Reactions of Furazano[3,4-*b*]quinoxalines with Phosphorus Ylides and an Unusual Oxidative Transformation of the Transylidation Product

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Reactions of furazano[3,4-*b*]quinoxalines **1** with phosphorus ylides **2** afford the transylidation product **3** and/or 4,9-dihydrofurazano[3,4-*b*]quinoxalines **4**. Oxidation of **3** with phenyliodide bis-trifluoroacetate gave the fused furan derivative **13** in high yield.

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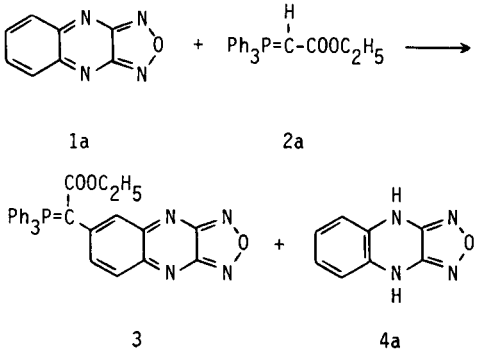
In a previous paper [1] we reported on the synthesis of furoxano[3,4-*b*]quinoxalines and on their deoxygenation to the corresponding furazano[3,4-*b*]quinoxalines. Furthermore, we recently described the reaction of some of the above mentioned furoxans with phosphorus ylides [2], with alkynes and alkenes [3], and finally with nitrile oxides [4]. These reactions resulted in substituted pyrazino[2,3-*b*]quinoxalines, pyrazino[2,3-*b*]quinoxaline 1,4-dioxides and *as*-triazino[5,6-*b*]quinoxaline 1,2,4-trioxides respectively. In all these studies there was generally observed that the chemical reactivity of furoxano[3,4-*b*]quinoxalines substantially differs from the one of benzofuroxan.

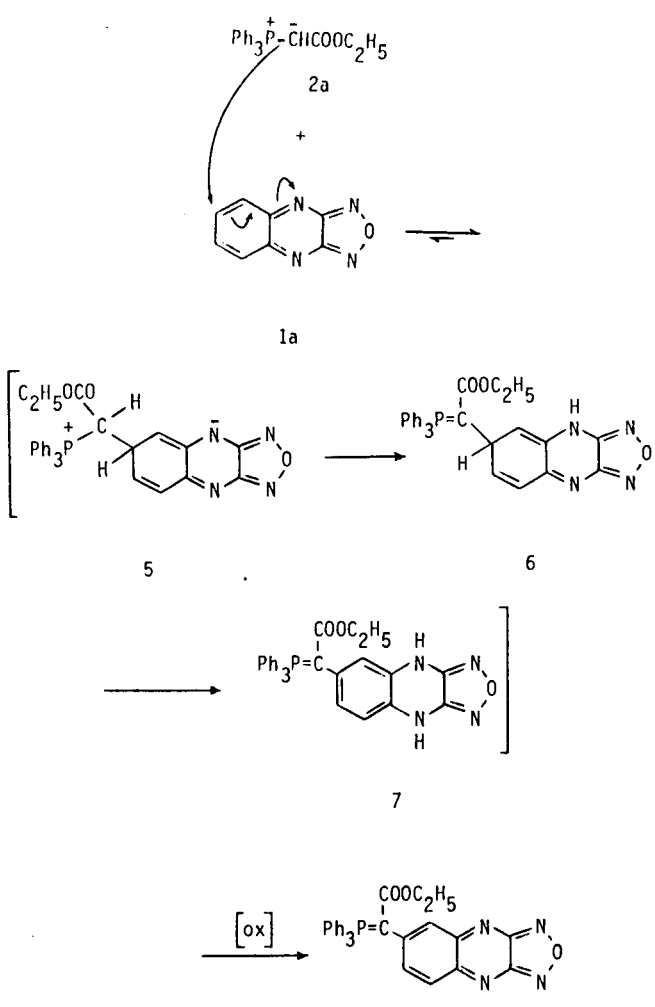
We now report on reactions of the title compounds with phosphorus ylides and further transformations of the products thus obtained. Equimolar amounts of furazano-[3,4-*b*]quinoxaline (**1a**) and ethoxycarbonylmethylenetriphenylphosphorane (**2a**) in methylene chloride were allowed to stand at room temperature for six (6) days. 4,9-Dihydrofurazano[3,4-*b*]quinoxaline (**4a**) (Scheme 1) was precipitated from the dark-blue reaction mixture as colorless crystals in 26% yield and α-(6-furazano[3,4-*b*]quinoxalinyl)-α-ethoxycarbonylmethylenetriphenylphosphorane (**3**) was separated from the filtrate in the form of blue crystals (36% yield) by column chromatography, followed by the starting quinoxaline **1a** (15%) and triphenylphosphine oxide (39%).

