Preparation of Pyrido- and Azepino-fused Cycl[3.2.2]azines[1)]

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Pyrido- and azepino-fused cycl[3.2.2]azines were obtained by the reaction of the corresponding pyrido- and azepino[*hi*]indolizines with electron-deficient acetylenes in the presence of appropriate oxidants. The reaction pathway of their preparation was proposed to be a sequence of Michael addition of indolizine to acetylene, 10π-electrocyclic reaction of Michael adduct, and dehydrogenation by means of the chemical conversions of the isolated intermediates.

Much attention has been paid for the synthesis of the heterocyclic compounds with new ring systems because of their chemical and physicochemical as well as biological interests.

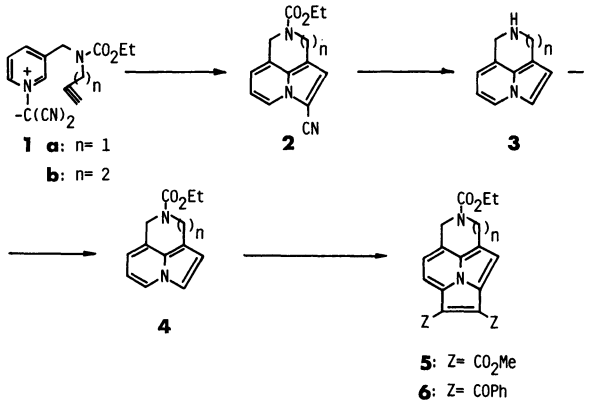
Recently, we reported the interesting physical properties of 4*H*-benzo[*hi*]pyrrolo[2,1,5-*cd*]indolizin-4-ones[2)] and cyclohepta[*hi*]pyrrolo[2,1,5-*cd*]indolizines,[3)] which were prepared by the oxidation of 5,6-dihydro-4*H*-benzo- and 4,5,6,7-tetrahydrocyclohepta[*hi*]pyrrolo [2,1,5-*cd*]indolizines,[4)] respectively. In the continuation of our studies on [*ef*]fused cycl[3.2.2]azine systems, our attention was focused on the synthesis of pyrido- and azepino-fused cycl[3.2.2]azines as aza-analogs of the above two systems.

We wish to report here the synthesis of 2,3-dihydro-1*H*-pyrido- and 1,2,3,4-tetrahydro[3,4,5-*hi*]pyrrolo[2, 1,5-*cd*]indolizines from the corresponding [*hi*]fused indolizines. A mechanistic aspect for the cyclazine synthesis was also described.

Results and Discussion

5-Cyano-2-ethoxycarbonyl-2,3-dihydro-1*H*-pyrido- (**2a**) and 6-cyano-2-ethoxycarbonyl-1,2,3,4-tetrahydroazepino [3,4,5-*hi*]pyrrolo[2,1,5-*cd*]indolizine (**2b**) were prepared by the intramolecular 1,3-dipolar addition of pyridinium-1-dicyanomethylides **1** according to the procedure developed by us.[5)] It was proved that the cyano group at 5 or 6-position of **2** hindered the reaction with acetylenes, so **2a** and **2b** were converted to 2,3-dihydro-1*H*-pyrido- (**3a**) and 1,2,3,4-tetrahydroazepino[3,4,5-*hi*]pyrrolo[2,1,5-*cd*]indolizine (**3b**), respectively, with alkaline hydrolysis followed by decarboxylation. In order to protect the amine moiety, **3a** was again converted to carbamate **4a**, which was allowed to react with dimethyl acetylenedicarboxylate (DMAD) in toluene under reflux for 20 h in the presence of palladium-charcoal (Pd/C) to give 2-ethoxycarbonyl-2,3-dihydro-5,6-bis(methoxycarbonyl)-1*H*-pyrido[3,4,5-*hi*]pyrrolo [2,1,5-*cd*]indolizine (**5a**) in 59% yield. The azepinopyrroloindolizine **5b** was also obtained from **4b** and DMAD in 68% yield.

The reactions of **4a** and **4b** with dibenzoylacetylene (DBZA) were carried out in tetrahydrofuran (THF) at 0°C in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to afford the expected pyrido- and azepinopyrroloindolizines, **6a** and **6b**, in 57 and 49% yields, respectively (Scheme 1).



