate Preparation of 9.**—A mixture of 0.50 g of 2-bromo-1-phenyl-3-(*p*-nitrophenyl)-2-propen-1-one[12] and 0.163 g of *o*-phenylenediamine and 0.152 g of triethylamine in 30 ml of 95% EtOH was heated to boiling. The mixture was allowed to stand overnight and then was filtered to remove a small amount of unreacted starting reagent. Most of the solvent was evaporated, the mixture cooled and filtered to give 0.21 g (48%) of crude **9**.

**1,1a-Dihydro-1-(*m*-nitrophenyl)-2-phenylazirino[1,2-*a*]quinoxaline (10)** was prepared in 65% yield by reaction of 10.0 g of 1-phenyl-2,3-dibromo-3-(*m*-nitrophenyl)-1-propanone, 2.70 g of *o*-phenylenediamine and 5.0 g of triethylamine according to the method employed for preparing **6**. After recrystallizing from 95% EtOH **10** melted at 139–140°.

*Anal.* Calcd for $C_{21}H_{15}N_3O_2$: C, 73.90; H, 4.42; N, 12.30. Found: C, 74.03; H, 4.33; N, 12.66.

**1,1a-Dihydro-1,2-diphenylazirino[1,2-*a*]quinoxaline (11)** was prepared in the same manner as **6** by reacting 9.72 g of *o*-phenylenediamine, 11.04 g of 1,3-diphenyl-2,3-dibromo-1-propanone and 6.06 g of triethylamine. The reaction mixture was allowed to stand 1 week at room temperature, yield 4.3 g (48%). An analytical sample of **11**, mp 123.5–125°, was prepared by recrystallizing **11** from 95% EtOH. The compound is yellow-orange but turns bright red upon exposure to light.

*Anal.* Calcd for $C_{21}H_{16}N_2$: C, 85.13; H, 5.41; N, 9.46. Found: C, 84.87; H, 5.63; N, 9.45.

**Isomerization of 9 to 2-(*p*-Nitrobenzyl)-3-phenylquinoxaline (12).**—To a solution of 2.00 g of **9** in 50 ml of boiling acetone was added 5 drops of concentrated hydrochloric acid. The solution rapidly turned deep red. The reaction mixture was cooled and the solvent evaporated to give 1.86 g of **12** which melted after recrystallization from 95% ethanol at 122–123°. An authentic sample of **12** prepared according to a literature[14] procedure was identical with respect to infrared absorption bands and melting point with **12** obtained by the isomerization of **9**.

**Isomerization of 10 to 2-(*m*-nitrobenzyl)-3-phenylquinoxaline (30)** was achieved by adding 1.0 ml of concentrated hydrochloric acid to a solution of 0.030 g of **10** in 45 ml of hot ethanol and benzene. Evaporation of the solvent gave 0.255 g of **30** melting at 120.5–122°. A genuine sample prepared by a literature method[15] melted 120°.

**The isomerization of 11 to 2-benzyl-3-phenylquinoxaline (31)** was accomplished in the same manner as the conversion of **9** to **12**. The structure of the product was confirmed by comparison of melting point and infrared absorption bands of **31** prepared by reaction of benzyl phenyl diketone and *o*-phenylenediamine.[16]

**Conversion of 11 into *trans*-Stilbene and 2-Phenylquinoxaline.**—A 300-mg sample of **11** was heated in a sublimator under reduced pressure at 138° for 24 hr. The sublimate (211 mg) was dissolved in methylene chloride and the methylene chloride solution was extracted with 6 *N* HCl. Neutralization of the acid layer with potassium hydroxide gave 101 mg (49%) of 2-phenylquinoxaline. Evaporation of the methylene chloride layer gave a quantitative yield of *trans*-stilbene.

**Conversion of 9 into 2-Phenylquinoxaline and *trans*-4,4′-Dinitrostilbene.**—A 200-mg sample of **9** was heated in a sublimator at 100° at reduced pressure (5 mm) for 12 hr. The sublimate was identified as 2-phenylquinoxaline (62 mg, 51%). The dark residue in the sublimator was extracted with a small volume of hot $CHCl_3$. Evaporation of the solvent gave a small quantity of *trans*-4,4′-dinitrostilbene.

