Tetrahydroquinolizinium Ylides: Preparation and 1,3-Dipolar Cycloaddition†

Elena I. Kostik,‡ Atsushi Abiko,‡ and Akira Oku*,§

Venture Laboratory and Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, 606-8585 Japan

oku@ipc.kit.ac.jp

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By the Cu(II)-catalyzed reaction of 2-(4-diazo-3-oxoalkyl)pyridines (**2**), 4-alkoxycarbonyl (or 4-acyl)-3-oxo-1,2,3,4-tetrahydroquinolizinium ylides (**3**) were obtained in high yields. From the cycloaddition reaction of **3** with acetylenic esters (propynoates or acetylenedicarboxylates) the labile [2 + 3] cycloadducts, 3-oxo-3*H*-2a,4,5,8a-tetrahydropyrrolo[2,1,5-*de*]quinolizine-2a-carboxylates (**8** or **12**), were identified, which further reacted with DMAD (dimethyl acetylenedicarboxylate) to afford azocine derivatives (**15** or **16**) and produced pyrrolodihydroquinolizines (**9** or **20**) by dealkoxycarbonylation.

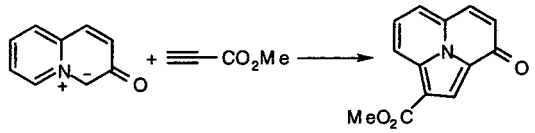
Introduction

Iminium ylides have attracted much attention because of the possible application to the synthesis of a wide variety of novel heterocyclic systems.[1] The 1,3-dipolar cycloaddition reaction of iminium ylides leading to pyrrolidine derivatives has been explored intensively. Recently many efforts are driven to the synthesis of the aza-acenaphthylene ring system ([3,3,2]-cyclazine) by dipolar cycloaddition, especially after the discovery of a new family of coccinellid alkaloids having an aza-acenaphthylene moiety.[2] These tricyclic systems could be accessible from the bicyclic iminium ylides, possessing a nitrogen atom at the ring juncture position, via a 1,3-dipolar cycloaddition reaction (Scheme 1).

The prototype of these bicyclic iminium ylides, 3-oxoquinolizinium betaine, was isolated from the corresponding salt in 1965[3] and was used later as a dipole in the synthesis of [2.2.3]cyclazines.[4] Recently, the synthesis and decarboxylation reaction of stable substituted dihydro-1-oxoquinolizinium ylides were reported.[5] However, only little is known about the chemical and physical properties of iminium ylides having a partially saturated quinolizinium structure, presumably because of limited availability of the precursor, 3-oxotetrahydroquinolizinium salts.

Among the synthetic approaches toward iminium ylides, the reaction of carbenes (or carbenoids) with imines seems to be particularly interesting from its diversity and generality.[6] Stable isoquinolinium and pyridinium ylides, derived from isoquinolines or pyridines and carbenes with electron-withdrawing substituents, have been synthesized and extensively studied. In the last 10 years, such an approach was successfully applied to the intramolecular reaction of carbenes and nitrogen atoms to generate ammonium and iminium cyclic ylides.[7,8] Padwa et al. demonstrated the ability of a variety of α-diazocarbonyl compounds possessing imine moiety to produce bicyclic iminium ylides by the action of rhodium(II) catalysts.[8a] So far, such iminium ylides have been generated in the presence of dipolarophiles and only characterized as 1,3-dipolar cycloadducts.

Scheme 1



In this article, we would like to report syntheses of a series of tetrahydroquinolizinium ylides as stable ylides by the Cu(II)-catalyzed cyclization of 2-(4-diazo-3-oxoalkyl)-pyridines. Investigation of the physical and chemical properties of these quinolizinium ylides, including a detailed study on the 1,3-dipolar cycloaddition reaction of these ylides, is described.

Results and Discussion

Synthesis of Tetrahydroquinolizinium Ylide. The diazocarbonyl-substituted pyridines, requisite for the present study, were prepared by the alkylation of the dianion of 1,3-dicarbonyl compounds with 2-(α-chloroalkyl)pyridines, followed by the reaction with arenesulfonyl azides (Scheme 2). Using this simple protocol a variety of diazo pyridines **2** were prepared conveniently.

† Part 1 of "The Studies on Tetrahydroquinolizinium Ylides".
‡ Venture Laboratory.
§ Department of Chemistry and Materials Technology.

(1) (a) Tsuge, O.; Kanemasa, *S. Adv. Heterocycl. Chem.* **1989**, *45*, 231−349. (b) Claus, P. K. In *Houben-Weyl, Methoden der Organischen Chemie;* Klamann, D., Hagemann, H., Eds.; Thieme: Stuttgart, 1990; E14b, 2, pp 1−221. (c) Beall, L. S.; Padwa, A. In *Advances in Nitrogen Heterocycles;* Moody, C. J., Ed.; Jai Press Inc.: Greenwich, CT, 1998; Vol. 3, pp 117−158.
(2) King, A. G.; Meinwald, J. *Chem. Rev.* **1996**, *96*, 1105.
(3) Duke, P. A.; Fozard, A.; Jones, G. *J. Org. Chem.* **1965**, *30*, 526.
(4) Farquhar, D.; Gough, T. T.; Leaver, D.; Miller, J. F.; Dick, J. W.; Jessep, M. A. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2553.
(5) Matsuda, Y.; Katou, K.; Nishiyori, T.; Uemura, T.; Urakami, M. *Heterocycles* **1997**, *45*, 2197.
(6) (a) Surpateanu, G.; Catteau, J. P.; Karafiloglou, P.; Lablashe-Combier, A. *Tetrahedron* **1976**, *32*, 2647. (b) Padwa, A.; Hornbuckle, S. *Chem. Rev.* **1991**, *91*, 263.
(7) Naidu, B. N.; West, F. G. *Tetrahedron* **1997**, *53*, 16565.
(8) (a) Padwa, A.; Austin, D. J.; Precedo, L.; Zhi, L. *J. Org. Chem.* **1993**, *58*, 1144. (b) Padwa, A.; Dean, D. C.; Osterhout, M. H.; Precedo, L.; Semones, M. A. *J. Org. Chem.* **1994**, *59*, 5347.

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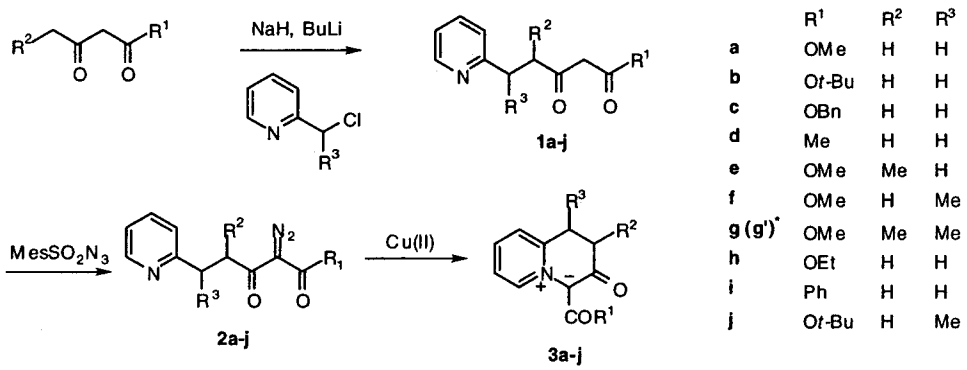
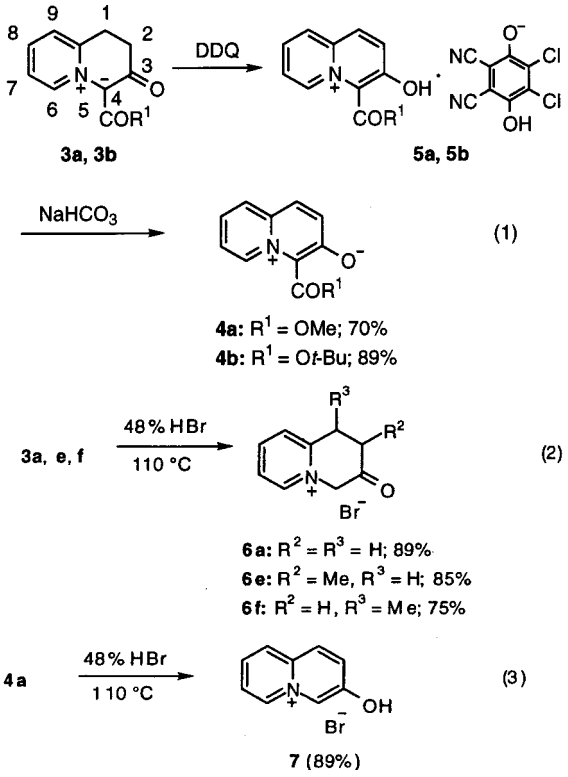
Scheme 2



	R^1	R^2	R^3
a	OMe	H	H
b	O*t*-Bu	H	H
c	OBn	H	H
d	Me	H	H
e	OMe	Me	H
f	OMe	H	Me
g (g')*	OMe	Me	Me
h	OEt	H	H
i	Ph	H	H
j	O*t*-Bu	H	Me

In the survey of the reaction conditions of the transition-metal-catalyzed decomposition of **2**, copper(II) bis(trifluoroacetylacetonate) was found to be superior to rhodium(II) acetate. Thus, stirring a mixture of **2** and the copper catalyst (2.5 mol %) in dry benzene at 80 °C for 25 min afforded 3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ides (**3**) in high yields.