Scheme 1.

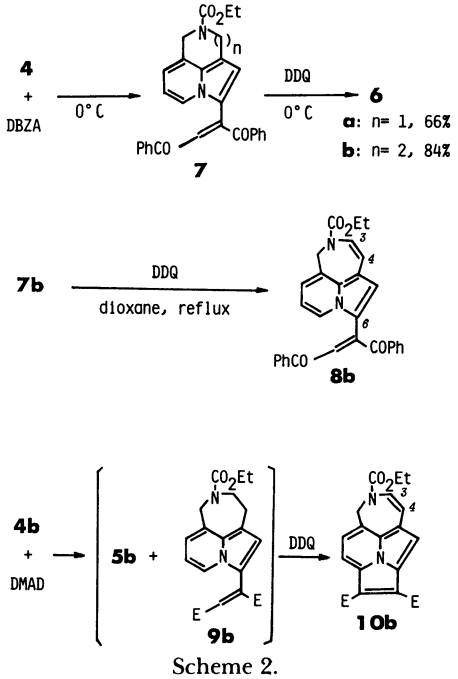
The analytical data and spectroscopic properties of **5** and **6** were consistent with the proposed structures. Especially, in ^{1}H NMR spectrum of **6a** or **6b**, one pair of the signals assignable to ethyl, methylene, and olefin protons were observed. The spectra of **6a** in deuteriochloroform at elevated temperatures revealed that the signals corresponding to two isomers were coalesced at *ca.* 50°C and sharpened again with an increase of the temperature. From these findings, we concluded that **6** in the solution was consisted of two conformational isomers concerning to the azepine ring.

In recent investigations of the mechanism on the cyclazine synthesis from indolizine, the isolation of intermediary products under the conditions without dehydrogenating reagents and their chemical conversions revealed considerably reliable reaction profiles.[6,7)] A proposed mechanism[7)] for the reaction with electron-deficient acetylene is as follows: Indolizine **A** attacks nucleophilically on acetylene to give the zwitterionic intermediate **B**, which leads to Michael adduct **C** and [8+2] cycloadduct **D**. The cycloadduct **D** is converted to more stable isomer(s) by the migration of hydrogen atom and finally dehydrogenated to the cyclazine.

In the synthesis of the benzo- and cyclohepta-fused cyclazines,[4)] some, at least more than two, intermediary products leading to cyclazines were also detected by ^{1}H NMR spectra and thin-layer chromatographies (TLC) of the reaction mixtures and, however, had not been identified owing to their thermodynamically

liablities. The 6-vinylindolizine derivative **7b**, the initially-formed product, was isolated in 62% yield as a pure form at the first time in the reaction of **4b** with DBZA in THF at 0 °C without DDQ. The structural elucidation of **7b** was accomplished on the basis of its spectral data and elemental analysis. Particularly, its ^{1}H NMR spectrum showed a broad doublet at δ 8.46 assignable to the proton at 8-position. The similar reaction of **4a** with DBZA gave the 5-vinylindolizine **7a**, whose structure was confirmed by its ^{1}H NMR spectral data compared with those of **7b**.

While the treatment of **7b** with an equimolar DDQ in THF at 0 °C gave the cyclazine **6b** in 84% yield, the similar treatment in dioxane under reflux afforded 6-(1,2-dibenzoylvinyl)-2-ethoxycarbonyl-1,2-dihydroazepino[3,4,5-*hi*]indolizine (**8b**) in 73% yield, which was formed by the oxidation of cyclic methylene moiety of **7b**. On the other hand, the reaction of **4b** with DMAD in dioxane without Pd/C gave a (1:4) mixture of **5b** and an intermediate **9b** similar to **7b**. The mixture was treated with an equimolar DDQ under reflux to give a mixture of **5b**, **9b**, and 2-ethoxycarbonyl-1,2-dihydroazepino[3,4,5-*hi*]pyrrolo[2,1,5-*cd*]indolizine (**10b**), then, with two equimolar DDQ to give **10b** in 66% yield as a sole product (Scheme 2).