Scheme 1



Reactions of **1a** with α-methoxycarbonylethylidenetriphenylphosphorane (**2b**) and of **1b** with ylides **2a** and **2b** did not afford a product similar to **3**. A polymeric residue was precipitated, whereof the respective compounds **4a** and **4b** were separated by column chromatography in relatively low yields. The filtrate yielded only unchanged **1a** or **1b** and triphenylphosphine oxide. The reaction of 6,7-dimethylfurazano[3,4-*b*]quinoxaline (**1b**) with ylides **2a** and

Scheme 2



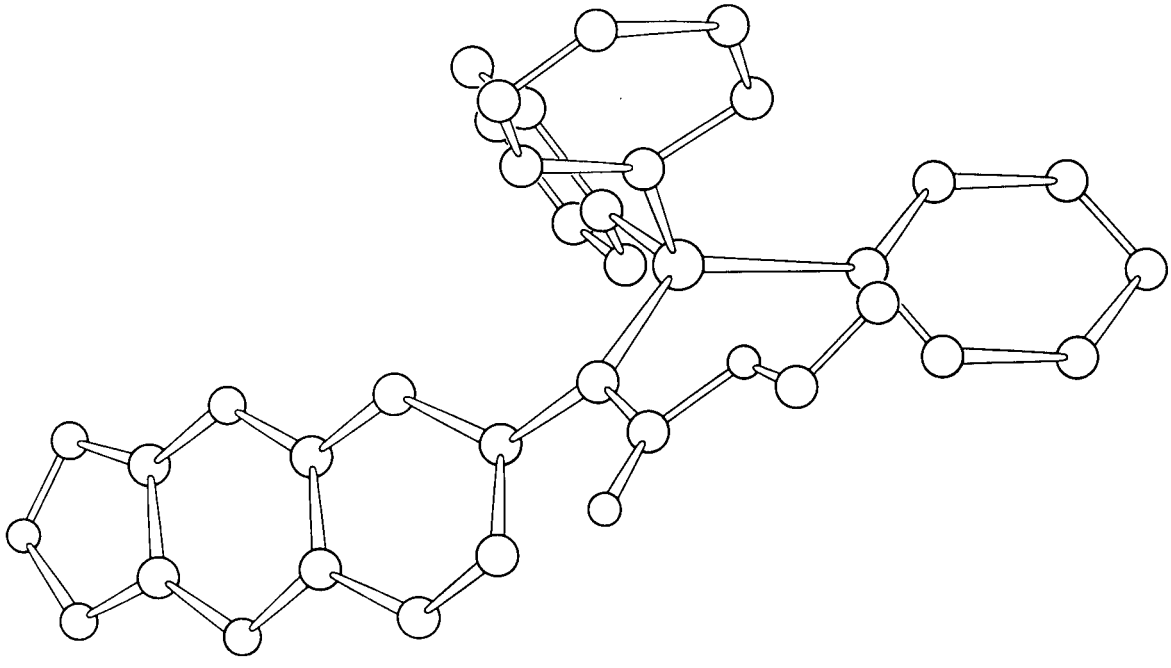


Figure 1. Perspective view of compound **3**.

2b resulted furthermore in dimethyl *cis*- and/or *trans*-dimethylbutenodioates **8**.

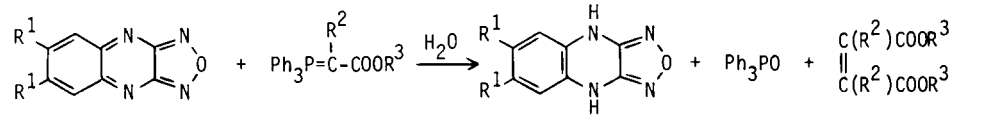
The formation of ylide **3** may be rationalized mechanistically by considering that compound **1a** undergoes a nucleophilic attack at the 6-position by ylide **2a**, leading to not isolated ylide **7** *via* the intermediates **5** and **6**. Further oxidation of **7** affords the ylide **3** (Scheme 2). The proposed nucleophilic attack could be considered as an 1,4- or 1,6-Michael addition to the conjugated system **1**. This long conjugation and the quinoid structure render the 6,7-positions of the furazano[3,4-*b*]quinoxalines electrophilic center. Analogous nucleophilic attacks to quinoid compounds have been reported in the literature [5]. The quinoid structure of furazano[3,4-*b*]quinoxalines is reflected in their ^{1}H nmr spectra where the allylic coupling ($^5J_{H\text{-}H}$ = 1 Hz) at compound **1b** appears between H-5 and the methyl protons.

