Ring Transformations Involving Pyrido[1,2-*b*]cinnolin-6-ium Hydroxide Inner Salts

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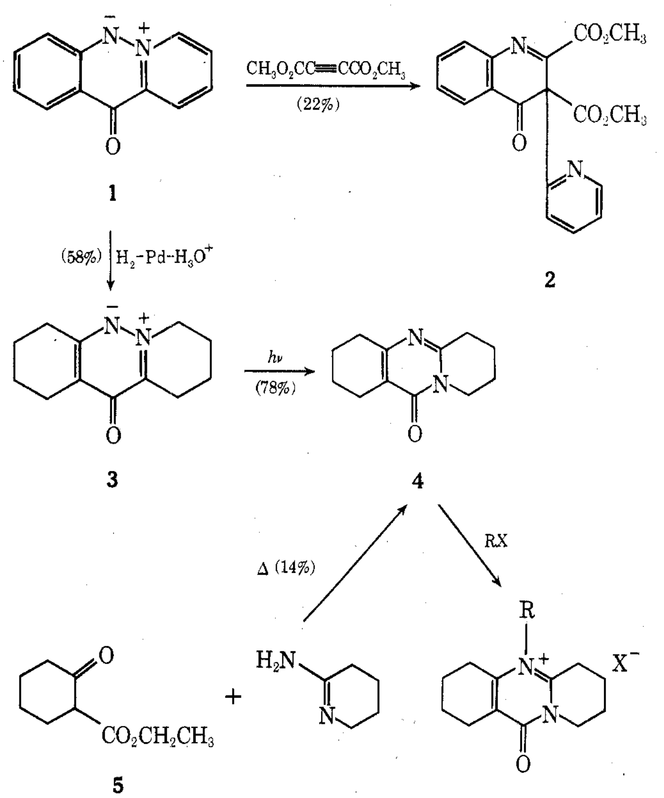
The heating of the mesoionic 5,11-dihydro-11-oxopyrido[1,2-*b*]cinnolin-6-ium hydroxide inner salt (1) with dimethyl acetylenedicarboxylate afforded 2,3-dicarbomethoxy-3,4-dihydro-3-(2-pyridyl)quinolin-4-one (2). The 1,2,3,4,7,8,9,10-octahydro derivative of 1 (3) undergoes photoisomerization, in high yield, to 1,2,3,4,6,7,8,9-octahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (4). Structures of 2 and 4 (as the hydrobromide salt **7b**) were unambiguously established by X-ray crystallography. Compound 4 was also directly synthesized.

We recently reported[1] on the preparation and chemistry of 5,11-dihydro-11-oxopyrido[1,2-*b*]cinnolin-6-ium hydroxide inner salt (**1**)[2] and related compounds. In the course of further investigation of these novel substances, we encountered two products (**2** and **4**) which resulted from unusual rearrangements. The structures of these products were unambiguously established by X-ray crystallography. We wish to record these rearrangements as interesting examples of ring transformation reactions.[3]



7a, R = H; X = ClO_4^-
b, R = H; X = Br^-
c, R = CH_3; X = $CH_3SO_4^-$

Recent interest in dipolar cycloadditions involving six-membered mesoionic ring systems[4,5] prompted us to treat **1** with dimethyl acetylenedicarboxylate. The sluggishness of the reaction necessitated the heating (100°) of **1** in undiluted dimethyl acetylenedicarboxylate for 30 hr. The only product we could isolate from the complex reaction mixture was **2**, obtained in 22% yield. Several aspects of the spectral properties of **2**, especially the very different carbonyl frequencies (1760 and 1715 cm^{-1}) of the carbomethoxy groups, were inconsistent with simple 1:1 cycloadducts. The eventual assignment of structure **2** by X-ray crystallography confirmed our suspicion of the occurrence of an extensive rearrangement.