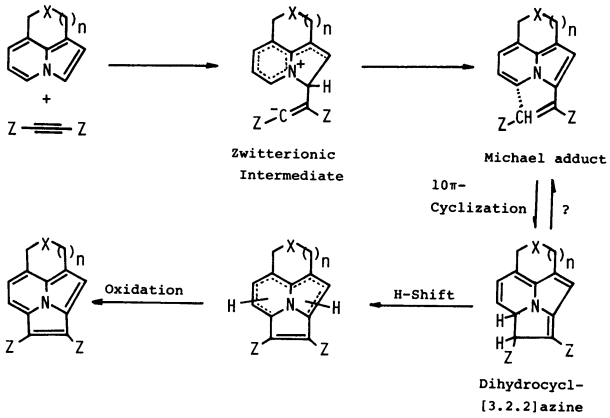


Scheme 2.

These results implied the possibility of the conversion of Michael adduct **C** to cyclazine system in the above-mentioned pathway or, circumstantially, of the interconversion between these two systems, which had been overlooked by preceding investigators.

In the actual synthesis of **6b** from **4b** and DBZA in the presence of DDQ, the examination by TLC revealed that the 6-vinylindolizine **7b** was converted to another intermediate, which was oxidized to the cyclazine **6b** finally.

From these results, we believe that the cyclazine synthsis from [*hi*]fused indolizines and acetylenes proceeds in a stepwise manner than in a concerted one.[8] Also, we suggest that vinylindolizines such as **7** or **9**, the Michael type adducts, would undergo 10π-electrocyclic reaction to give 1,2,3,4,7,7a-hexahydroazepino- or 2,3,6,6a-tetrahydro-1*H*-pyrido[3,4,5-*hi*]pyrrolo[2,1,5-*cd*]indolizines, which are converted to more stable isomer(s) and oxidized to the cyclazines (Scheme 3).



Scheme 3.

Experimental

All melting points are uncorrected. The IR spectra were measured on a JASCO IRA-1 spectrometer as potassium bromide pellets. ^{1}H NMR spectra were obtained on a JEOL JMN-MH-100 spectrometer with tetramethylsilane as an internal standard. Mass spectra were determined with a JEOL JMS-D mass spectrometer equipped with a direct inlet and at an ionization energy of 75 eV. Elemental analyses were performed on a Hitachi 026 CHN analyzer. The TLC was accomplished on 0.2 mm precoated plates of silica gel 60 F-254 (Merck) or on 0.2 mm precoated plates of aluminium oxide 60 F-254 type E (Merck). Visualization was made with ultraviolet light (254 and 365 nm). For the preparative column chromatography, Wakogel C-300 was used.

Preparations of Cyanoindolizines **2**: The pyridinium-1-dicyanomethylides **1** were prepared from the corresponding 3-(aminomethyl)pyridines and tetracyanooxirane and converted to cyanoindolizines **2** by the heating in toluene similarly to the reported method.[5]

*3-[N-(Ethoxycarbonyl)propargylaminomethyl]pyridinium-1-dicyanomethylide (**1a**)*: Yield 58%; yellow prisms; mp 81—84 °C.

Found: C, 64.05; H, 5.16; N, 19.56%. Calcd for $C_{15}H_{14}N_4O_2$: C, 63.82; H, 5.00; N, 19.85%; M, 282.

*3-[N-(Ethoxycarbonyl)-3-butynylaminomethyl]pyridinium-1-dicyanomethylide (**1b**)*: Yield 55%; yellow prisms; mp 119—120 °C.

Found: C, 65.09; H, 5.48; N, 18.96%. Calcd for $C_{16}H_{16}N_4O_2$: C, 64.85; H, 5.44; N,18.91; M, 296.

*5-Cyano-2-ethoxycarbonyl-2,3-dihydro-1H-pyrido[3,4,5-hi]indolizine (**2a**)*: Yield 75%; colorless needles; mp 104—105 °C; IR (KBr) 2200 (CN) and 1700 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, t, $-CH_3$, J=7 Hz), 4.20 (2H, q, $-CH_2-$, J=7 Hz),

4.8 (4H, m, 1 and 3-H), 6.7—6.9(2H, m, 8 and 9-H), 7.09 (1H, s, 4-H), and 8.06 (1H, br d, 7-H, J=6 Hz).