**Reaction of 9 with Nitrosobenzene.**—A mixture of 3.00 g of **9** and 0.943 g of nitrosobenzene in 50 ml of dry toluene was stirred and refluxed for 1 hr. The solvent was evaporated and a small quantity of 95% EtOH was added to the residue. The reaction mixture was cooled and filtered. There was obtained 1.85 g (87%) of N-phenyl-α-*p*-nitrophenylnitrone. Concentration of the ethanolic filtrate gave 1.81 g (94%) of 2-phenylquinoxaline. The nitrone **13** was identical with a genuine sample prepared by a literature method.[17]

**Diethyl 1,3a-dihydro-1-(*p*-nitrophenyl)-4-phenyl-*s*-triazolo[4,3-*a*]quinoxaline-2,3-dicarboxylate (14)** was prepared by refluxing a mixture of 2.00 g of **9** and 1.05 g of diethyl azodicarboxylate in 45 ml of dry toluene with vigorous stirring for 17–20 min. The reaction mixture was immediately chilled. The solvent was evaporated and a small amount of EtOH was added to the residue. The crude **14** was filtered and weighed 1.97 g (65%). This compound is very heat sensitive and recrystallization was best effected by saturating hot acetonitrile with **14** and quickly filtering the solution into a flask previously placed in an ice bath. Three recrystallizations gave bright yellow plates of **14** melting with decomposition at 156–157°.

*Anal.* Calcd for $C_{27}H_{25}N_5O_6$: C, 62.91; H, 4.89; N, 13.58. Found: C, 63.09; H, 4.90; N, 13.52.

**Conversion of 14 into 1-(*p*-Nitrophenyl)-4-phenyl-*s*-triazolo[4,3-*a*]quinoxaline (15).**—A mixture of 0.50 g of **14** and 0.50 g of potassium hydroxide in 30 ml of $CH_3OH$ was stirred at room temperature for 12 hr. The reaction mixture was filtered to give 0.27 g of crude **15**. Compound **15** was recrystallized from EtOH to give orange needles melting at 215–230°. The crude **15** was then dissolved in $CHCl_3$ and passed through a column of silica gel. The solvent was evaporated and the residue was recrystallized from an ethanol–pyridine mixture to give **15**, mp 255–256°. The infrared spectra of **15** and of a genuine sample prepared by a literature method[18] were identical. A mixture melting point determination showed no depression of the melting point.

**Diethyl 1-(*p*-Nitrophenyl)-4-phenylpyrrolo[1,2-*a*]quinoxaline-2,3-dicarboxylate (16). Method A.**—A mixture of 2.00 g of **9** and 0.833 g of dimethyl acetylenedicarboxylate in 30 ml of dry toluene was refluxed with vigorous stirring for 1 hr. The solvent was evaporated and the residue triturated with warm EtOH. The mixture was cooled and filtered to give 1.51 g (54%) of crude **16**, mp 234–237°. A molecular weight determined by means of mass spectroscopy was 481.

*Anal.* Calcd for $C_{27}H_{19}N_3O_6$: C, 67.35; H, 3.98; N, 8.73. Found: C, 67.69; H, 4.09; N, 8.76.

**Preparation of 16 (Method B).**—A mixture of 1.00 g of **9**, 0.721 g of chloranil, and 0.416 g of dimethyl acetylenedicarboxylate in 30 ml of dry toluene was refluxed with stirring for 40 min. The solvent was evaporated and the residue was warmed with a small quantity of methanol. The mixture was cooled and filtered to give 1.16 g of **16** (82%). Evaporation of the filtrate gave impure 2,3,5,6-tetrachlorohydroquinone.

**1-(*p*-Nitrophenyl)-4-phenylpyrrolo[1,2-*a*]quinoxaline (17).**—A mixture of 0.500 g of **16** and 2.0 g of potassium hydroxide in 50 ml of distilled water was refluxed with stirring for 13 hr. The mixture was cooled and made acid with 6 *N* HCl and filtered. The yield of the crude diacid of **16**, mp 298–305°, was 0.443 g (94%). The diacid (0.425 g), 3 ml of quinoline and 30 mg of copper chromite was heated at 210° for 75 min. The mixture was cooled and 25 ml of methylene chloride was added. After filtering, the mixture was made acid with 6 *N* HCl. The layers were separated and the aqueous layer was extracted with methylene chloride. The organic layers were combined and the solvent evaporated to give 310 mg (90%) of **17**. The crude **17** was dissolved in chloroform and passed through a column of silica gel. The solvent was evaporated and the residue was recrystallized three times from toluene to give yellow crystals of **17** melting at 222–224°.

*Anal.* Calcd for $C_{23}H_{15}N_3O_2$; C, 75.60; H, 4.14; N, 11.50. Found: C, 76.01; H, 4.01; H, 11.36.