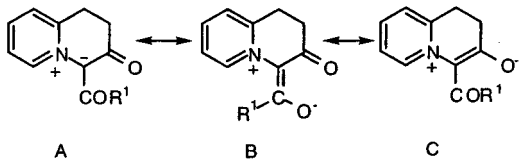
Scheme 3



Most of **3** could be isolated as stable crystals and characterized spectroscopically as well as by elemental analyses. Ylides **3a** and **3b** were readily converted to quinolizinium-3-olates **4a** and **4b** in 70% and 89% yields, respectively, by the oxidation with DDQ followed by neutralization of the resulting DDQH salt (Scheme 3 (1)). Treatment of **3a**, **e**, **f** and **4a** in 48% aqueous HBr at 110 °C for 2 h afforded the corresponding decarboxylated salts **6a**, **e**, **f** (Scheme 3 (2)) and **7** (Scheme 3 (3)), respectively, in high yields. Similarly, the perchlorate salt **6a′** was obtained in 70% yield by the treatment of **3b** with 40% $HClO_4$.[9] Bromide **7** was identical in all respects to the reported specimen.[3,10] Thus, the structures of **4a** and **3a** were unambiguously established.

In the ^1H NMR spectra of compounds **3a**−**j**, four aromatic protons (H6−9, see Scheme 3) appeared at lower fields in comparison with those of pyridine precursors **2**, the H6 proton being observed around δ 9.1, which were similar to those[5] reported for 1,4-dihydroquinolizinium ylides. ^{13}C NMR spectra of 4-alkoxycarbonyl-3-oxo-1,2,3,4-tetrahydroquinolizinium ylides (**3a**−**c**, **3e**−**h**, **3j**) showed the signal of C-4 ylidic carbon around δ 106−109, while those of 4-acyl-3-oxo-l,2,3,4- tetrahydroquinolizinium ylides (**3d** and **3i**) and quinolizinium-3-olates (**4a** and **4b**) appeared around δ 118−123. The IR spectra of the ylides showed carbonyl absorptions at lower frequencies: a 3-carbonyl absorption maximum at 1677 cm^{-1} for *tert*-butyl ester **3b**, at 1656−30 cm^{-1} for other esters **3a**, **c** and **3e**−**h**, and at 1620 cm^{-1} for acyl ylide **3d**. The differences in both the ^{13}C NMR chemical shift of C-4 and the 3-carbonyl IR absorptions suggest that alkoxycarbonyl-substituted ylides (**3a**−**c**, **3e**−**h**, **3j**) mainly exist in a keto form, i.e., canonical structure A (Scheme 4), whereas acyl-substituted (**3d**, **3i**) and dehydrogenated ylides (**4a**, **4b**) do in enolate forms, i.e., canonical structures B and C (Scheme 4).

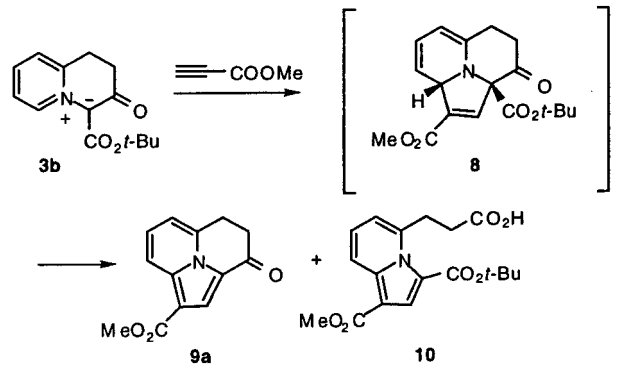
Scheme 4



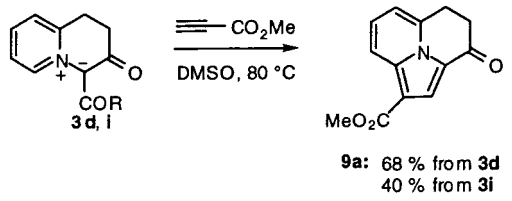
1,3-Dipolar Cycloaddition of Tetrahydroquinolizinium Ylides. Dipolar reactivity of quinolizinium ylides has been reported.[4,8a] Quinolizinium-3-olate reacted with acetylenic dipolarophiles to afford cyclazines via 1,3-dipolar cycloaddition followed by oxidation. The similar transformation, accompanied by the deacylative cleavage of a carbon−carbon bond, was also reported for the reaction of acetyl-substituted ylide with DMAD.[8a] The 1,3-dipolar cycloaddition of isoquinolinium dimethoxycarbonylmethylides with DMAD was explored extensively, and sometimes relatively stable adducts were isolated without oxidation,[6a] whereas it was also reported that the 1,5-dipolar cycloaddition of isoquinolinium diethoxycarbonylmethylides with DMAD produced oxazepines.[8a]

(9) Kröhnke, F. *Chem. Ber.* **1939**, *72*, 83.
(10) Schrtifstitter, E. *Angew. Chem.* **1962**, *74*, 874.

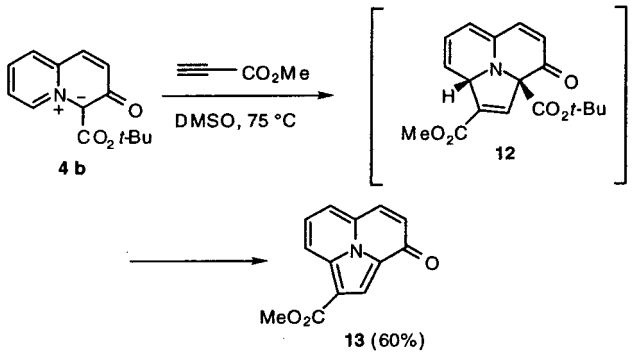
Scheme 5



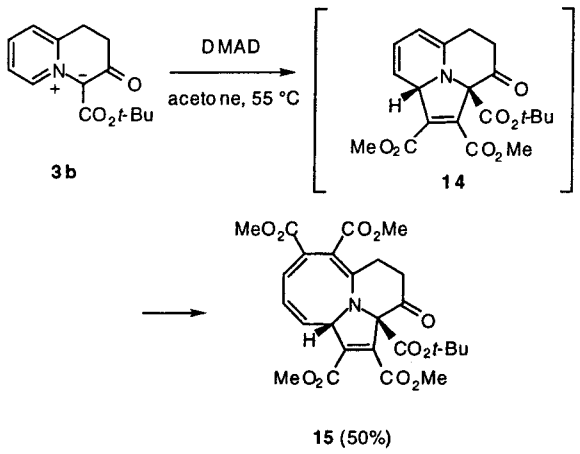
Scheme 6



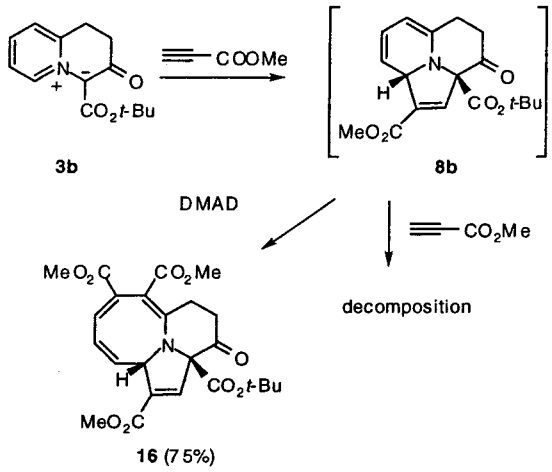
Scheme 7



Scheme 8



Scheme 9



In this regard we were interested in examining the reaction behavior of tetrahydroquinolizinium ylides (**3**) in dipolar cycloadditions. The 1,3-dipolar cycloadducts of ylides **3** should have higher stability toward oxidative transformation to indolizines, because the oxidative aromatization had to proceed through C−C bond cleavage and elimination of alkoxycarbonyl group. Thus, we expected it would be possible to investigate the reaction course in detail by isolating the primary cycloadducts.

Tetrahydroquinolizinium ylides **3** were inert toward ethylenic dipolarophiles but reacted readily with acetylenic esters.[11] For example, ylide **3b** in acetone-d_6 at 55 °C reacted with methyl propynoate within 15 min to furnish 1,3-dipolar cycloadduct **8** as a sole product. Adduct **8** was not stable enough to be isolated, and the structure was assigned on the basis of NMR spectra of the reaction mixture. When the reaction mixture was heated longer in acetone or treated with silica gel, initial monoadduct **8** was transformed into two isolable products, i.e., aromatic cyclazine **9a** and indolizinepropionic acid **10**, with concomitant considerable decomposition. The reaction proceeded more smoothly in DMSO.[12] Thus, in the reaction of **3b** with methyl propynoate in DMSO-d_6 at 75 °C for 10 min, formation of the primary cycloadduct **8** was confirmed by NMR. When the reaction mixture was heated longer (75 °C, 45 min) in DMSO, **9a** (30%) and **10** (14%) were isolated. It should be noted that *t*-BuOH (about 30%) was also detected in the NMR spectra of the reaction mixture (Scheme 5).