Found: C, 65.96; H, 5.12; N, 16.23%. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46%; M, 255.

*6-Cyano-2-ethoxycarbonyl-1,2,3,4-tetrahydroazepino[3,4,5-hi]-indolizine (**2b**)*: Yield 87%; colorless prisms; mp 126—127 °C; IR (KBr) 2200 (CN) and 1960 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ=1.2—1.4 (3H total, m, $-CH_3$), 3.1—3.2 (2H, m, 4-H), 3.8 (2H, t, 3-H, J=6 Hz), 4.0—4.2 (2H, m, $-CH_2-$), 4.74 (2H, br s, 1-H), 6.7 (2H, m, 9 and 10-H), and 8.04 (1H, br d, 8-H, J=6 Hz).

Found: C, 67.05; H, 5.65; N, 15.34%. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.61%; M, 269.

*Conversion of Cyanoindolizines **2** to Indolizines **3** (Typical Procedure)*: **2a** (3.9 mmol) was refluxed in 15% ethanolic potassium hydroxide (100 ml) for 10 h and ethanol was removed to give a residue. The residue was made acidic with concd hydrochloric acid (150 ml) and refluxed for 3 h. The solution was concentrated *in vacuo* and made basic with sodium hydroxide and extracted with ether (50 ml×5). The ethereal layer was collected, dried, and evaporated to give the indolizine **3a** (0.56 g, 91%).

*2,3-Dihydro-1H-pyrido[3,4,5-hi]indolizine (**3a**)*: Colorless prisms; mp 97—99 °C; IR (KBr) 3200 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ=2.3 (1H, s, NH), 3.96, 4.12 (2H each, 2s, 1 and 3-H), 6.15 (1H, d, 9-H, J=6 Hz), 6.34 (1H, t, 8-H, J=6 Hz), 6.50 (1H, d, 4-H, J=2 Hz), 7.12 (1H, d, 5-H, J=2 Hz), and 7.62 (1H, d, J=6 Hz); MS m/z 158(M^+).

Found: C, 75.93; H, 6.42; N, 17.57%. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71%; M, 158.

*1,2,3,4-Tetrahydroazepino[3,4,5-hi]indolizine (**3b**)*: Yield 98%; colorless needles; mp 87—89 °C; IR (KBr) 3260 cm^{-1} (NH); ^1H NMR($CDCl_3$) δ=2.0 (1H, s, NH), 3.0—3.2 (4H, m, 3 and 4-H), 4.06 (2H, s, 1-H), 6.3 (2H, m, 9 and 10-H), 6.52 (1H, d, 5-H, J=2 Hz), 7.18 (1H, d, 6-H, J=2 Hz), and 7.62 (1H, dd, 8-H, J=5 and 3 Hz); MS m/z 172 (M^+).

Found: C, 76.54; H, 7.18; N, 16.24%. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27%; M, 172.

Reaction of [hi]Fused Indolizines with DMAD (Typical Procedure): To a solution of **3a** (4.65 mmol) and triethylamine (6 mmol) in THF (20 ml), ethyl chloroformate (5 mmol) was added and the mixture was allowed to stand at room temperature overnight. After being filtrated the precipitates, the filtrate was concentrated to give a residue, which was treated with a short column chromatography (silica gel-chloroform) to afford **4a** quantitatively. Without further purification, **4a** was reacted with DMAD (5 mmol) in toluene (30 ml) under reflux in the presence of 0.5 g of 5% Pd/C overnight and the reaction mixture was worked up usually to give the cyclazine **5a**.

*2-Ethoxycarbonyl-2,3-dihydro-1H-pyrido[3,4,5-hi]indolizine (**4a**)*: Pale yellow oil; ^1H NMR ($CDCl_3$) δ=1.20 (3H, t, $-CH_3$, J=7 Hz), 4.12 (2H, q, $-CH_2-$, J=7 Hz), 4.62, 4.72 (2H each, 2s, 1 and 3-H), 6.1—6.3 (2H, m, 8 and 9-H), 6.46 (1H, d, 4-H, J=2 Hz), 7.03 (1H, d, 5-H, J=2 Hz), and 7.46 (1H, br d, 7-H, J=6 Hz).