No product analogous to ylide **3** is obtained from the reactions of **1b** with occupied electrophilic positions, nor from reactions of ylide **2b**. Although a similar nucleophilic attack could not be excluded in these cases, it is obvious that the betaine **5** formed is less stable than the reactants, since its further stabilization towards the isomerization depicted in Scheme 2 is impossible.

Atmospheric oxygen oxidizes probably the intermediate **7**. It is unlikely that the quinoxaline **1a** acts as the oxidant at this step being reduced to **4a**, because this assumption is unable to explain the generation of triphenylphosphine oxide. Compound **1a** may only partially participate in this oxidation step. Dihydroquinoxalines **4** should be formed by a parallel competitive reaction pathway, in the same way as in the reaction of **1a** with ylide **2b** or of **1b** with ylides **2a-b**. An attack by the ylide **2a-b** at the *N*-atom of the pyrazine ring is likely in this reaction pathway, possibly *via* free radicals. Hydrolytic transformation of the adducts by moisture affords in a complicated manner dihydro compounds **4** and triphenylphosphine oxide (Scheme 3). The formation of polymers reinforces the suggested free radical intermediates.

The structure of compounds **3** and **4a-b** has been assigned by means of their elemental analysis and spectral data, further by the transformation reactions presented in

Scheme 3



1 a-b 2 a-b 4 a-b 8 a-b

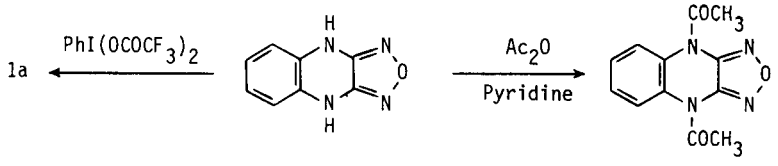
1a : R^1 = H
b : R^1 = CH_3

2a : R^2 = H, R^3 = C_2H_5
b : R^2 = R^3 = CH_3

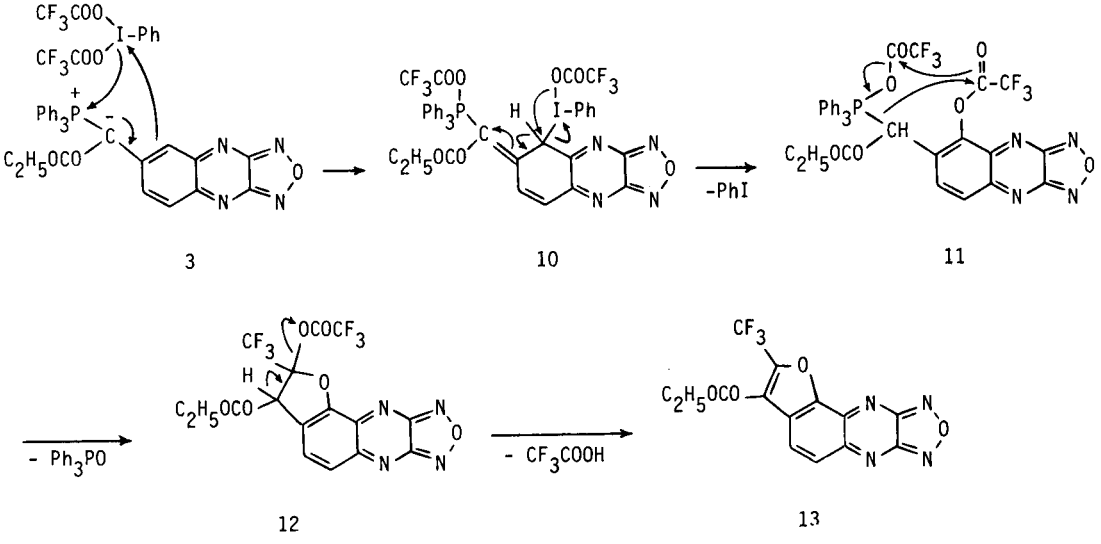
4a : R^1 = H
b : R^1 = CH_3

8a : R^2 = H, R^3 = C_2H_5
b : R^2 = R^3 = CH_3

Scheme 4



Scheme 5