We have described earlier[1] the catalytic hydrogenation of **1** over Raney nickel in tetrahydrofuran to yield the octahydro derivative **3**. In the course of preparing larger amounts of compound **3**, we found that more consistent results were obtained if palladium on carbon and aqueous hydrochloric acid were used as catalyst and solvent, respectively. When **3** was photolyzed with a medium-pressure mercury lamp, isomerization occurred cleanly. The photoproduct[6] was isolated in 78% yield. After structure **4** was established by X-ray crystallographic analyses of its hydrobromide salt, **7b**, confirmation of **4** by synthesis was easily achieved by the condensation of 2-carbethoxycyclohexanone (**5**) with 2-iminopiperidine (**6**).

Several salts of **4** were prepared. The presence of the carbonyl bands (1700 cm^{-1}) in the infrared spectra of the perchlorate, hydrobromide, and the quaternary methylsulfonate salts **7a**, **7b**, and **7c**, respectively, are consistent with protonation and alkylation on nitrogen rather than oxygen.

Mechanisms. Plausible mechanisms for the formation of **2** and **4** are shown in Scheme I. The initial 1,3-dipolar cycloaddition to **1** leading to intermediate A is reasonable.[5,7] Subsequent ring opening (to B) and reclosure as shown completes the transformation to the quinolinone **2**.

The most likely intermediate in the photolysis of **3** is the diaziridine[8,9] C. Ring-fused diaziridines have been isolated from photoisomerization of the ylide form of 1,5-dimethyl-6-phenyl-2,3-dihydrodiazepin-4-one,[10] and implicated in the photorearrangements of acyliminopyridinium *N*-ylides[11-14] and iminoquinolinium *N*-ylides.[15,16] The diaziridine C can open to the intermediate ketene D, which cyclizes to give **4**. It is of interest to note that the ketene intermediates B and D belong to the class of α-acyl-, α-thioacyl-, and α-imidoylketene intermediates which apparently readily undergo 1,4-cycloaddition reactions in the manner similar to those proposed here.[17]

Crystallography.[18] Crystal structure analyses were done for **2**, **4**, and **7b**. The cell dimensions for each compound were obtained from a least-squares fit of 14 well-centered reflections with $30° < 2\theta < 40°$. Intensity data for all three compounds were measured on a Hilger-Watts four-circle diffractometer (θ–2θ scans, Ni filtered Cu Kα radiation, plus height discrimination). The structures of **2** and **4** were solved by a multiple solution procedure[19] and that of **7b** by Patterson and Fourier methods. All refinements were carried out by full-matrix least squares. The unweighted discrepancy index is given by $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and the weighted index by $R_w = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$.

Crystal data for **2** are: triclinic, space group $P\bar{1}$, $a = 7.586$ (5), $b = 8.625$ (4), $c = 12.091$ (6) Å, $\alpha = 86.93$ (3), $\beta = 86.19$