Reactions of acyl-substituted ylides **3d,i** with methyl propynoate in DMSO at 75 °C afforded cyclazine **9a** in 68% and 40% yield, respectively (Scheme 6). The formation of 1 equiv (vs **9a**) of acid (acetic or benzoic acid, respectively) was confirmed by the NMR analysis of the reaction mixture.

The same type of primary cycloadduct **12** could be detected in the reaction of quinolizinium ylide **4b** with methyl propynoate in DMSO at 75 °C, and **12** was converted to cyclazine **13**[4] in 60% yield within 40 min of stirring (Scheme 7).

It should be mentioned that the reactions of ylides **3d**, **i** and **4a**, **b** with acetylenic esters proceeded significantly slower than that of **3b**, presumably as a result of the enolate structure of the former (vide supra). However, the reactions were accelerated in polar solvents and by using an excess amount of dipolarophile.

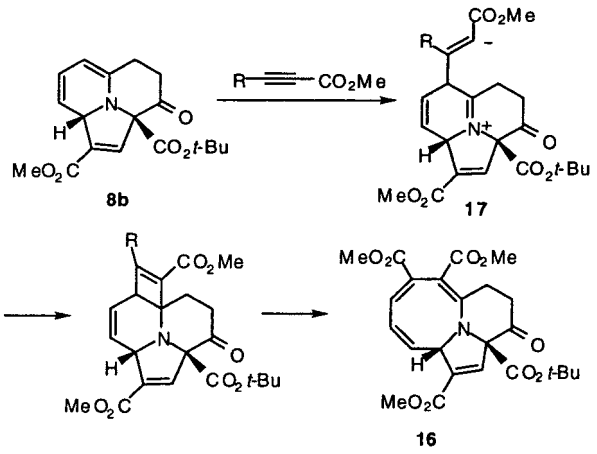
Reaction of ylide **3b** with dimethyl acetylenedicarboxylate (DMAD) proceeded differently from that with propynoates. The cycloaddition reaction in acetone at 55 °C

(11) Ylides **3a** and **3b** showed similar reactivities in the cycloaddition reactions.

(12) This may be attributed to the nucleophilic attack of DMSO to facilitate the oxidative decarboxylation (or decarbonylation).

(13) The structure of the pentamethyl ester analogue of **15** was determined by X-ray analysis. We thank Prof. Toshiro Harada, Kyoto Institute of Technology, for the analysis.

Scheme 10



did not stop at the stage of monocycloadduct (**14**) but furnished the bisadduct, azocine **15**, in 50% yield.[13] It should be noted that the bisadducts of this type were not detected in the reaction with excess methyl propynoate. Furthermore, the addition of an additional 1 equiv of methyl propynoate to the reaction mixture containing monoadduct **8** and heating at 55 °C caused complete decomposition of **8**, more rapidly than the control reaction of **8** without additional dipolarophile under the same conditions. In contrast, the reaction of monoadduct **8** with DMAD gave the bisadduct, azocine **16**, in 75% yield (Schemes 8 and 9).

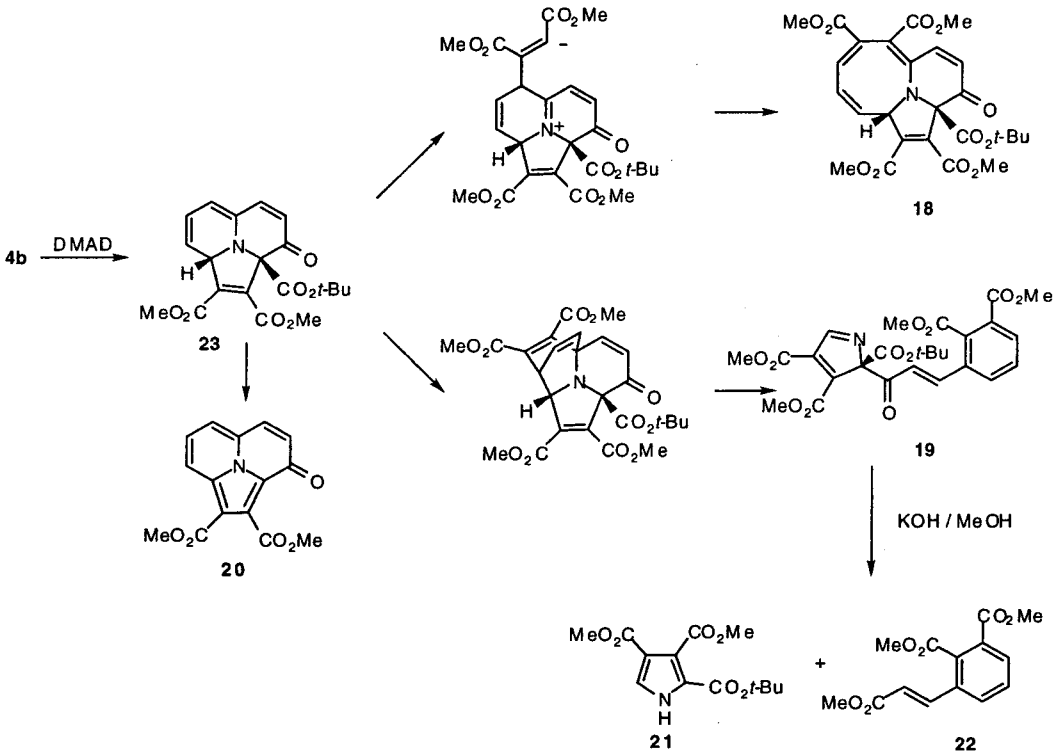
The striking difference between the reactions with DMAD and propynoate can be explained by the difference in the stability and reactivity of the initial Michael type addition intermediate **17** (Scheme 10).

The reaction of quinolizinium ylide **4b** with DMAD in chloroform afforded azocine **18** (21%) as well as another type of bisadduct **19** (19%) along with aromatic cyclazine **20** (15%). Apparently **19** was formed from the Diels–Alder addition of a second molecule of DMAD to the diene moiety of the primary monoadduct, followed by aromatization through a retro-Diels–Alder reaction. Product **19** was isolated as an oil, which upon treatment with KOH/MeOH solution afforded two stable products, **21** and **22**, quantitatively (Scheme 11). It should be noted that the reaction proceeded rather slowly compared to the reaction of **3b** with DMAD. This may be because the introduction of additional unsaturation in **4b** caused reduction in the reactivity of primary monoadduct **23** as an enamine to **18** more significantly than as a diene to **19**.

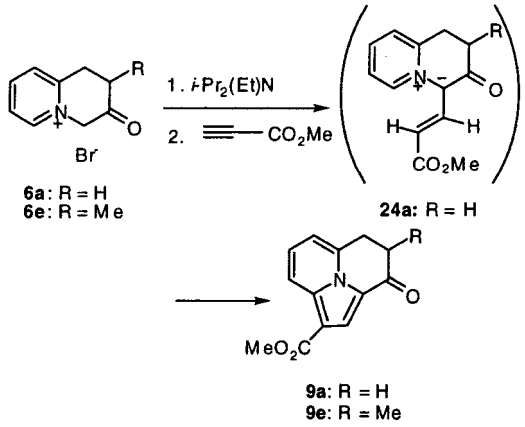
Tetrahydroquinolizinium salts **6a** and **6e** with methyl propynoate in acetonitrile at 60 °C rapidly formed cyclazines **9a** and **9e**, respectively, in the presence of $(i\text{-Pr})_2$NEt. Mechanism of the cycloaddition may be stepwise rather than concerted, because when the reaction of **6a** was carried out in chloroform, acrylate betaine **24a** was isolated as a byproduct in 15–20% yield together with 40% of **9a**. Betaine **24a** was also formed exclusively from **6a** in methanol in the presence of potassium carbonate. The TLC analysis of the reaction in acetonitrile showed that **24a** was detected in the beginning, but it was gradually converted to **9** (Scheme 12).

In conclusion, a variety of tetrahydroquinolizinium ylides were synthesized in high yields by the Cu-catalyzed reaction of diazo pyridines. The labile primary cycloadducts **8** and **12** formed between tetrahydroquinolizinium (or quinolizinium) ylides and methyl propynoate were identified spectroscopically. From the primary adducts **8**, two more types of transformation were characterized: (1) Michael type addition of the enamine moiety of **8** to an acetylenic ester leading to azocine derivatives and (2) facile decarbonylative oxidation leading to oxodihydropyrroloquinolizines ([2,3,3]-cyclazines) by the aid of a nucleophilic species such as DMSO.

Scheme 11



Scheme 12



Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra were measured in $CDCl_3$, unless otherwise noted, and assignment was done on the basis of CH-COSY, HMBC, and NOE procedures. All reactions were performed in oven-dried glassware under nitrogen atmosphere. Solutions were evaporated under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using ethyl acetate−hexane mixture as an eluent unless specified otherwise.

General Procedure for the Preparation of 4-Alkoxycarbonyl (or 4-Acyl)-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ides. To a solution of the dianion $R^1C(O^-Li^+)$═CHC-(O^-Na^+)═CHR^2 in THF (100 mL), prepared from the parent 1,3-dicarbonyl compound $R^1C(O)CH_2C(O)CH_2R^2$ (40 mmol) according to the described procedure,[14] 2-(α-chloroalkyl)pyridine in 8 mL of THF was added at 0 °C. The 2-(α-chloroalkyl)-pyridine, in turn, was prepared from its hydrochloride (45 mmol) by the treatment with saturated sodium bicarbonate solution, extraction with methylene chloride, drying over magnesium sulfate, and evaporation of the solvent under reduced pressure. The reaction mixture was allowed to warm slowly to room temperature, stirred for 30 min, and quenched with 6.8 mL of hydrochloric acid in 20 mL of water (pH 7−8). The aqueous layer was further extracted with 2 × 40 mL of ether. The extracts were combined, washed with water and brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The resulting residue was subjected to flash column chromatography to give **1**.