**1-(*p*-Nitrophenyl)-4-phenyl-2,3-dibenzoylpyrrolo[1,2-*a*]quinoxaline (18).**—A mixture of 1.00 g of **9**, 0.687 g of dibenzoylacetylene, and 0.721 g of chloranil in 30 ml of dry toluene was refluxed with vigorous stirring for 1 hr. The solvent was evaporated, the residue washed with a small quantity of 95% EtOH, and the mixture filtered. A crude yield of 1.44 g (85%) of **18** was obtained. Five recrystallizations from 1-propanol gave **18** melting at 269.5–71.5°. The nmr spectrum of **18** in $CDCl_3$ showed no aliphatic protons. The molecular weight determined by mass spectroscopy was 573 (calculated 573.6).

*Anal.* Calcd for $C_{37}H_{23}N_3O_4$: C, 77.48; H, 4.04; N, 7.33. Found: C, 77.22; H, 4.22; N, 7.13.

**1,2-Dihydro-1,2-di(*p*-nitrophenyl)-4-phenyl-3aH-oxazolo[3,2-*a*]-**

(14) N. H. Cromwell and G. D. Mercer, *J. Amer. Chem. Soc.*, **79**, 3823 (1957).
(15) S. Bodforss, *Ber.*, **49**, 2795 (1916).
(16) O. Widman, *ibid.*, **49**, 477 (1916).
(17) O. H. Wheeler and P. H. Gore, *J. Amer. Chem. Soc.*, **78**, 3363 (1956).
(18) D. Shiho and S. Tagami, *ibid.*, **82**, 4044 (1960).

**quinoxaline (27a).**—A mixture of 3.00 g of **9** and 1.40 g of *p*-nitrobenzaldehyde in 70 ml of dry toluene was refluxed with vigorous stirring for 75 min. Most of the solvent was evaporated and the residue was treated with a small amount of 95% EtOH. The mixture was filtered to give 3.46 g (79.7%) of **27a**. Four recrystallizations from $CH_3CN$ gave **27a** decomposing at 178–181° with considerable darkening of **27a** near the decomposition point.

*Anal.* Calcd for $C_{28}H_{20}N_4O_5$: C, 68.29; H, 4.09; N, 11.37. Found: C, 68.05; H, 4.26; N, 11.54.

**1,2-Dihydro-1,2,4-triphenyl-3aH-oxazolo[3,2-*a*]quinoxaline (28).**—A mixture of 1.00 g of **11** and 0.358 g of benzaldehyde in 30 ml of toluene was refluxed with stirring for 1 hr. The solvent was evaporated and the oily residue was induced to crystallize by warming in 95% EtOH. Filtration gave 0.390 g (29%) of **28**. Recrystallization three times from $CH_3CN$ gave **28**, mp 151.6 dec.

*Anal.* Calcd for $C_{28}H_{22}N_2O$: C, 83.55; H, 5.51; N, 6.96. Found: C, 83.68; H, 5.53; N, 7.03.

**1,2-Dihydro-1-(*p*-nitrophenyl)-2,4-diphenyl-3aH-oxazolo[3,2-*a*]quinoxaline (29).**—A mixture of 3.00 g of **9** and 1.40 g of benzaldehyde in 70 ml of dry toluene was refluxed with vigorous stirring for 90 min. The reaction mixture was worked up as for **28** to give 2.33 g (59%) of **29**. Recrystallization once from toluene and thrice from $CH_3CN$ gave **29**, mp 178–180°.

*Anal.* Calcd for $C_{28}H_{21}N_3O_3$: C, 75.15; H, 4.73; N, 9.39. Found: C, 74.75; H, 4.95; N, 9.68.

**6a,6b,12b,13-Tetrahydro-13-*p*-nitrophenyl-6-phenylacenaphtho[1′,2′:3,4]pyrrolo[1,2-*a*]quinoxaline (19).**—A mixture of 2.05 g of **9** and 1.00 g of acenaphthylene in 50 ml of dry toluene was refluxed for 1 hr with vigorous stirring. The reaction mixture was cooled and filtered to give 2.06 g of crude **19**. Five crystallizations from *p*-xylene gave **19** decomposing at 231–233°. The product darkens considerably near the decomposition point. This reaction was also carried out in 1-propanol with comparable yields.

*Anal.* Calcd for $C_{33}H_{23}N_3O_2$: C, 80.31; H, 4.70; N, 8.51. Found: C, 80.45; H, 4.79; N, 8.25.