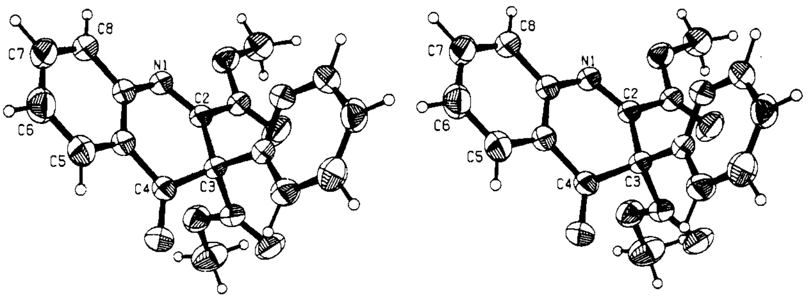
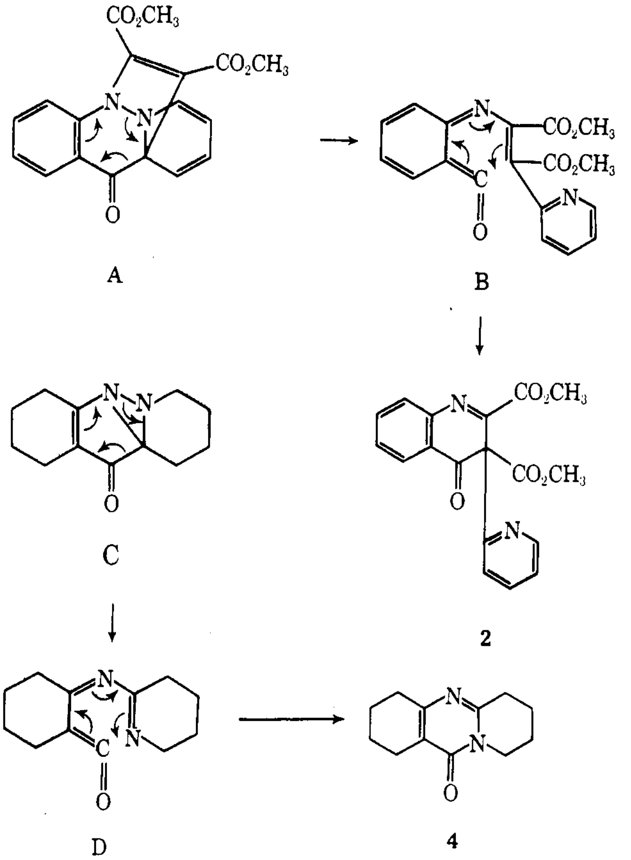


Figure 1. A stereodrawing of the structure of **2**.

Scheme I



(5), γ = 82.55 (4)°, Z = 2, μ (Cu Kα) = 9.04 cm^{-1}. The crystal used for data collection was 0.12 × 0.25 × 0.40 mm in size. Of the 3217 accessible reflections with $\theta < 76°$, 2571 had intensities which were significantly greater than background [$I > 2.5\sigma(I)$].

In the initial (isotropic) refinement of **2** the carbon and nitrogen atoms were all assigned the carbon scattering curve. The nitrogen atoms were identified at the conclusion of this refinement on the basis of their isotropic temperature factors. In the final refinement anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors for the hydrogen atoms. The hydrogen atom parameters were refined. The final R is 0.046 for the 2571 observed reflections. The final difference Fourier has no features greater than 0.1eÅ^{-3} in magnitude. The structure of **2** is shown by the stereodrawing in Figure 1. Using the numbering of the atoms in Figure 1 and indicating the nitrogen and carbon atoms of the pyridine ring as N′ and C′ respectively, the distances and angles about the two nitrogen atoms are, C(8a)-N(1), 1.418 (3) Å; N(1)-C(2), 1.271 (3) Å; C(8a)-N(1)-C(2), 119.2 (2)°; C(6′)-N(1′), 1.342 (3) Å; N(1′)-C(2′), 1.335 (3) Å; C(6′)-N(1′)-C(2′), 117.4 (2)°.

Crystal data for **4** are: monoclinic, space group Pn, a = 9.887 (6), b = 6.328 (5), c = 9.578 (8) Å, β = 117.05 (4)°, Z = 2, μ (Cu Kα) = 6.6 cm^{-1}. There were 1048 accessible reflections with $\theta < 76°$ of which 661 were considered observed. Although the gross structure was obtained easily, the analysis did not succeed in distinguishing between carbon and nitrogen atoms. Owing to this failure, an X-ray analysis of **7b** was undertaken.