To a mixture containing 10 mmol of 1,3-dicarbonyl compound **1** and 11 mmol of mesitylenesulfonyl azide in 2.9 mL of acetonitrile was added 3.5 mL of triethylamine. The reaction was stirred for 30 min and concentrated under reduced pressure. The resulting residue was refluxed with 45 mL of hexane for 15 min and filtered still warm. The procedure was repeated two more times. The cooled combined hexane solution was once more filtered, and after removal of the solvent and flash column chromatography of the resulting residue, **2** were obtained.

A solution containing 7.9 mmol of **2** and 56 mg (2.5 mol %) of copper(II) trifluoroacetylacetonate in 81 mL of dry benzene was stirred at 80 °C for 20−25 min until no more nitrogen was evolved. The reaction mixture with precipitated ylide was cooled at 10 °C. Filtration and washing with dry ether gave ylides **3** (in some cases partial removal of benzene and addition of pentane was necessary for precipitation to occur).

Methyl 3-Oxo-5-(2-pyridyl)pentanoate (1a). Yield 88%; pale yellow oil; IR (KBr) 1747, 1716, 1592 cm^{-1}; ^{1}H NMR δ 3.05 (2H, m; H4), 3.11 (2H, m; H5), 3.57 (2H, s; H2), 3.72 (3H, s; MeO), 7.11 (1H, dd, J = 7.3 and 5.0 Hz; H5′), 7.19 (1H, d, J = 7.6 Hz; H3′), 7.58 (1H, dd, J = 7.6 and 7.3 Hz; H4′), 8.48 (1H, d, J = 5.0 Hz; H6′); ^{13}C NMR δ 31.4, 41.5, 49.2, 52.3, 121.3, 123.2, 136.3, 149.1, 159.8, 167.6, 202.0.

Methyl 2-Diazo-3-oxo-5-(2-pyridyl)pentanoate (2a). Yield 90%; thick pale yellow oil; IR (KBr) 2139, 1724, 1656, 1593 cm^{-1}; ^{1}H NMR δ 3.14 (2H, t, J = 7.2 Hz; H4), 3.50 (2H, t, J = 7.2 Hz; H5), 3.83 (3H, s; MeO), 7.10 (1H, t, J = 7.8 Hz; H5′), 7.22 (1H, d, J = 7.8 Hz; H3′), 7.58 (1H, dt, J = 1.7, 7.8 and 7.8 Hz; H4′), 8.51 (1H, m; H6′); ^{13}C NMR δ 31.9, 39.4, 52.1, 75.0, 121.1, 123.0, 136.2, 149.1, 160.2, 161.7. 191.6.

4-Methoxycarbonyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (3a). Yield 86%; yellow crystal; mp 151−152 °C; IR (KBr) 1639, 1614, 1589 cm^{-1}; ^{1}H NMR δ 2.53 (2H, t, J = 6.8 Hz; H2), 3.13 (2H, t, J = 6.8 Hz; H1), 3.87 (3H, s; MeO), 7.50 (1H, t, J = 7 Hz; H7), 7.51 (1H, d, J = 8.2 Hz; H9), 7.73 (1H, dd, J = 7 and 8.2 Hz; H8), 9.12 (1H, d, J = 6.8 Hz; H6); ^{13}C NMR δ 28.4 (C1), 33.7 (C2), 51.0 (OMe), 108.0 (C4), 123.0 (C7), 124.5 (C9), 136.1 (C8), 142.0 (C6), 150.1 (C9a), 165.0 (CO_2), 181.9 (C3). Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.82. Found: C, 64.08; H, 5.39; N, 6.81. HRMS calcd for $C_{11}H_{11}NO_3$ 205.0739, found 205.0739. UV λ (log ε) nm: 245 (4.49), 274.5 (3.29), 386 (3.32).

***tert*-Butyl 3-Oxo-5-(2-pyridyl)pentanoate (1b).** Yield 72%; yellow oil; ^{1}H NMR δ 1.45 (9H, s), 3.04 (1H, dd, J = 6.9 and 2.1 Hz), 3.05 (1H, brd, J = 6.9 Hz), 3.09 (1H, brd, J = 6.9 Hz), 3.11 (1H, dd, J = 6.9 and 2.1 Hz), 3.40 (2H, s), 7.10 (1H, dd, J = 7.6 and 5.1 Hz), 7.19 (1H, d, J = 7.6 Hz), 7.58 (1H, t, J = 7.6 Hz), 8.49 (1H, d, J = 5.1 Hz); ^{13}C NMR δ 27.9, 31.4, 41.6, 50.7, 81.8, 121.2, 123.2, 136.3, 149.1, 160.0, 166.4, 202.6.

***tert*-Butyl 2-Diazo-3-oxo-5-(2-pyridyl)pentanoate (2b).** Yield 95%; thick yellow oil; ^{1}H NMR δ 1.52 (9H, s), 3.13 (2H, t, J = 7.3 Hz), 3.32 (2H, t, J = 7.3 Hz), 7.09 (1H, dd, J = 7.3 and 5.0 Hz), 7.21 (1H, d, J = 7.3 Hz), 7.58 (lH, t, J = 7.3 Hz), 8.51 (1H, d, J = 5.0 Hz); ^{13}C NMR δ 28.2, 32.0, 39.5, 76.6, 83.1, 121.1, 123.0, 131.8, 136.3, 149.2, 160.5, 192.2.

4-*tert*-Butoxycarbonyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (3b). The cooled reaction mixture was filtered through a glass filter to remove the tiny powder of catalyst, and approximately half of the solvent was removed under reduced pressure to afford **3b** (82%) as yellow crystals: mp 134−135 °C; IR (KBr) 1678, 1645, 1541 cm^{-1}; ^{1}H NMR δ 1.59 (9H, s; C(Me)$_3$), 2.47 (2H, t, J = 6.9 Hz; H2); 3.11 (2H, t, J = 6.9 Hz; H1), 7.46 (1H, t, J = 7.1 Hz; H7), 7.48 (1H, d, J = 7.6 Hz; H9), 7.68 (1H, dd, J = 7.1 and 7.6 Hz; H8), 9.0 (1H, d, J = 7.1 Hz; H6); ^{13}C NMR δ 28.5 (C1), 28.7 (Me), 33.8 (C2), 79.6 (C(Me)$_3$), 109.4 (C4), 122.8 (C7), 124.5 (C9), 135.3 (C8), 145.7 (C6), 149.8 (C9a), 164.1 (CO_2), 181.1 (C3). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.89; H, 6.88; N, 5.43.

Benzyl 3-Oxo-5-(2-pyridyl)pentanoate (1c). Yield 50%; yellow oil; ^{1}H NMR δ 3.03 (1H, dt, J = 2.0, 6.3 and 6.3 Hz; H4), 3.04 (1H, d, J = 6.3 Hz; H4), 3.08 (1H, d, J = 6.3 Hz; H5), 3.09 (1H, dt, J = 2.0, 6.3 and 6.3 Hz; H5), 3.56 (2H, s; H2), 5.16 (2H, s; CH_2Ph), 7.09 (1H, dd, J = 4.7 and 7.6 Hz; H5′), 7.16 (1H, d, J = 7.6 Hz; H3′), 7.30∼7.40 (5H, m; Ph), 7.56 (1H, t, J = 7.6 Hz; H4′), 8.47 (1H, d, J = 4.7 Hz; H6′); ^{13}C NMR δ 31.4, 41.5, 49.3, 67.0, 121.3, 123.1, 128.3, 128.4, 128.5, 135.3, 136.3, 149.1, 159.7, 167.0, 201.9.

4-Benzyloxycarbonyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (3c). Yield 75% (2 steps); yellow crystal; mp 135−136 °C; IR (KBr) 1641, 1618, 1589 cm^{-1}; ^{1}H NMR δ 2.50 (2H, brt, J = 6.7 Hz; H2), 3.10 (2H, brt, J = 6.7 Hz; H1), 5.36 (2H, s; CH_2Ph), 7.24 (1H, t, J = 7.4 Hz; Ph-*p*-H), 7.34 (2H, t, J = 7.4 Hz; Ph-*m*-H), 7.45 (1H, t, J = 7.1 Hz; H7), 7.47 (1H, d, J = 7.1 Hz; H9), 7.54 (2H, d, J = 7.4 Hz; Ph-*o*-H), 7.68 (1H, t, J = 7.1 Hz; H8), 9.07 (1H, d, J = 7.1 Hz; H6); ^{13}C NMR δ 28.4 (C1), 33.8 (C2), 65.0 (CH_2Ph), 108.0 (C4), 123.0 (C7), 124.6 (C9), 127.1 (Ph-*p*-C), 127.2 (Ph-*o*-C), 128.2 (Ph-*m*-C), 136.0 (Ph-*ipso*-C), 137.5 (C8), 141.8 (C6), 150.0 (C9a), 164.3 (CO_2), 181.9 (C3). Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.38; N, 4.98. Found: C, 72.29; H, 5.40; N, 4.86.