*2-Ethoxycarbonyl-2,3-dihydro-5,6-bis(methoxycarbonyl)-1H-pyrido[3,4,5-hi]pyrrolo[2,1,5-cd]indolizine (**5a**)*: Yellow prisms; mp 95—96 °C; IR (KBr) 1725 and 1675 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ=1.34 (3H, t, $-CH_3$, J=7 Hz), 4.01, 4.05 (3H each, 2s, $-CH_3$), 4.23 (2H, q, $-CH_2-$, J=7 Hz), 5.2—5.3 (4H, br, 1 and 3-H), 7.36 (1H, br s, 4-H), 7.68 (1H, d, 8-H, J=8 Hz), and 8.35 (1H, d, J=8 Hz); MS m/z 370 (M^+).

Found: C, 61.65; H, 4.98; N, 7.89%. Calcd for $C_{19}H_{18}N_2O_6$: C, 61.61; H, 4.90; N, 7.56%; M, 370.

*2-Ethoxycarbonyl-1,2,3,4-tetrahydroazepino[3,4,5-hi]-indolizine (**4b**)*: Pale yellow oil; ^1H NMR ($CDCl_3$) δ=1.1—1.3 (3H total, m, $-CH_3$), 3.1—3.3 (2H total, m, 4-H), 3.7—3.9 (2H total, m, 3-H), 4.0—4.2 (2H total, m, $-CH_2-$), 4.64, 4.68 (2H total, 2s, 1-H), 6.4 (2H, m, 9 and 10-H), 6.58 (1H, br s, 5-H), 7.24 (1H, br s, 6-H), and 7.70 (1H, br d, 8-H, J=6 Hz).

*2-Ethoxycarbonyl-1,2,3,4-tetrahydro-6,7-bis(methoxycarbonyl)-azepino[3,4,5-hi]pyrrolo[2,1,5-cd]indolizine (**5b**)*: Yellow prisms; mp 133—135 °C; IR (KBr) 1730, 1690, and 1665 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ=1.2—1.3 (3H total, m, $-CH_3$), 3.4—3.5 (2H total, m, 4-H), 3.94 (2H total, m, $-CH_2-$), 5.15, 5.20 (2H total, 2s, 1-H), 7.4 (1H, br s, 5-H), 7,60, 7.63 (1H total, 2d, 9-H, J=8 Hz each), 8.30, and 8.32 (1H total, 2d, 8-H, J=8 Hz each); MS m/z 384 (M^+).

Found: C, 62.51; H, 5.23; N, 7.31%. Calcd for $C_{20}H_{20}N_2O_6$: C, 62.49; H, 5.24; N, 7.29%; M, 384.

Reaction of [hi]Fused Indolizines with DBZA (Typical Procedure): To a cooled at 0 °C and stirred solution of **4a** (1 mmol) in THF (10 ml), DBZA (1 mmol) in THF (5 ml) was added dropwise for 10 min. After the consumption of the starting materials being confirmed by TLC, DDQ (1.1 mmol) in THF (5 ml) was added to the mixture, which was allowed to stir for additional 10 min at the same temperature. The resultant hydroquinone was filtered off and the filtrate was evaporated to dryness. Chromatography on silica gel with chloroform as an eluent gave **6a** (264 mg, 57%).

*5,6-Dibenzoyl-2-ethoxycarbonyl-2,3-dihydro-1H-pyrido[3,4,5-hi]pyrrolo[2,1,5-cd]indolizine (**6a**)*: Yellow prisms; mp 69—71 °C; IR (KBr) 1690 and 1655 cm^{-1}(CO); ^1H NMR ($CDCl_3$) δ=1.35 (3H, t, $-CH_3$, J=7 Hz), 4.30 (2H, q, $-CH_2-$, J=7 Hz), 5.3(4H, br, 1 and 3-H), 7.3—7.6 (7H, m, 8-H and phenyl protons), 7.6—7.9 (5H, m, 4-H and phenyl protons), and 8.14 (1H, d, 7-H, J=8 Hz); MS m/z 462 (M^+).