Crystal data for **7b** are: orthorhombic, space group $P2_12_12_1$, a = 6.106 (5), b = 11.924 (10), c = 17.192 (15) Å, Z = 4, μ (Cu Kα) = 47.9 cm^{-1}. The size of the crystal used for data collection was 0.2 × 0.2 × 0.5 mm. Of the 2575 accessible reflections ($\theta < 76°$, *hkl* and *hkl* octants), 2166 were considered observed. These data were corrected for absorption. The crystal structure of **7b** was solved (except for the C vs. N ambiguity) by straightforward application of the heavy-atom method. In the preliminary stages of refinement all atoms except the oxygen and bromine were treated as carbon atoms and the imaginary part of the anomalous dispersion correction ($\Delta f''$) was set to zero. The first few cycles of least squares were done using isotropic temperature factors for all atoms. This refinement was followed by four cycles of least squares in which all atoms had anisotropic thermal parameters. At this point two sets of structure factors were calculated, one using the correct value of $\Delta f''$ and the other with the sign of $\Delta f''$ reversed (equivalent to refining the antipode). The absolute configuration of the crystal structure of **7b** was taken as the one corresponding to the lower R_w value (R_w = 0.082 and 0.088). The complete anomalous dispersion correction was used in all subsequent refinements.

It was apparent from the anisotropic thermal parameters that there was a disorder involving atoms C(12) and C(13) (see Figure 2 for the atom labeling scheme). That is, the ring containing these two atoms randomly assumes either of two conformations in the crystal. To account for this disorder, the two atoms C(12) and C(13) were replaced by four atoms, C(12)A, C(12)B, C(13)A, and C(13)B, each with an atom multiplier of 0.5. Isotropic temperature factors were used for these half-carbons in all subsequent refinements. Following refinement of the trial structure including the half-atoms a difference map was calculated. Peaks were found at reasonable positions for hydrogen atoms about those atoms not involved in the disorder, including a peak of 0.8 Å from the atom at position 4 [N(4) in Figure 2]. The positions of all hydrogen atoms were calculated. Two sets of eight half-hydrogens were used for the hydrogen atoms about the carbon atoms involved in the disorder. The refinement was continued for the structure including the hydrogen atoms. At the end of this refinement the discrepancy indices were R = 0.0453 and R_w = 0.0658.

All that remained to be done at this point was to identify the nitrogen atoms. It was assumed that both nitrogens were part of the central ring and that the atom bonded to O(1) was a carbon. Thus there were ten possible trial struc-

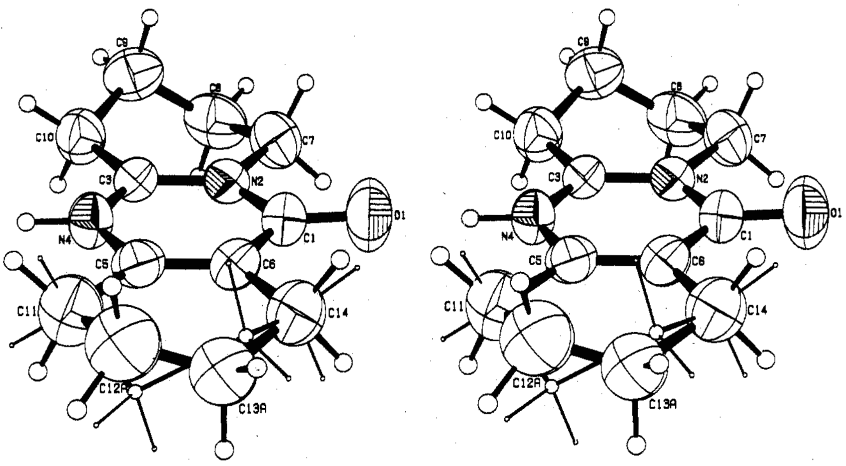


Figure 2. A stereodrawing of the cation of **7b.** The anisotropic atoms and C(12)A and C(13)A are scaled to the 50% probability level. The hydrogen atoms, including those which are part of the conformer containing C(12)A and C(13)A, are shown as spheres of a fixed arbitrary size. The carbon atoms C(12)B and C(13)B and the hydrogen atoms which are part of the other conformer are shown as very small spheres connected by thin bonds.