3-Diazo-6-(2-pyridyl)hexane-2,4-dione (2d). Yield 60% (2 steps); yellow oil; ^{1}H NMR δ 2.44 (3H, s), 3.17 (1H, m), 3.18 (1H, d, J = 5.1 Hz), 3.20 (1H, d, J = 5.1 Hz), 3.21 (1H, m), 7.12 (1H, dd, J = 7.6 and 5.1 Hz), 7.21 (1H, d, J = 7.6 Hz),

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7.59 (1H, t, J = 7.6 Hz), 8.50 (1H, d, J = 5.1 Hz); ^{13}C NMR δ 28.7, 31.7, 39.0, 84.4, 121.3, 123.1, 136.3, 149.2, 159.6, 189.8.

4-Acetyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (3d). The cooled reaction mixture was filtered through a glass filter to remove the tiny powder of catalyst, and pentane was added to the solution until precipitation started to afford yellow crystals: yield 82%; mp 150−152 °C; IR (KBr) 1620, 1585, 1537 cm^{-1}; ^{1}H NMR δ 2.52 (2H, t, J = 6.8 Hz; H2), 2.60 (3H, s; COMe), 3.12 (2H, t, J = 6.8 Hz; H1), 7.51 (1H, dd, J = 6.4 and 7.7 Hz; H7), 7.53 (1H, d, J = 7.7 Hz; H9), 7.80 (1H, t, J = 7.7 Hz; H8), 9.24 (1H, d, J = 6.4 Hz; H6); ^{13}C NMR δ 28.2 (C1), 29.6 (COMe), 33.7 (C2), 119.6 (C4), 122.7 (C7), 124.5 (C9), 137.1 (C8), 143.2 (C6), 149.9 (C9a), 183.0 (COMe), 184.6 (C3). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.87; H, 5.86; N, 7.40. Found: C, 69.71; H, 5.92; N, 7.26.

Methyl 4-Methyl-3-oxo-5-(2-pyridyl)pentanoate (1e). Yield 80%; yellow oil; ^{1}H NMR δ 1.16 (3H, d, J = 6.9 Hz), 2.81 (1H, dd, J = 14.3 and 6.2 Hz), 3.23 (1H, dd, J = 14.3 and 7.7 Hz), 3.30 (1H, m), 3.54 (1H, A of ABq, J_{AB} = 15.6 Hz), 3.59 (1H, B of ABq, J_{AB} = 15.6 Hz), 3.70 (3H, s), 7.11 (1H, dd, J = 7.6 and 4.7 Hz), 7.13 (1H, d, J = 7.6 Hz), 7.58 (1H, t, J = 7.6 Hz), 8.50 (1H, d, J = 4.7 Hz); ^{13}C NMR δ 16.3, 40.7, 45.8, 48.1, 52.2, 121.4, 123.6, 136.3, 149.2, 158.9, 167.7, 205.9.

Methyl 2-Diazo-4-methyl-3-oxo-5-(2-pyridyl)pentanoate (2e). Yield 95%; yellow oil; ^{1}H NMR δ 1.16 (3H, d, J = 6.9 Hz), 2.81 (1H, dd, J = 13.9, and 7.0 Hz), 3.28 (1H, dd, J = 13.9 and 7.4 Hz), 3.83 (3H, s), 4.08 (1H, m), 7.09 (1H, dd, J = 4.7 and 7.7 Hz), 7.20 (1H, d, J = 7.7 Hz), 7.57 (1H, t, J = 7.7 Hz), 8.50 (1H, d, J = 4.7 Hz); ^{13}C NMR δ 16.8, 40.9, 42.1, 52.2, 75.6, 121.2, 123.6, 136.2, 149.2, 159.5, 161.5, 195.7.

4-Methoxycarbonyl-2-methyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (3e). The cooled reaction mixture was filtered through a glass filter to remove the tiny powder of catalyst, and pentane was added to a solution until precipitation started to afford yellow crystals: yield 83%; mp 126−127 °C (134−136 °C, crystallosovate, benzene); IR (KBr) 1657, 1552 cm^{-1}; ^{1}H NMR δ 1.15 (3H, d, J = 7.1 Hz; Me), 2.44 (1H, ddq, J = 10.5, 4.2 and 7.1 Hz; H2), 2.87 (1H, dd, J = 15.3 and 10.5 Hz; H1), 3.15 (1H, dd, J = 15.4 and 4.2 Hz; H1), 3.85 (3H, s; OMe), 7.48 (1H, dd, J = 6.4 and 7.1 Hz; H7), 7.50 (1H, d, J = 7.8 Hz; H9), 7.72 (1H, dd, J = 7.1 and 7.8 Hz; H8), 9.13 (1H, d, J = 6.4 Hz; H6); ^{13}C NMR δ 14.5 (Me), 35.6 (C1), 36.7 (C2), 51.0 (OMe), 107.1 (C4), 123.0 (C7), 124.9 (C9), 135.5 (C8), 141.5 (C6), 149.1 (C9a), 165.4 (CO_2), 184.1 (C3). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.93; H, 5.96; N, 6.32. Anal. Calcd for ($C_{12}H_{13}NO_3C_6H_6$): C, 72.71; H, 6.44; N, 4.71. Found: C, 72.30; H, 6.39; N, 4.76.

Methyl 3-Oxo-5-(2-pyridyl)hexanoate (1f). Yield 65%; yellow oil; ^{1}H NMR δ 1.30 (3H, d, J = 6.8 Hz), 2.80 (1H, dd, J = 17.2 and 6.2 Hz), 3.21 (1H, dd, J = 17.2 and 7.7 Hz), 3.42 (1H, A of ABq, J_{AB} = 15.6 Hz), 3.48 (1H, B of ABq, J_{AB} = 15.6 Hz), 3.50 (1H, m), 3.71 (3H, s), 7.10 (1H, dd, J = 7.6 and 5.0 Hz), 7.20 (1H, d, J = 7.6 Hz), 7.60 (1H, t, J = 7.6 Hz), 8.49 (1H, d, J = 5.0 Hz); ^{13}C NMR δ 21.0, 36.8, 48.7, 49.5, 52.2, 121.4, 122.3, 136.5, 149.0, 164.1, 167.6, 201.8.

Methyl 2-Diazo-3-oxo-5-(2-pyridyl)hexanoate (2f). Yield 94%; yellow oil; ^{1}H NMR δ 1.33 (3H, d, J = 6.8 Hz), 3.12 (1H, m), 3.50 (1H, m), 3.52 (1H, m), 3.83 (3H, s), 7.09 (1H, dd, J = 7.6 and 4.8 Hz), 7.23 (1H, d, J = 7.6 Hz), 7.50 (1H, t, J = 7.6 Hz), 8.51 (1H, d, J = 4.8 Hz); ^{13}C NMR δ 20.9, 37.3, 46.4, 52.2, 76.1, 121.2, 122.0, 136.3, 149.1, 161.8, 164.7, 191.4.

4-Methoxycarbonyl-l-methyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (3f). Yield 92%; yellow crystal; mp 163−165 °C; IR (KBr) 1637, 1612, 1589 cm^{-1}; ^{1}H NMR δ 1.46 (3H, d, J = 6.9 Hz; Me), 2.35 (1H, dd, J = 15.8 and 10.9 Hz; H2), 2.56 (1H, dd, J = 15.8 and 4.3 Hz; H2), 3.24 (1H, m; H1), 3.86 (3H, s; MeO), 7.51 (1H, dd, J = 6.5 and 7.3 Hz; H7), 7.53 (1H, d, J = 8.6 Hz; H9), 7.81 (1H, dd, J = 7.3 and 8.6 Hz; H8), 9.10 (1H, d, J = 6.5 Hz; H6); ^{13}C NMR δ 15.7 (Me), 32.6 (C1), 42.0 (C2), 51.1 (OMe), 107.9 (C4), 122.4 (C7), 122.8 (C9), 136.4 (C8), 142.2 (C6), 153.8 (C9a), 165.1 (CO_2), 181.1 (C3). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.46; H, 5.95; N, 6.14.

Methyl 4-Methyl-3-oxo-5-(2-pyridyl)hexanoate (1g). Yield 34%; yellow oil; ^{1}H NMR δ 0.91 (3H, d, J = 6.3 Hz), 1.28 (3H, d, J = 6.2 Hz), 3.15 (2H, m), 3.55 (1H, A of ABq, J_{AB} = 15.7 Hz), 3.60 (1H, B of ABq, J_{AB} = 15.7 Hz), 3.75 (3H, s), 7.13 (1H, d, J = 7.6 Hz), 7.14 (1H, dd, J = 7.6 and 4.6 Hz), 7.61 (1H, t, 7.6 Hz), 8.56 (1H, d, J = 4.6 Hz); ^{13}C NMR δ 15.4, 19.1, 44.2, 49.1, 51.5, 52.3, 121.6, 122.9, 136.5, 149.4, 163.3, 167.6, 206.4.