Schemes 4 and 5. The structure of compound **3** whose perspective view is shown in Figure 1, was unequivocally confirmed by X-ray analysis [6]. Ylide **3** shows the carbonyl stretching band at 1640 cm^{-1} and furthermore at the mass spectrum (70 eV) the molecular ion (very low intensity). The H-5 and H-8 chemical shifts appear at δ 6.60 and 8.40 respectively. Its ^{13}C nmr shifts are also in good agreement with the values expected from the structure of **3**. Compounds **4a-b** show also a very good agreement in their ir, ms, ^{1}H and ^{13}C nmr spectra with the structures proposed. An alternate structure where the 1- and 3- instead of 4- and 9-nitrogen atoms were reduced is easily excluded when considering the ^{1}H and ^{13}C nmr spectra which indicate that the quinoxaline ring has undergone a change.

Oxidation of compound **4a** with phenyliodine bis-trifluoroacetate (PIT) gave in 75% yield the starting compound **1a**, while treatment of **4a** with acetic anhydride in pyridine afforded 4,9-dihydro-4,9-diacetylfurazano[3,4-*b*]-quinoxaline **9** in 96% yield (Scheme 4).

Ylide **3** is very stable, due to its long conjugated system. So ylide **3** does not give the Wittig reaction with benzaldehyde at refluxing chloroform. However, it is easily converted by PIT to ethyl 2-trifluoromethylfuro[3,2-*h*]furazano[3,4-*b*]quinoxaline-3-carboxylate (**13**) in 94% yield. The mechanism proposed in Scheme 5 can account for the formation of this unexpected product. To our best knowledge [7], this reaction is the first example where the trifluoroacetoxy group of PIT participates in a ring formation concerning the reaction products. The analytical and spectral data (ir, ms, ^{1}H nmr, ^{13}C nmr) strongly support the proposed structure **13**. The C=O stretching band appears at 1720 cm^{-1}. The mass spectrum of this product shows the molecular ion and a fragmentation pattern in agreement with structure **13**. The ^{1}H nmr spectrum shows two doublets (AB system) for the two aromatic protons, while the ^{13}C nmr is more enlighting. An assignment of this latter is shown in Figure 2 [8].

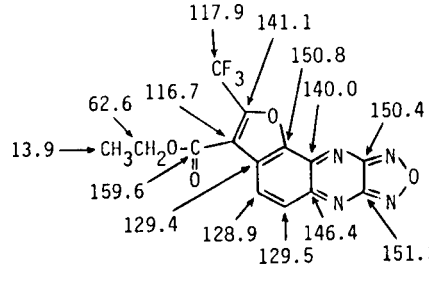
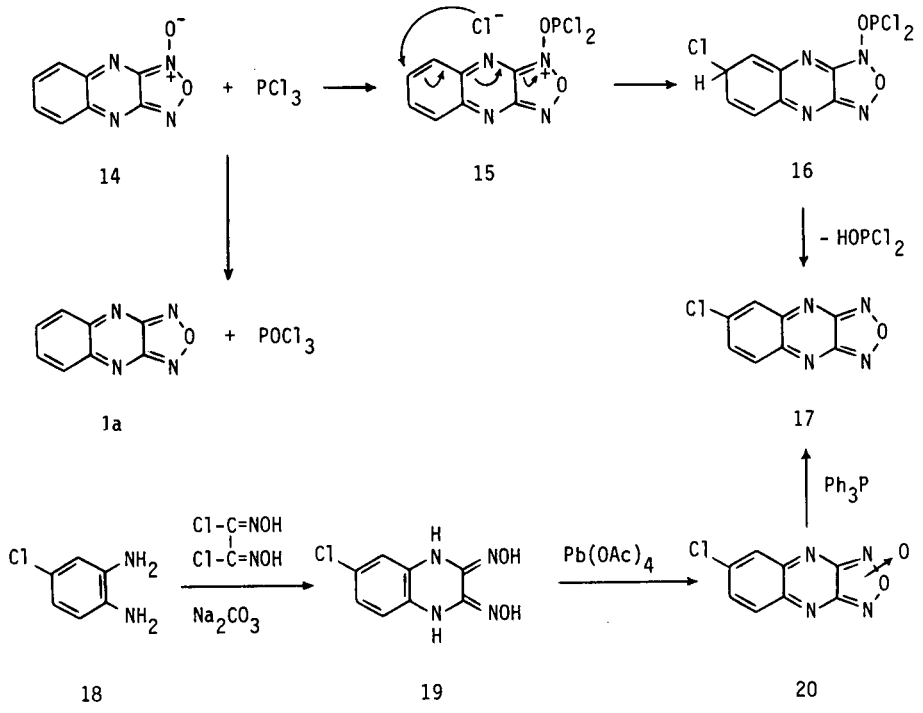


Figure 2. ^{13}C nmr assignment of compound **13**.