Table I
***R* Factors for the Various Trial Structures of 7b**

Positions of nitrogen atoms	R	R_w
2,3	0.0447	0.0654
2,4	0.0386	0.0591
2,5	0.0441	0.0656
2,6	0.0440	0.0654
3,4	0.0456	0.0658
3,5	0.0490	0.0707
3,6	0.0494	0.0713
4,5	0.0442	0.0650
4,6	0.0446	0.0649
5,6	0.0491	0.0712

Table II
Distances and Angles about the Atoms Comprising the Central Ring of 7b as Indicated in Figure 2

C(6)–C(1)	1.433 (8) Å	C(6)–C(1)–N(2)	115.8 (4)[a]
C(1)–N(2)	1.423 (6)	C(1)–N(2)–C(3)	122.2 (4)
N(2)–C(3)	1.316 (6)	N(2)–C(3)–N(4)	119.5 (4)
C(3)–N(4)	1.320 (6)	C(3)–N(4)–C(5)	122.6 (4)
N(4)–C(5)	1.384 (6)	N(4)–C(5)–C(6)	119.9 (4)
C(5)–C(6)	1.324 (7)	C(5)–C(6)–C(1)	119.8 (4)
C(1)–O(1)	1.225 (7)	C(6)–C(1)–O(1)	124.7 (5)
N(2)–C(7)	1.485 (7)	N(2)–C(1)–O(1)	119.5 (5)
C(3)–C(10)	1.495 (7)	C(1)–N(2)–C(7)	115.1 (4)
C(5)–C(11)	1.497 (8)	C(3)–N(2)–C(7)	122.6 (4)
C(6)–C(14)	1.513 (7)	N(2)–C(3)–C(10)	122.3 (5)
		N(4)–C(3)–C(10)	118.2 (4)
		N(4)–C(5)–C(11)	114.5 (5)
		C(6)–C(5)–C(11)	125.6 (5)
		C(5)–C(6)–C(14)	121.5 (5)
		C(1)–C(6)–C(14)	118.6 (5)

tures in which the remaining five atoms of the central ring could be assigned as two nitrogen and three carbon atoms. The discrepancy indices for these ten trial structures are listed in Table I. The *R* factor ratio test of Hamilton[20] was used to compare the R_w values of the various trial structures in Table I with the R_w value of the structure with nitrogen atoms at positions 2 and 4. These other nine trial structures could be rejected at a significance level of 0.005 (two-dimensional hypothesis, 2023 degrees of freedom). Thus it is established that the nitrogen atoms are located at positions 2 and 4 (Figure 2).

Further evidence that N(4) is a nitrogen atom is provided by the fact that it is hydrogen bonded to the bromide ion. The N···Br distance is 3.23 Å and the N–H···Br angle is 177°. The bond distances and angles about the atoms comprising the central ring are given in Table II. In the final refinement isotropic temperature factors were used for the hydrogen atoms and the four half-weighted carbon atoms and anisotropic thermal parameters were used for all other atoms. The hydrogen atoms were included in the structure factor calculations, but they were not refined. The final discrepancy index is $R = 0.039$ for the 2166 observed reflections. There were two peaks (-0.5 and $-0.6e\text{Å}^{-3}$), both about 0.85 Å from the bromide ion, on the final difference Fourier. There were no other peaks greater than $0.4e\text{Å}^{-3}$ in magnitude.

Experimental Section

All melting points were taken in capillaries, heated in oil baths, and are corrected. Infrared spectra were determined on a Beckman IR-9 or a Perkin-Elmer 621 grating spectrometer, mass spectra on a Jeolco 01SG or a CEC-21-110 spectrometer, nuclear magnetic resonance spectra on a Varian A-60 or a Varian HA-100 spectrometer, using tetramethylsilane as internal standard, and ultraviolet spectra with a Cary 14M or 15 recording spectrometer. Solvents used were of reagent grade purity. Petroleum ether used boils at 30–60°. Unless otherwise specified, all solvents were evaporated on a Büchi Rotavapor evaporator under water-aspirator pressure using a water bath set at 30–80°. The progress of reactions was routinely followed by thin layer chromatography (TLC).