**Preparation of 6a,6b,12b,13-tetrahydro-6,13-diphenylacenaphtho[1′,2′:3,4]pyrrolo[1,2-*a*]quinoxaline** was prepared the same way as **19** with 0.592 g of **11**, 0.304 g of acenaphthylene in 10 ml of toluene. Recrystallization of the product from 50:50 EtOH–$C_6H_6$ gave material decomposing at 207–210°. A molecular weight determination by mass spectroscopy gave a value of 448.

*Anal.* Calcd for $C_{33}H_{24}N_2$: C, 88.36; H, 5.39; N, 6.25. Found: C, 88.31; H, 5.35; N, 6.16.

**Hydrolysis of 6 to *p*-Nitrobenzyl Phenyl Diketone.**—To 5 ml of cold concentrated $H_2SO_4$ was added 300 mg of **6**. The mixture was poured over 200 g of ice and allowed to stand overnight and filtered. A yield of 0.261 (94.7%) of the diketone was obtained. It was converted into **12** by reaction with *o*-phenylenediamine. The hydrolysis of **7** and **8** were carried out analogously and the resulting $\alpha$ diketones reacted with *o*-phenylenediamine to give the known quinoxalines **30** and **31**.

**Registry No.**—**6**, 18039-27-5; **7**, 18039-28-6; **8**, 18039-29-7; **9**, 18039-30-0; **10**, 18039-31-1; **11**, 18039-32-2; **12**, 18039-33-3; **14**, 18039-34-4; **16**, 18039-35-5; **17**, 18067-01-1; **18**, 18039-36-6; **19**, 18067-02-2; **27a**, 18039-37-7; **28**, 18039-38-8; **29**, 18039-39-9; **30**, 18039-40-2; 6a, 6b, 12b, 13-tetrahydro-6,13-diphenylacenaphtho[1′,2′,3,4]pyrrolo[1,2-*a*]quinoxaline, 18039-41-3.

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# 1,2,3-Oxathiazolidines—a New Heterocyclic System[1]

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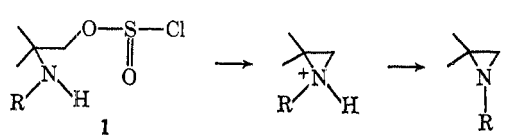
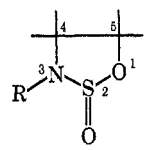
The reactions of $\beta$-amino alcohols with thionyl chloride in the presence of base leads to 2-oxo-1,2,3-oxathiazolidines (a previously unreported heterocyclic system) in good to excellent yields. Evidence is presented for the general structure of these compounds. The existence of the asymmetry at sulfur in these compounds is discussed and the anisotropic nature of the S–O bond is used to assign stereochemistry.

The conversion of $\beta$-amino alcohols to $\beta$-haloamines followed by base-catalyzed cyclization (Gabriel synthesis) constitutes one of the more useful routes to aziridines.[2] Our desire to develop milder routes to functionally substituted aziridines has prompted us to investigate alternative techniques for ring closure of amino alcohols. A possible modification of the Gabriel synthesis consisted of the reaction of amino alcohols with thionyl chloride in the presence of base. Our hope was that conditions could be derived which would be favorable to initial formation of a chlorosulfite ester (**1**) and its subsequent intramolecular decomposition to an aziridine.



**1**

We have prepared a variety of amino alcohols which have bulky or electron-withdrawing groups on nitrogen. These compounds were treated with thionyl chloride in the presence of tertiary amines in nonpolar solvents. The products from these reactions clearly did not correspond to the desired aziridines. In each case, elemental and mass spectral analysis revealed that the products contained, in addition to those atoms expected for the aziridine, the elements of $SO_2$. We have assigned to these products the 2-oxo-1,2,3-oxathiazolidine structure (**2**). This structure constitutes



**2**

the first example of the 1,2,3-oxathiazolidine heterocyclic ring system.[3,4] For this reason we would like to

(1) Support of this work by the National Science Foundation Grants GP-5531 and GP-8044 is gratefully acknowledged.

(2) P. E. Fanta in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part 1, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1964, p 528.

(3) McCombie and Parkes reported the preparation of 2-oxo-1,2,3-oxathiazoles (the unsaturated analog of **2**) from thionyl chloride and certain $\alpha$-amino ketones.[4]

(4) H. McCombie and J. W. Parkes, *J. Chem. Soc.*, **101**, 1991 (1912).