Found: C, 75.49; H, 5.10; N, 5.87%. Calcd for $C_{29}H_{22}N_2O_4$: C, 75.31; H, 4.80; N, 6.06%; M, 462.

*6,7-Dibenzoyl-2-ethoxycarbonyl-1,2,3,4-tetrahydroazepino[3,4,5-hi]pyrrolo[2,1,5-cd]indolizine (**6b**)*: Yellow prisms; mp 147—150 °C; IR (KBr) 1700 and 1650 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ=1.2—1.4 (3H total, m, $-CH_3$), 3.4—3.5 (2H total, m, 4-H), 3.95 (2H, br t, 3-H, J=7 Hz), 4.1—4.3 (2H total, m, $-CH_2-$), 5.22, 5.27 (2H total, 2s, 1-H), 7.2—7.5 (7H, m, 5-H and phenyl protons), 8.15, and 8.19 (1H total, 2d, 8-H, J=8 Hz each); MS m/z 476 (M^+).

Found: C, 75.50; H, 5.10; N, 5.67%. Calcd for $C_{30}H_{24}N_2O_4$: C, 75.61; N, 5.08; N, 5.88%; M, 476.

*Identification of Primarily-formed Intermediates in the Reaction of [hi]Fused Indolizines **4** with DBZA or DMAD (Typical Procedure)*: DBZA (1 mmol) in THF (5 ml) was added to a solution of **4b** (1 mmol) in THF (10 ml) for 10 min at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for additional 10 min at the same conditions, evaporated to dryness, and a reddish crystalline **7b** (296 mg, 62%) was obtained from ether.

*6-(1,2-Dibenzoylvinyl)-2-ethoxycarbonyl-1,2,3,4-tetrahydroazepino[3,4,5-hi]indolizine (**7b**)*: Red prisms, mp 170—171 °C; IR (KBr) 1690 and 1650 cm^{-1} (CO);^1H NMR ($CDCl_3$) δ=1.99 (3H, t, $-CH_3$, J=7 Hz), 2.9—3.1 (2H, m, 4-H), 3.72 (2H, br t, 3-H, J=6 Hz), 4.07 (2H, q, $-CH_2-$, J=7 Hz), 4.6—4.8 (2H, br s, 1-H), 6.6—6.8 (3H, m, 5, 9, and 10-H), 7.3—7.6 (7H, m, vinyl and phenyl protons), 7.8—8.0 (4H, m, phenyl protons), and 8.46 (1H, br d, 8-H, J=6 Hz); MS m/z 478 (M^+).

Found: C, 75.13; H, 5.60; N, 6.02%. Calcd for $C_{30}H_{26}N_2O_4$: C, 75.29; H, 5.48; N, 5.85%; M, 478.

The reaction of **4a** with DBZA gave a reddish amorphous **7a** (62%), whose structure was confirmed by ^{1}H NMR spectral data without satisfactory analytical data.

*5-(1,2-Dibenzoylvinyl)-2-ethoxycarbonyl-2,3-dihydro-1H-pyrido-[3,4,5-hi]indolizine (**7a**)*: ^{1}H NMR ($CDCl_3$) δ=1.90 (3H, t, $-CH_3$, J=7 Hz), 4.32 (2H, q, $-CH_2-$, J=7 Hz), 4.70, 4.75 (2H each, 2s, 1 and 3-H), 6.6—6.8 (3H, m, 4, 8, and 9-H), 7.2—7.6 (7H, m, vinyl and phenyl protons), 7.7—8.0 (4H, m, phenyl protons), and 8.33 (1H, br d, 7-H, J=6 Hz).

The formation of 6-vinylindolizine **9b** from **4b** and DMAD was elucidated by the ^{1}H NMR spectrum of the reaction mixture in octadeuteriodioxane. It showed three singlets at δ 3.78 and 3.92 (methyl protons), 6.04 (vinyl proton), and a doublet at δ 8.00 (8-H, J=6 Hz) besides the other protons overlapped with those of **5b**.