2,3-Dicarbomethoxy-3,4-dihydro-3-(2-pyridyl)quinolin-4-one (2). A mixture of 5,11-dihydro-11-oxopyrido[1,2-*b*]cinnolin-6-ium hydroxide inner salt[1] (**1**, 20.0 g, 10.2 mmol) and 60 ml of dimethyl acetylenedicarboxylate (Aldrich Chemical Co.) was heated in a stoppered flask on a steam bath for 30 hr. On cooling, the dark, viscous oil was triturated three times with 100-ml portions of boiling ether. The combined ethereal solutions were filtered and concentrated to near dryness, giving 3.0 g of slightly impure **2** as colorless prisms, mp 151–153°. The crystals were dissolved in ether. The ethereal solution was filtered through a pad of neutral alumina (10 g), which was then washed with ether. The combined ethereal filtrate and washing was evaporated. The solid residue was recrystallized from ethyl acetate–hexane to give 2.5 g of large, colorless prisms, mp 157–160°. These crystals were used for X-ray crystallographic analysis.

The ether-insoluble portion of the original product mixture was dissolved in a small volume of tetrahydrofuran and applied to the top of a short column of alumina (100 g of Woelm activity I grade) which was packed in ether. Elution of this column with ether afforded pure **2**, which after crystallization from ethyl acetate–hexane weighed 5.1 g as colorless prisms, mp 156–159°. The total yield was 7.6 g (22%): ir (KBr) 1760, 1715, and 1685 cm^{-1}; uv max (CH_3CN) 244 nm (ϵ 30,800), 331 (4300); NMR (DMSO-d_6) δ 3.68 (s, 3, CH_3), 3.81 (s, 3, CH_3), 7.28–8.40 ppm (m, 8, aromatic); mass spectrum *m/e* 338 (M^+).

Anal. Calcd for $C_{18}H_{14}N_2O_5$: C, 63.91; H, 4.17; N, 8.28. Found: C, 63.64; H, 4.07; N, 8.09.

1,2,3,4,5,7,8,9,10,11-Decahydro-11-oxopyrido[1,2-*b*]cinnolin-6-ium Hydroxide Inner Salt (3).[1] A suspension of 90 g (0.46 mol) of 5,11-dihydro-11-oxopyrido[1,2-*b*]cinnolin-6-ium hydroxide inner salt (1) and 100 g of 10% palladium on carbon in 3 l. of 0.2 *N* aqueous hydrochloric acid was hydrogenated under 1 atm hydrogen at room temperature. After 20 hr the uptake of hydrogen became sluggish and TLC indicated that the reaction was essentially complete. The catalyst was removed by filtration. The filtrate was basified (pH 9) with 6 *N* sodium hydroxide. The product was isolated by extraction with methylene chloride. On crystallization from acetonitrile, 54.5 g (58%) of **3** was obtained, mp 198–200°. This material was identical with that which we reported earlier[1] (mp 196–198°).

1,2,3,4,6,7,8,9-Octahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (4). A. From Photoisomerization of 3. A solution of 35.5 g (0.175 mol) of **3** in 4 l. of tetrahydrofuran was photolyzed under nitrogen with a 250-W medium-pressure mercury lamp (Hanovia 654A) through quartz. The quartz well was cleaned when it became coated with a brown film in the course of the photolysis. After 5 days, TLC indicated a clean and complete conversion. Solvent was evaporated. Trituration of the residue with ether afforded 27.7 g (78%) of amorphous **4**, mp 168–170°. Recrystallization from acetone–hexane afforded colorless prisms: mp 168–170°; ir (KBr) 1660 cm^{-1}; molecular ion *m/e* 204 (calcd 204); uv max (CH_3CN) 232 nm (ϵ 5660) and 276 (5460); NMR ($CDCl_3$) δ 1.6–2.1 (m, 8, 4 CH_2), 2.3–2.7 (m, 4, 2 CH_2), 2.85 (t, 2, CH_2), and 3.92 ppm (t, 2, CH_2).

Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.71. Found: C, 70.47; H, 7.75; N, 13.72.

B. By Synthesis. A solution of 2.5 g (18.5 mmol) of 2-iminopiperidine hydrochloride in 5.5 g (~32 mmol) of ethyl 2-cyclohexanone carboxylate (both reagents from Aldrich Chemical Co.) containing 0.5 ml of glacial acetic acid was heated under reflux, under nitrogen, for 20 hr. The reaction mixture was partitioned between methylene chloride and water which was basified with dilute ammonium hydroxide. The methylene chloride layer was washed with water, dried (Na_2SO_4), and evaporated. Crystallization of the residual oil from ether afforded 0.52 g (14%) of **4**, mp 162–165°. This material was found to be identical (TLC, ir) with the sample from the photoisomerization of **3** as described above.

The perchlorate salt (**7a**) was prepared by dissolving the free base **4** with a slight excess of concentrated perchloric acid (70%) in a mixture of methylene chloride and tetrahydrofuran. Solvents were evaporated. Crystallization from acetone–ether afforded the perchlorate salt in 76% yield as light tan prisms, mp 182–184°, ir (KBr) 1700 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}N_2O \cdot HClO_4$: C, 47.30; H, 5.62; N, 9.19 Found: C, 47.53; H, 5.72; N, 9.30.

The hydrobromide salt (**7b**) was prepared by passing gaseous hydrogen bromide into a solution of the free base in methylene chloride. The salt crystallized from methylene chloride–ethyl acetate in 94% yield, mp 288–292° dec, ir (KBr) 1700 cm^{-1}. The crystals (light amber rods) used in X-ray crystallography were obtained by slow crystallization resulting from the solution of the free base in ethyl bromoacetate which contained some hydrogen bromide.

Anal. Calcd for $C_{12}H_{16}N_2O \cdot HBr$: C, 50.54; H, 6.01; N, 9.82; Br^-, 28.02. Found: C, 50.60; H, 6.03; N, 10.11; Br^-, 28.19.

Thermal Stability of 3. Three melting point capillaries containing **3** (mp 196–198°) were heated in an oil bath at 199–200°. The capillaries were withdrawn one at a time after 5, 15, and 45 min. TLC of the melted samples showed that the bulk of **3** was intact and that little or none of the photoproduct **4** was formed.

5-Methyl-1,2,3,4,6,7,8,9-octahydro-11-oxo-11*H*-pyrido[2,1-*b*]quinazolin-5-ium Methylsulfate (7c). A mixture of 4.08 g (20 mmol) of **4** and 10 ml of dimethyl sulfate was heated on a steam bath for 0.5 hr. The clear solution was diluted with ether, affording 4.6 g (70%) of light tan prisms, mp 155–157°. Recrystallizations from acetone afforded light tan needles, mp 153–155°, ir (KBr) 1700 cm^{-1}.

Anal. Calcd for $C_{14}H_{22}N_2O_5S$: C, 50.89; H, 6.71; N, 8.48. Found: C, 50.56; H, 6.79; N, 8.32.

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Registry No.—**1**, 53114-16-2; **2**, 55450-47-0; **3**, 53114-22-0; **4**, 55450-48-1; **5**, 1655-07-8; **6** HCl, 16011-96-4; **7a**, 55450-49-2; **7b**, 55450-50-5; **7c**, 55450-52-7; dimethyl acetylenedicarboxylate, 762-42-5.

Supplementary Material Available. Tables of the positional and thermal parameters for the structures of **2** and **7b** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (100 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W. Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2201.

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