Methyl 2-Diazo-4-methyl-3-oxo-5-(2-pyridyl)hexanoate (2g). Yield 79%; colorless needle (hexane); mp 75−77 °C; IR (KBr) 2144, 1720, 1647 cm^{-1}; ^{1}H NMR δ 0.88 (3H, d, J = 6.9 Hz), 1.27 (3H, d, J = 6.8 Hz), 3.25 (1H, dq, J = 9.7 and 6.8 Hz), 3.86 (3H, s), 4.05 (1H, dq, J = 9.7 and 6.9 Hz), 7.12 (1H, dd, J = 7.3 and 4.5 Hz), 7.16 (1H, d, J = 7.7 Hz), 7.60 (1H, dd, J = 7.3 and 7.7 Hz), 8.57 (1H, d, J = 4.5 Hz); ^{13}C NMR δ 16.0, 19.2, 44.7, 46.8, 52.2, 76.3, 121.4, 122.7, 136.2, 149.4, 161.5, 163.7, 196.2. Anal. Calcd for $C_{13}H_{15}N_3O_3$: C, 59.76; H, 5.79; N, 16.08. Found: C, 59.58; H, 5.70; N, 15.79.

4-Methoxycarbonyl-1,2-dimethyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (3g). Yield 80% from **2g** as a mixture with 20% of the stereoisomer **3g′**; yellow solid; IR (KBr) 1630, 1610, 1585 cm^{-1}; ^{1}H NMR δ 0.90 (3H, br; 2-Me), 1.37 (3H, br; 1-Me), 2.53 (1H, br; H2), 3.29 (1H, br; H1), 3.87 (3H, s; OMe), 7.49 (1H, dd, J = 6.4 and 7.7 Hz; H7), 7.50 (1H, d, J = 7.7 Hz; H9), 7.76 (1H, t, J = 7.7 Hz; H8), 9.12 (1H, d, J = 6.4 Hz; H6); ^{13}C NMR δ 14.6 (1-Me), 15.0 (2-Me), 39.4 (C1), 43.7 (C2), 51.1 (OMe), 106.3 (C4), 122.9 (C7), 124.3 (C9), 135.9 (C8), 141.5 (C6), 152.3 (C9a), 165.5 (CO_2), 183.4 (C3). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.01. Found: C, 67.03; H, 6.51; N, 5.85.

Methyl 4-Methyl-3-oxo-5-(2-pyridyl)hexanoate (**1g′**, diastereomer of **1g**). Yield 29% (isolated from a mixture with **1g**); yellow oil; ^{1}H NMR δ 1.17 (3H, d, J = 6.4 Hz), 1.28 (3H, d, J = 6.5 Hz), 3.25 (2H, overlapped), 3.38 (1H, A of ABq, J_{AB} = 15.7 Hz,), 3.47 (1H, B of ABq, J_{AB} = 15.7 Hz,), 3.66 (3H, s), 7.10 (1H, dd, J = 4.7 and 6.9 Hz), 7.14 (1H, d, J = 7.7 Hz), 7.59 (1H, dd, J = 6.9 and 7.7 Hz), 8.49 (1H, d, J = 4.7 Hz); ^{13}C NMR δ 13.8, 17.5, 43.5, 48.7, 50.7, 52.1, 121.4, 122.7, 136.5, 148.9, 163.9, 167.7, 206.6.

Methyl 2-Diazo-4-methyl-3-oxo-5-(2-pyridyl)hexanoate (2g′, diastereomer of **2g**). Yield 84% from **1g′**; colorless needle (hexane); 56−57 °C; IR (KBr) 2141, 1724, 1655, 1591 cm^{-1}; ^{1}H NMR δ 1.19 (3H, d, J = 7.0 Hz), 1.29 (3H, d, J = 7.1 Hz), 3.33 (1H, dq, J = 8.3 and 7.0 Hz), 3.83 (3H, s), 4.08 (1H, dq, J = 8.3 and 7.1 Hz), 7.06 (1H, dd, J = 7.4 and 4.7 Hz), 7.22 (1H, d, J = 7.8 Hz), 7.56 (1H, dd, J = 7.4 and 7.8 Hz), 8.48 (1H, d, J = 4.7 Hz); ^{13}C NMR δ 14.2, 17.3, 43.2, 46.5, 52.1, 75.5, 121.1, 122.6, 136.2, 148.9, 161.5, 164.6, 196.0. Anal. Calcd for $C_{13}H_{15}N_3O_3$: C, 59.76; H, 5.79; N, 16.08. Found: C, 59.72; H, 5.59; N, 16.00.

4-Methoxycarbonyl-1,2-dimethyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (3g′, diastereomer of **3g**). Yield 78% from **2g′**; yellow crystal; mp 131−133 °C; IR (KBr) 1630, 1610, 1585 cm^{-1}; ^{1}H NMR δ 1.08 (3H, d, J = 7.2 Hz; 2-Me), 1.42 (3H, d, J = 7.1 Hz; 1-Me), 2.28 (1H, dq, J = 6.9 and 7.2 Hz; H2), 2.93 (1H, dq, J = 6.9 and 7.1 Hz; H1), 3.86 (3H, s; OMe), 7.50 (1H, dd, J = 6.5 and 7.6 Hz; H7), 7.53 (1H, d, J = 7.6 Hz; H9), 7.77 (1H, t, J = 7.6 Hz; H8), 9.14 (1H, d, J = 6.5 Hz; H6); ^{13}C NMR δ 14.7 (1-Me), 15.0 (2-Me), 39.4 (C1), 43.7 (C2), 51.0 (OMe), 106.7 (C4), 122.7 (C7), 124.2 (C9), 135.8 (C8), 141.7 (C6), 153.0 (C9a), 165.4 (CO_2), 183.4 (C3). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.01. Found: C, 66.80; H, 6.54; N, 5.83.

Ethyl 2-Diazo-3-oxo-5-(2-pyridyl)pentanoate (2h). Yield 73% (2 steps); yellow oil; ^{1}H NMR δ 1.34 (3H, t, J = 7.0 Hz), 2.46 (2H, t, J = 7 Hz), 3.09 (2H, t, J = 7 Hz), 4.28 (2H, q, J = 7.0 Hz), 7.45 (1H, t, J = 7 Hz), 7.48 (1H, d, J = 7.6 Hz) 7.70 (1H, dd, J = 7.1 and 7.6 Hz), 9.04 (1H, d, J = 6.8 Hz); ^{13}C NMR δ 14.2, 32.0, 39.5, 61.3, 75.9, 121.1, 123.0, 136.2, 149.1, 160.3, 161.3, 191.7.

4-Ethoxycarbonyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (3h). Yield 90%; yellow crystal; mp 144−145 °C; IR (KBr) 1637, 1610, 1591 cm^{-1}; ^{1}H NMR δ 1.40 (3H, t, J = 7.1 Hz; CH_3CH_2O), 2.50 (2H, brt, J = 6.9 Hz; H2), 3.13 (2H, brt, J = 6.7 Hz; Hi), 4.32 (2H, q, J = 7.1 Hz; OCH_2CH_3), 7.49 (1H, dd, J = 6.4 and 7.7 Hz; H7), 7.53 (1H, d, J = 7.7 Hz; H9), 7.74 (1H, t, J = 7.7 Hz; H8), 9.09 (1H, d, J = 6.4 Hz; H6); ^{13}C

NMR δ 14.6 ($\underline{C}H_3CH_2O$), 28.4 (C1), 33.7 (C2), 59.6 ($O\underline{C}H_2CH_3$), 108.2 (C4), 123.0 (C7), 124.5 (C9), 135.9 (C8), 142.0 ($\underline{C}$6), 150.0 (C9a), 164.7 (CO_2), 181.7 (C3). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.54; H, 5.89; N, 6.32.

1-Phenyl-5-(2-pyridyl)pentane-1,3-dione (1i). Yield 40%; yellow oil; ^{1}H NMR (major enol isomer) δ 2.94 (2H, t, J = 7.6 Hz), 3.18 (2H, t, J = 7.6 Hz), 6.19 (1H, s), 7.12 (1H, dd, J = 7.1 and 4.9 Hz; H5′), 7.21 (1H, d, J = 7.7 Hz; H3′), 7.44 (2H, t, J = 7.3 Hz, Ph-*m*-H), 7.50 (1H, t, J = 7.3 Hz, Ph-*p*-H), 7.60 (1H, dd, J = 7.1 and 7.7 Hz; H4′), 7.84 (2H, d, J = 7.3 Hz; Ph-*o*-H), 8.54 (1H, brd, J = 4.9 Hz; H6′); ^{13}C NMR δ 33.5, 38.7, 96.4, 121.4, 123.1, 126.9, 128.6, 132.2, 134.7, 136.5, 149.3, 160.1, 182.3, 196.4.

2-Diazo-1-phenyl-5-(2-pyridyl)pentane-1,3-dione (2i). Yield 84%; yellow oil; ^{1}H NMR δ 3.20 (2H, t, J = 7.2 Hz), 3.45 (2H, t, J = 7.2 Hz), 7.11 (1H, dd, J = 7.2 and 5.0 Hz), 7.24 (1H, d, J = 7.8 Hz), 7.48 (2H, t, J = 7.6 Hz), 7.57 (1H, t, J = 7.6 Hz), 7.59 (1H, dd, J = 7.6 and 7.8 Hz), 7.63 (2H, d, J = 7.6 Hz), 8.51 (1H, d, J = 5.0 Hz); ^{13}C NMR δ 32.2, 40.4, 83.2, 121.2, 123.1, 127.3, 128.8, 132.6, 136.3, 137.4, 149.2, 160.2, 185.1, 192.4.