It is noteworthy that all efforts to bring about a similar reaction between benzofurazan and ylide **2a**, failed, even under forced conditions such as prolonged refluxing in methylene chloride, chloroform or *o*-xylene.

An additional reaction related to those described above

Scheme 6



again demonstrating the electrophilic character of 6,7-positions of furazano[3,4-*b*]quinoxaline system, is the reaction between furoxano[3,4-*b*]quinoxaline (**14**) and phosphorus trichloride, where besides the expected compound **1a** there was obtained 6-chlorofurazano[3,4-*b*]quinoxaline (**17**) in 16% yield, obviously according to the reaction sequence shown in Scheme 6. Compound **17** is also prepared according to the general method [1], depicted in Scheme 6. Similar chlorinations with simultaneous deoxygenation of *N*-oxides are known in the literature [9] from reactions of heterocyclic *N*-oxides with phosphorus oxychloride. However compound **14** did not react with phosphorus oxychloride at refluxing chloroform. For comparison we report that neither benzofuroxan did react with phosphorus trichloride nor with phosphorus oxychloride even at refluxing chloroform for an extended period.

In conclusion, the reactions studied in this paper show that furazano[3,4-*b*]quinoxalines have a tendency to hydrogenate at the two *N*-atoms of the pyrazine ring and furthermore the 6,7-positions are electrophilic centers which can be attacked by nucleophiles like phosphorus ylides. Benzofurazan is inert towards the above mentioned reagents.

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. The ir spectra were obtained with a Perkin-Elmer 297 spectrophotometer. The ^{1}H nmr spectra were obtained at 200 MHz on a Varian XL-200 spectrometer, with tetramethylsilane as the internal standard. The ^{13}C nmr spectra were obtained at 25 MHz on a JEOL FX-100 nmr spectrometer or at 50 MHz on a Varian XL-200 spectrometer, referenced to the solvent [deuteriochloroform δ 77.0, d_6-dimethyl sulfoxide δ 39.5]. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6L spectrometer, with ionization energy 70 eV. Microanalyses were performed on a Perkin-Elmer 240B elemental analyzer. Commercially available reagents and solvents were used without further purifications. Silica gel (Merck 60, 70-230 mesh) was used for column chromatography. Compounds **1a**, **1b** and **14** were prepared according to literature methods [1,2]. Ylides **2a** and **2b** were also made by standard procedures [10].

Reaction of Furazano[3,4-*b*]quinoxaline (**1a**) with Ylide **2a**.

A solution of furazano[3,4-*b*]quinoxaline (**1a**) (0.15 g, 0.87 mmole) and ylide **2a** (304 mg, 0.87 mmole) in methylene chloride (15 ml) was allowed for 6 days at room temperature. The color of the solution became gradually dark blue and crystals were precipitated. The crystals were filtered, washed with hexane and characterized as 4,9-dihydrofurazano[3,4-*b*]quinoxaline (**4a**) (40 mg, 26%), mp 244-246°; ir (Nujol): 3200, 1625, 1585 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 6.62 (AA'BB', 4H), 9.84 (s, 2H); ^{13}C nmr (DMSO-d_6): δ 114.6 (C-5), 121.9 (C-6), 128.2 (C-4a), 147.0 (C-3a); ms: m/z (%) 175 (M^++1, 11), 174 (M^+, 100), 172 (10), 144 (38), 143 (19), 142 (12), 117 (16), 92 (13), 90 (35).

Anal. Calcd. for $C_8H_6N_4O$: C, 55.17; H, 3.47; N, 32.17. Found: C, 55.28; H, 3.44; N, 32.06.