*Reactions of 6-Vinylindolizines **7** with DDQ (Typical Procedure)*: A mixture of **7b** (0.21 mmol) and DDQ (0.22 mmol) in THF (5 ml) was stirred at 0 °C for 30 min and evaporated *in vacuo* to give a residue. The residue was treated with a short column chromatography (silica gel-chloroform) to give **6b** (84 mg, 84%).

A mixture of **7b** (0.42 mmol) and DDQ (0.44 mmol) in dioxane (10 ml) was refluxed for 10 min. After the usual working-up, 145 mg(73%) of **8b** was obtained.

*6-(1,2-Dibenzoylvinyl)-2-ethoxycarbonyl-1,2-dihydroazepino[3,4,5-hi]indolizine (**8b**)*: Red prisms; mp 132—134 °C; IR (KBr) 1690 and 1655 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ=1.26 (3H, t, $-CH_3$, J=7 Hz), 4.18 (2H, q, $-CH_2-$, J=7 Hz), 4.61 (2H, br s, 1-H), 5.90 (1H, d, 4-H, J=8 Hz), 6.60 (1H, d, 3-H, J=8 Hz), 6.7—6.8 (3H, m, 5, 9, and 10-H), 7.3—7.6 (7H, m, vinyl and phenyl protons), 7.8—8.0 (4H, m, phenyl protons), and 8.51 (1H, dd, 8-H, J=6 and 4 Hz); MS m/z 476 (M^+).

Found: C, 75.52; H, 5.14; N, 5.82%. Calcd for $C_{30}H_{24}N_2O_4$: C, 75.61; H, 5.08; N, 5.88%; M, 476.

*Reactions of 6-Vinylindolizine **9b** with DDQ (Typical Procedure)*: DDQ (3.5 mmol) was added to a (1:4) mixture of **5b** and **9b**, from indolizine **4b** (1.64 mmol) and DMAD (1.76 mmol), in dioxane (20 ml) and the reaction mixture was refluxed for 30 h. The resultant hydroquinone was removed by filtration and the filtrate was worked up usually to give **10b** (412 mg, 66%).

*2-Ethoxycarbonyl-6,7-bis(methoxycarbonyl)-1,2-dihydroazepino-[3,4,5-hi]pyrrolo[2,1,5-cd]indolizine (**10b**)*: Orange prisms; mp 118—120 °C, IR (KBr) 1720 and 1700 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ=1.28 (3H, t, $-CH_3$, J=7 Hz), 4.04, 4.07 (3H each, 2s, $-CH_3$), 4.24 (2H, q, $-CH_2-$, J=7 Hz), 5.21 (2H, s, 1-H), 6.43 (1H, d, 4-H, J=8 Hz), 6.84 (1H, br d, 3-H, J=8 Hz), 7.42 (1H, s, 5-H), 7.70 (1H, d, 9-H, J=8 Hz), and 8.34 (1H, d, 8-H, J=8 Hz); MS m/z 476 (M^+).

Found: C, 75.50; H, 5.10; N. 5.67%. Calcd for $C_{30}H_{24}N_2O_4$: C, 75.61; H, 5.08; N, 5.88%; M, 476.

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References

1) Studies on Nitrogen-bridged Heterocycles. V. Part IV in this series: M. Noguchi, N. Tanigawa, H. Okumura, and S. Kajigaeshi, submitted to *Heterocycles*.

2) M. Noguchi, N. Tanigawa, T. Yamamoto, and S. Kajigaeshi, *Chem. Lett.*, **1985**, 873.

3) M. Noguchi, N. Tanigawa, H. Okumura, and S. Kajigaeshi, submitted to *Heterocycles*.

4) M. Noguchi, N. Tanigawa, and S. Kajigaeshi, *J. Heterocycl. Chem.*, **22**, 1049 (1985).

5) M. Noguchi, H. Kan, and S. Kajigaeshi, *Chem. Pharm. Bull.*, **31**, 3342 (1983).

6) S. Ikeda, S. Kajigaeshi, and S. Kanemasa, *Chem. Lett.*, **1976**, 367.

7) Y. Yamashita, D. Suzuki, and M. Masumura, *Heterocycles*, **22**, 705 (1984).

8) A. Galbraith, T. Small, R. A. Barnes, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 453 (1961).