4-Phenacyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (3i). Yield 85%; yellow crystal; mp 132−133 °C; IR (KBr) 1633, 1608, 1531 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.29 (2H, t, J = 7.0 Hz; H2), 3.22 (2H, t, J = 7.0 Hz; H1), 7.28 (3H, m; Ph), 7.38 (2H, d, J = 6.9 Hz; Ph), 7.72 (1H, dd, J = 6.4 and 7.7 Hz; H7), 7.87 (1H, d, J = 7.7 Hz; H9), 8.05 (1H, t, J = 7.7 Hz; H8), 9.31 (1H, d, J = 6.4 Hz; H6); ^{13}C NMR δ 28.2 (C1), 30.8 (C2), 118.6 (C4), 123.1 (C7), 124.9 (C9), 127.3, 127.5 (Ph-*o*-C and Ph-*m*-C), 128.2 (Ph-*ipso*-C), 128.9 (Ph-*p*-C), 137.3 (C8), 142.8 (C6), 150.1 (C9a), 182.2 ($\underline{C}$OPh), 183.4 (C3).

***tert*-Butyl 3-Oxo-5-(2-pyridyl)hexanoate (1j).** Yield 52%; yellow oil; ^{1}H NMR δ 1.31 (3H, d, J = 7.0 Hz), 1.45 (9H, s), 2.81 (1H, dd, J = 17.3 and 6.4 Hz), 3.19 (1H, dd, J = 17.3 and 7.4 Hz), 3.31 (1H, A of ABq, J_{AB} = 15.2 Hz), 3.37 (1H, B of ABq, J_{AB} = 15.2 Hz), 3.49 (1H, m), 7.09 (1H, dd, J = 7.3 and 4.9 Hz), 7.20 (1H, d, J = 7.8 Hz), 7.58 (1H, dd, J = 7.3 and 7.8 Hz), 8.50 (1H, d, J = 4.9 Hz); ^{13}C NMR δ 20.9, 27.8, 36.6, 48.8, 50.9, 81.6, 121.2, 122.1, 136.3, 148.9, 164.3, 166.3, 202.3.

***tert*-Butyl 2-Diazo-3-oxo-5-(2-pyridyl)hexanoate (2j).** Yield 80%; yellow oil; ^{1}H NMR δ 1.35 (3H, d, J = 6.8 Hz), 1.52 (9H, s), 3.12 (1H, dd, J = 16.8 and 6.0 Hz), 3.46 (1H, dd, J = 17.0 and 7.6 Hz), 3.50 (1H, m), 7.08 (1H, dd, J = 7.3 and 4.9 Hz), 7.22 (1H, d, J = 7.9 Hz), 7.59 (1H, dd, J = 7.3 and 7.9 Hz), 8.51 (1H, d, J = 4.9 Hz); ^{13}C NMR δ 21.0, 28.3, 37.2, 46.4, 76.9, 83.0, 121.2, 122.1, 136.3, 149.1, 160.5, 164.9, 191.9.

4-*tert*-Butoxycarbonyl-1-methyl-3-oxo-1,2,3,4-tetrahydroquinolizinium-3-ide (3j). Yield 81%; yellow oil; ^{1}H NMR δ 1.46 (3H, d, J = 6.9 Hz; Me), 1.59 (9H, s; C(Me)$_3$), 2.30 (1H, dd, J = 15.8 and 11.6 Hz; H2), 2.53 (1H, dd, J = 15.8 and 4.4 Hz; H2), 3.23 (1H, m; H1), 7.44 (1H, dd, J = 6.4 and 7.6 Hz; H7), 7.48 (1H, d, J = 7.8 Hz; H9), 7.73 (1H, dd, J = 7.6 and 7.8 Hz; H8), 8.99 (1H, d, J = 6.4 Hz; H6); ^{13}C NMR δ 15.8 (1-Me), 28.8 (Me$_3$), 32.6 (C1), 41.7 (C2), 79.7 ($\underline{C}$(Me)$_3$), 109.3 (C4), 122.2 (C7), 122.6 (C9), 135.7 (C8), 142.2 (C6), 153.7 (C9a), 164.1 (CO_2), 180.6 (C3).

Oxidation of Ylides 3. Preparation of 4-Methoxycarbonyl-3-oxyquinolizinium 2,3-Dichloro-5,6-dicyano-4-oxy-phenyloxide (5a) and 4-Methoxycarbonyl- and 4-*tert*-Butoxycarbonylquinolizinium-3-olate (4a, 4b). To a stirred solution of **3a** (1.01 g, 4.9 mmol) in methylene chloride (96 mL) was added a warm solution of DDQ (1.12 g, 4.9 mmol) in methylene chloride (193 mL). The dark-purple reaction mixture gradually became light with a brownish precipitate. Big particles of solid were ground, and the stirring was continued until the precipitate became homogeneous. The precipitate was separated by filtration and washed with methylene chloride to give 1.96 g (92%) of **5a**.

4-Methoxycarbonyl-3-oxyquinolizinium 2,3-Dichloro-5,6-dicyano-4-oxy-phenyloxide (5a). Needles (MeOH); mp 195−196 °C; IR (KBr) 2231, 1722, 1606, 1514 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 4.00 (3H, s), 7.73 (1H, d, J = 9.6 Hz; H1), 7.80 (1H, dd J = 6.9 and 7.7 Hz), 7.9 (1H, dd, J = 7.7 and 8.3 Hz), 8.25 (1H, d, J = 9.6 Hz; H2), 8.32 (1H, d, J = 8.3 Hz), 8.85 (1H, d, J = 6.9 Hz); ^{13}C NMR (DMSO-d_6) δ 53.5, 99.5, 115.5, 121.0, 124.4, 127.7, 129.0, 130.1, 130.8, 131.1, 132.9, 134.6, 151.7, 158.7, 162.7. Anal. Calcd for $C_{19}H_{11}Cl_2N_3O_5$: C, 52.80; H, 2.56; N, 9.72. Found: C, 52.66; H, 2.65; N, 9.67.

4-Methoxycarbonylquinolizinium-3-olate (4a). Compound **5a** (1.96 g, 4.5 mmol) was treated with ammonia−water, and the resulting yellow solution was extracted three times with chloroform. Combined extracts were washed with brine and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave 0.69 g of **4a** (76%) as a yellow oil, which gradually solidified upon standing.

4-Methoxycarbonyl-quinolizinium-3-olate (4a). Yellow needles (ether); mp 112−113 °C; IR (KBr) 1720, 1608, 1520 cm^{-1}; ^{1}H NMR δ 4.40 (3H, s; MeO), 7.36 (1H, dd, J = 6.7 and 7.2 Hz; H7), 7.38 (1H, dd, J = 7.2 and 7.9 Hz; H8), 7.50 (1H, d, J = 9.7 Hz; H2), 7.55 (1H, d, J = 9.7 Hz; H1), 7.67 (1H, d, J = 7.9 Hz; H9), 8.95 (1H, d, J = 6.7 Hz; H6); ^{13}C NMR δ 52.7 (MeO), 119.8 (C4), 122.4 (C7), 125.9 (C8), 126.7 (C1), 127.1 (C9), 129.3 (C6), 132.0 (C9a), 139.5 (C2), 165.5 (CO_2), 167.9 (C3); MS *m*/*z* (relative intensity) 203 (M$^+$, 100), 175 (53), 172 (16), 144 (68), 128 (26), 117 (91), 89 (31), 69 (19), 63 (12), 57 (10); HRMS calcd for $C_{11}H_9NO_3$, 203.0583, found 203.0568.

4-Methoxycarbonyl-3-oxyquinolizinium Perchlorate ($HClO_4$ salt of 4a). Colorless crystal (*i*-PrOH); mp 147−147.5 °C; IR (KBr) 1730, 1630 cm^{-1}. Anal. Calcd for $C_{11}H_{10}ClNO_7$: C, 43.51; H, 3.32; N, 4.61. Found: C, 43.29; H, 3.30; N, 4.53.

Analogously, **4b** was obtained in 86% yield via 4-*tert*-butoxycarbonyl-3-oxyquinolizinium 2,3-dichloro-5,6-dicyano-4-oxy-phenyloxide (**5b**) from **3b**.

4-*tert*-Butoxycarbonyl-quinolizinium-3-olate (4b). Yellow needles (ether); mp 167−167.5 °C; IR (KBr) 1697, 1604, 1518 cm^{-1}; ^{1}H NMR δ 1.68 (9H, s; *t*-BuO), 7.26 (1H, dd, J = 8.2 and 7.1 Hz; H8), 7.31 (1H, dd, J = 6.9 and 7.1 Hz; H7), 7.46 (1H, d, J = 9.6 Hz; H2), 7.54 (1H, d, J = 9.6 Hz; H1), 7.64 (1H, d, J = 8.2 Hz; H9), 8.43 (1H, d, J = 6.9 Hz; H6); ^{13}C NMR δ 28.2 (Me$_3$), 83.6 ($\underline{C}$Me$_3$), 122.2 (C7), 123.1 (C4), 124.0 (C8), 126.5 (C1), 126.7 (C9), 127.1 (C6), 130.2 (C9a), 138.8 (C2), 163.9 (CO2), 166.8 (C3). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.08; H, 6.13; N, 5.40.