The filtrate was chromatographed on silica gel with hexane/ethyl acetate as eluant to give at first the unreacted starting furazano[3,4-*b*]quinoxaline (**1a**) (23 mg, 15%), mp 178-181° (lit [1] mp 181-182°). Then blue crystals of α-(6-furazano[3,4-*b*]quinoxalinyl)-α-ethoxycarbonylmethylenetriphenylphosphorane (**3**) were eluted (162 mg, 36%), mp 178-182°; ir (Nujol): 1640, 1610 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 0.81 (t, J = 7 Hz, 3H), 3.89 (q, J

= 7 Hz, 2H), 6.60 (s, 1H), 7.5 (m, 10H), 7.75 (m, 6H), 8.40 (dd, J = 9.5 × 2 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 14.0 (prim aliphatic), 58.8 (sec aliphatic), 59.7 (ylidic C, d, $^{1}J_{C-P}$ = 117.2 Hz), 120.0 (C-5, d, $^{3}J_{C-P}$ = 7.3 Hz), 125.0 (C-1', d, $^{1}J_{C-P}$ = 91.6 Hz), 127.2 (C-8), 129.1 (C-3', d, $^{3}J_{C-P}$ = 12.2 Hz), 132.7 (C-4'), 133.5 (C-2', d, $^{2}J_{C-P}$ = 9.8 Hz), 141.1 (C-7, d, $^{3}J_{C-P}$ = 9.8 Hz), 149.1 (C-6, d, $^{2}J_{C-P}$ = 11 Hz), 150.2 (C-4a), 151.1 (C-8a), 151.5 (C-3a), 152.2 (C-9a), 167.6 (C=O, d, $^{2}J_{C-P}$ 13.4 Hz); ms: m/z 518 (M$^+$).

Anal. Calcd. for $C_{30}H_{23}N_4O_3P$: C, 69.49; H, 4.47; N, 10.81. Found: C, 69.65; H, 4.22; N, 11.05.

Triphenylphosphine oxide was then eluted (96 mg, 39%).

Reaction of 6,7-Dimethylfurazano[3,4-*b*]quinoxaline (**1b**) with Ylide **2a**.

A solution of compound **1b** (200 mg, 1 mmole) and ylide **2a** (348 mg, 1 mmole) in methylene chloride (20 ml) was refluxed for 72 hours. The precipitated residue was passed through a silica gel column with methylene chloride/ethyl acetate to yield at first unreacted starting compound **1b** (8 mg, 4%) and then 4,9-dihydro-6,7-dimethylfurazano[3,4-*b*]quinoxaline (**4b**) (15 mg, 7%), 235-238°; ir (Nujol): 3200, 1615, 1570 cm^{-1}; ^{1}H nmr (DMSO-d$_6$): δ 2.09 (s, 6H), 6.46 (s, 2H), 9.79 (s, 2H); ^{13}C nmr (DMSO-d$_6$): δ 18.5 (CH_3), 115.7 (C-5), 125.5 (C-6), 129.1 (C-4a), 147.0 (C-3a); ms: m/z (%) 202 (M$^+$, 100), 201 (14), 200 (15), 186 (15), 185 (24), 172 (90), 171 (38), 170 (49), 157 (27), 156 (40), 145 (27), 118 (33), 116 (26), 91 (39), 87 (39), 75 (25), 51 (30), 43 (75).

Anal. Calcd. for $C_{10}H_{10}N_4O$: C, 59.39; H, 4.98; N, 27.71. Found: C, 59.11; H, 4.92; N, 27.83.

The filtrate was chromatographed on silica gel, eluted by hexane/ethyl acetate to give triphenylphosphine oxide (166 mg, 60%).

Reaction of Furazano[3,4-*b*]quinoxaline (**1a**) with Ylide **2b**.

A solution of **1a** (172 mg, 1 mmole) and **2b** (348 mg, 1 mmole) in methylene chloride (20 ml) was allowed to stand at room temperature for 8 days. The solid residue precipitated was passed through a silica gel column with hexane/ethyl acetate as eluant to give 4,9-dihydrofurazano[3,4-*b*]quinoxaline (**4a**) (20 mg), 239-241°. The solution was then chromatographed on silica gel eluted by hexane/ethyl acetate to yield the following components:

a) Dimethyl *trans*-dimethylbutenodioate (**8**).

Five mg (6%) of **8** were obtained, mp 38-40° (lit [12] mp 41°); ir (Nujol): 1730 cm^{-1}; ^{1}H nmr (carbon tetrachloride): δ 2.0 (s), 3.75 (s); ms: m/z 172 (M$^+$).

b) Mixture of Furazano[3,4-*b*]quinoxaline (**1a**) and 4,9-Dihydrofurazano[3,4-*b*]quinoxaline (**4a**).

These two compounds were separated by dissolving **1a** in chloroform (5 ml) and filtering to give unchanged **1a** (20 mg, 12%) and 4,9-dihydrofurazano[3,4-*b*]quinoxaline (**4a**) (20 mg), mp 243-245°. Total yield of compound **4a** 40 mg (23%).

c) Triphenylphosphine Oxide.

Two hundred fifty mg (90%) were obtained.

Reaction of 6,7-Dimethylfurazano[3,4-*b*]quinoxaline (**1b**) with Ylide **2b**.

As in the previous experiment, from **1b** (200 mg, 1 mmole) and **2b** (348 mg, 1 mmole) in methylene chloride (20 ml) and refluxed for 120 hours, a solid residue precipitated, from which 4,9-dihydro-6,7-dimethylfurazano[3,4-*b*]quinoxaline (**4b**) (16 mg, 8%) was isolated by chromatography on silica gel and eluted with hexane/ethyl acetate. The solution was chromatographed also on silica gel using the same eluant to give:

a) Dimethyl *trans*-Dimethylbutenodioate (**8**).

Compound **8** was obtained in 20% yield (17 mg).

b) Dimethyl *cis*-Dimethylbutenodioate (**8'**).

This compound was obtained in 15% yield (13 mg) as an oil (lit [12] bp 106°/12 Tor); ir (Nujol): 1730 cm^{-1}; ^{1}H nmr (carbon tetrachloride): δ 1.9 (s), 3.65 (s); ms: m/z 172 (M$^+$).

c) Triphenylphosphine Oxide.

Two hundred mg (72%), were obtained.

Oxidation of 4,9-Dihydrofurazano[3,4-*b*]quinoxaline (**4a**) with Phenyliodine bis-Trifluoroacetate.

To a suspension of **4a** (50 mg, 0.287 mmole) in methylene chloride (10 ml) phenyliodine bis-trifluoroacetate (125 mg, 0.29 mmole) was added and the mixture was allowed to stand at room temperature for 2 hours. The reaction mixture was then chromatographed on silica gel with methylene chloride to give at first phenyliodide and then furazano[3,4-*b*]quinoxaline (**1a**) (37 mg, 75%).

4,9-Dihydro-4,9-diacetylfurazano[3,4-*b*]quinoxaline (**9**).

To a solution of 4,9-dihydrofurazano[3,4-*b*]quinoxaline (**4a**) (100 mg, 0.575 mmole) in dry pyridine (10 ml) an excess of acetic anhydride (1.5 ml) was added and the solution was allowed to stand at room temperature for 24 hours. It was then poured into water (250 ml) and extracted twice with ethyl ether (50 ml). The etherial solution was dried over sodium sulfate and the solvent removed to yield 144 mg of compound **9** (97%), mp 142-145° (hexane/chloroform); ir (Nujol): ν C=O 1705 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.60 (s, 6H), 7.30 and 7.83 (AA'BB', 4H); ^{13}C nmr (deuteriochloroform): δ 125.2 (C-5), 126.6 (C-6), 129.9 (C-4a), 149.9 (C-3a), 167.6 (C=O); ms: m/z (%) 258 (M$^+$, 3), 216 (6), 186 (3), 175 (4), 174 (32), 144 (12), 86 (35), 84 (53), 79 (100), 52 (72), 43 (75).

Anal. Calcd. for $C_{12}H_{10}N_4O_3$: C, 55.81; H, 3.90; N, 21.70. Found: C, 55.92; H, 3.72; N, 21.63.

Ethyl 2-Trifluoromethylfuro[3,2-*h*]furazano[3,4-*b*]quinoxaline-3-carboxylate (**13**).

To a solution of α-(6-furazano[3,4-*b*]quinoxalinyl)-α-ethoxycarbonylmethylenetriphenylphosphorane (**3**) (0.259 g, 0.5 mmole) in methylene chloride (20 ml) phenyliodine bis-trifluoroacetate (0.215 g, 0.5 mmole) was added and the blue color turned immediately to yellow. Chromatographic separation on silica gel using hexane/ethyl acetate as eluant yielded firstly phenyliodide, then compound **13** (0.165 g, 94%), mp 116-117° (methylene chloride/hexane); ir (Nujol): ν C=O 1720 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.50 (t, J = 7 Hz, 3H), 4.54 (q, J = 7 Hz, 2H), 7.92 and 8.48 (dd, AB, J = 9.5 Hz, 2H); ^{13}C nmr (deuteriochloroform): δ 13.9, 62.6, 116.7 (q, $^{3}J_{C-F}$ = 2.5 Hz), 117.9 (q, $^{1}J_{C-F}$ = 272 Hz), 128.9, 129.4, 129.5, 140.0, 146.4, 141.1 (q, $^{2}J_{C-F}$ = 44 Hz), 150.4, 150.8, 151.3, 159.6; ms: m/z (%) 352 (M$^+$, 11), 322 (13), 307 (2), 294 (5), 278 (4), 248 (3), 180 (4), 152 (44), 135 (12), 115 (14), 108 (37), 99 (32), 93 (40), 85 (37), 83 (22), 59 (34), 57 (24), 55 (44), 43 (100).

Anal. Calcd. for $C_{14}H_7N_4O_4F_3$: C, 47.74; H, 2.00; N, 15.90. Found: C, 47.81; H, 2.22; N, 15.78.

Triphenylphosphine oxide was then eluted (0.13 g, 94%).

2,3-Bis[hydroxyimino]-6-chloro-1,2,3,4-tetahydroquinoxaline (**19**).

To a cold solution of 4-chloro-1,2-phenylenediamine (**18**) (1.71 g, 12 mmoles) and dichloroglyoxime (2.0 g, 12.5 mmoles) in methylene chloride (50 ml) an aqueous 2*N* sodium carbonate solution (50 ml) was added dropwise with strong stirring over a period of 30 minutes. The precipitated solid was collected with filtration, washed thoroughly with water and methylene chloride and dried *in vacuo* to give 2.28 g (84%) of compound **19**. The crude product was used further for oxidation without purification. For purification, it was passed through silica gel column with ethyl acetate/-methanol as eluant to give the pure compound, mp 230-232°.

Anal. Calcd. for $C_8H_7ClN_4O_2$: C, 42.40; H, 3.11; N, 24.72. Found: C, 42.39; H, 2.99; N, 24.52.

6-Chlorofuroxano[3,4-*b*]quinoxaline (**20**).

To a suspension of 2,3-bis[hydroxyimino]-6-chloro-1,2,3,4-tetrahydroquinoxaline (**19**) (1.14 g, 5 mmoles) in methylene chloride (50 ml) lead tetraacetate (5.4 g, 12 mmoles) was added and the reaction mixture was allowed to stand at room temperature for 4 hours. The red solution was filtered, the solvent was removed under reduced pressure and the product was passed through siliga gel column with methylene chloride as eluant to give 0.27 g (24%) of compound **20**, mp 138-140° (chloroform/hexane); ^{1}H nmr (deuteriochloroform): δ 7.65 (dd, J = 10 × 2 Hz, 1H), 7.85 (d, J = 10 Hz, 1H), 7.87 (d, J = 2 Hz, 1H); ms: m/z (%) 224 (M^++2, 6), 222 (M^+, 18), 208 (1), 206 (3), 194 (22), 192 (66), 178 (5), 176 (10), 164 (10), 162 (27), 127 (27), 126 (6), 124 (12), 100 (23), 76 (15), 75 (23), 30 (100).

Anal. Calcd. for $C_8H_3ClN_4O_2$: C, 43.17; H, 1.36; N, 25.17. Found: C, 42.88; H, 1.29; N, 24.82.

6-Chlorofurazano[3,4-*b*]quinoxaline (**17**). From 6-Chlorofuroxano[3,4-*b*]quinoxaline (**20**).

To a solution of compound **20** (170 mg, 0.76 mmole) in methylene chloride (20 ml), triphenylphosphine (262 mg, 1 mmole) was added and the red solution was immediately turned into yellow. The solvent was evaporated and the mixture was chromatographed on silica gel to give yellow-orange crystals of compound **17** (150 mg, 95%), mp 151-153° (chloroform); ^{1}H nmr (deuteriochloroform): δ 7.75 (dd, J = 10 × 2 Hz, 1H), 8.0 (m, 2H); ms: m/z (%) 208 (M^++2, 15), 206 (M^+, 46), 178 (34), 176 (100), 126 (23), 124 (69), 30 (52).

Anal. Calcd. for $C_8H_3ClN_4O$: C, 46.51; H, 1.46; N, 27.12. Found: C, 46.39; H, 1.41; N, 26.88.

From Furoxano[3,4-*b*]quinoxaline (**14**).

A solution of compound **14** (100 mg, 0.53 mmole) and phosphorus trichloride (100 mg, 0.73 mmole) in dry chloroform (10 ml) was refluxed for 5 hours. The yellow mixture produced was chromatographed on silica gel with hexane/chloroform as eluant to give first 6-chlorofurazano[3,4-*b*]quinoxaline (**17**) (18 mg, 16%), mp 148-149°, and then furazano[3,4-*b*]quinoxaline (**1a**) (20 mg, 22%), mp 178-180°.

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