Decarboxylation of Ylides 3, and 4a. Preparation of Tetrahydroquinolizinium Bromides (6a, 6a′, 6e and 6f) and Quinolizinium Bromide 7. Ylide **3a** (1.01 g, 4.9 mmol) was refluxed in 47% HBr for 2.5 h. After removal of water under reduced pressure the residue was triturated with ether to give **6a** (0.96 g, 4.2 mmol).

3-Oxo-1,2,3,4-tetrahydroquinolizinium Bromide (6a). Yield 89% from **3a**; colorless crystals (ethanol−ethyl acetate); mp 238−239 °C; IR (KBr) 1734, 1637, 1583, 1510 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.69 (2H, t, J = 6.5 Hz; H2), 3.60 (2H, t, J = 6.5 Hz; H1), 5.32 (2H, s; H4), 8.04 (1H, dd, J = 6.1 and 7.5 Hz; H7), 8.17 (1H, d, J = 7.9 Hz; H9), 8.57 (1H, dd, J = 7.5 and 7.9 Hz; H8), 8.94 (1H, d, J = 6.1 Hz; H6); ^{13}C NMR (DMSO-d_6) δ 26.7 (C1), 32.4 (C2), 63.8 (C4), 125.8, 127.7, 145.1, 145.8, 154.9, 201.3 (C3). Anal. Calcd for $C_9H_{10}BrNO$: C, 47.39; H, 4.42; N, 6.14. Found: C, 47.06; H, 4.38; N, 5.93.

2-Methyl-3-oxo-1,2,3,4-tetrahydroquinolizinium Bromide (6e). Yield 85% from **3e**; colorless needles (ethanol); mp 218−219 °C; IR (KBr) 1732, 1635, 1581 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.16 (3H, d, J = 6.8 Hz; Me), 2.77 (1H, ddq, J = 12.5, 4.9 and 6.8 Hz; H2), 3.45 (1H, dd, J = 16.0 and 12.5 Hz; H1), 3.67 (1H, dd, J = 16.0 and 4.9 Hz; H1), 5.41 (1H, A of ABq, J_{AB} = 18.1 Hz; H4), 5.47 (1H, B of ABq, J_{AB} = 18.1 Hz; H4), 8.06 (1H, dd, J = 6.0 and 7.4 Hz), 8.18 (1H, d, J = 7.8 Hz), 8.58 (1H, dd, J = 7.8 and 7.4 Hz), 9.02 (1H, d, J = 6.0 Hz); ^{13}C NMR (DMSO-d_6) δ 13.6, 33.5, 37.0, 63.3, 125.7, 127.6, 144.9, 145.7, 154.5, 203.0. Anal. Calcd for $C_{10}H_{12}BrNO$: C, 49.61; H, 4.99; N, 5.79. Found: C, 49.41; H, 4.95; N, 5.55.

1-Methyl-3-oxo-1,2,3,4-tetrahydroquinolizinium Bromide (6f). Yield 75% from **3f**; colorless needles (ethanol); mp 201−202 °C; IR (KBr) 1732, 1626, 1574, 1508 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.47 (3H, d, J = 6.9 Hz; Me), 2.53 (1H, dd, J = 17.6 and 9.4 Hz; H2), 2.87 (1H, dd, J = 17.6 and 4.9 Hz; H2), 3.89 (ddq, 1H, J = 9.4, 4.9 and 6.9 Hz; H1), 5.42 (1H, A of ABq, J_{AB} = 18.1 Hz; H4), 5.53 (1H, B of ABq, J_{AB} = 18.1 Hz; H4), 8.09 (1H, dd, J = 6.1 and 7.5 Hz), 8.19 (1H, d, J = 8.0 Hz), 8.64 (1H, dd, J = 7.5 and 8.0 Hz), 9.04 (1H, d, J = 6.1

Hz); ^{13}C NMR (DMSO-d_6) δ 16.7, 31.6, 40.0, 63.7, 125.7, 127.7, 145.2, 146.1, 157.8, 200.9. Anal. Calcd for $C_{10}H_{12}BrNO$: C, 49.61; H, 4.99; N, 5.79. Found: C, 49.65; H, 5.03; N, 5.75.

3-Hydroxyquinolizinium Bromide (7).[3,10] Yield 89% from **4a**; colorless needles (ethanol); mp 255−256 °C; IR (KBr) 1655, 1633, 1518 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.99 (1H, dd, J = 6.7 and 7.4 Hz), 8.04 (1H, d, J = 9.4 Hz), 8.14 (1H, dd, J = 7.4 and 9.4 Hz), 8.47 (2H, ABq, J_{AB} = 13.5 Hz; H1 and H2), 8.85 (1H, s; H4), 9.26 (1H, d, J = 6.7 Hz), 11.89 (1H, s; HO); ^{13}C NMR (DMSO-d_6) δ 121.1, 124.0, 127.0, 128.2, 130.0, 133.4, 135.3, 137.6, 154.0. UV λ (log ϵ) nm: 228 (4.40), 243 (4.36), 263 (3.72), 271 (3.90), 341 (3.90). Anal. Calcd for C_9H_8BrNO: C, 47.82; H, 3.56; N, 6.20. Found: C, 47.91; H, 3.56; N, 6.13.

3-Oxo-1,2,3,4-tetrahydroquinolizinium Perchlorate (6a′). Compound **3b** (0.3 g, 1.2 mmol) was treated with 40% $HClO_4$ solution (2 mL) at room temperature, followed by the treatment with dry ether to afford 0.21 g (70%) of precipitate of **6a′**: Colorless crystals (MeOH); mp 203−205 °C; IR (KBr) 1734, 1637 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.69 (2H, t, J = 6.5 Hz), 3.59 (2H, t, J = 6.5 Hz), 5.29 (s, 2H), 8.03 (1H, dd, J = 6.1 and 7.3 Hz), 8.16 (1H, d, J = 7.9 Hz), 8.56 (1H, dd, J = 7.3 and 7.9 Hz), 8.9 (1H, d, J = 6.1 Hz); ^{13}C NMR (DMSO-d_6) δ 26.5, 32.3, 63.6, 125.7, 127.6, 144.9, 145.7, 154.8, 201.2. Anal. Calcd for $C_9H_{10}ClNO_5$: C, 43.65; H, 4.07; N, 5.66. Found: C, 43.38; H, 3.99; N, 5.52.

Reactions of Ylides 3b, 4b with Methyl Propynoate. A solution of **3b** (30 mg, 0.12 mmol) and methyl propynoate (0.011 mL, 0.12 mmol) in acetone-d_6 (0.5 mL) was kept at 55 °C for 12 min[15] to afford **8** as a sole product. Attempted isolation of **8** caused decomposition.

***tert*-Butyl 1-Methoxycarbonyl-3-oxo-3*H*-2a,4,5,8a-tetrahydropyrrolo[2,1,5-*de*]quinolizine-2a-carboxylate (8).** ^{1}H NMR δ 1.51 (9H, s; *t*-BuO), 2.23 (1H, ddd, J = 19.0, 12.8 and 6.4 Hz; H4), 2.47 (1H, ddd, J = 13.6, 6.4 and 1.2 Hz; H5), 2.67 (1H, ddd, J = 13.6, 12.8 and 6.4 Hz; H5), 2.81 (1H, ddd, J = 19.0, 6.4 and 1.2 Hz; H4), 3.82 (3H, s; MeO), 4.74 (1H, d, J = 5.9 Hz; H6), 5.28 (1H, dd, J = 9.2 and 2.5 Hz; H8), 5.76 (1H, q, J = 2.5 Hz; H8a), 5.86 (1H, ddd, J = 9.2, 5.9 and 2.5 Hz; H7), 6.95 (1H, d, J = 2.5 Hz; H2); ^{13}C NMR δ 26.7 (C5), 27.8 ((Me)$_3$C), 35.9 (C4), 52.3 (MeO), 66.2 (C8a), 84.4 and 84.9 (C2a and C(Me)$_3$), 93.1 (C6), 109.2 (C8), 125.0 (C7), 136.9 (C2), 139.8 (C1), 140.5 (C5), 163.5 and 167.9 (CO2), 201.2 (C3); MS m/z (relative intensity) 331 (M$^+$, 16), 275 (26), 230 (93), 198 (100), 188 (40), 172 (35), 142 (24), 141 (20), 57 (26); HRMS calcd for $C_{18}H_{21}NO_5$ 331.1420, found 331.1430.

Methyl 4,5-Dihydro-3-oxo-3*H*-pyrrolo[2,1,5-*de*]quinolizine-1-carboxylate (9a). A solution of **3b** (0.50 g, 2 mmol) and methyl propynoate (0.185 mL, 2 mmol) in DMSO (15 mL) was stirred at 80 °C for 45 min and then poured into water. The solution was basified with ammonia water and extracted with ether. Combined ether extracts were washed with water and brine and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified on silica gel to give **9a** (0.14 g, 30%). The water layer was washed with methylene chloride, acidified with diluted HCl, and extracted with diethyl ether. Combined ether extracts were dried over anhydrous magnesium sulfate. Removal of the solvent gave **10**.

Data for 9a. Colorless needles (*i*-PrOH); mp 147−148 °C; IR (KBr) 1700, 1645 cm^{-1}; ^{1}H NMR δ 2.82 (2H, t, J = 7.6 Hz; H4), 3.42 (2H, t, J = 7.6 Hz; H5), 3.92 (3H, s; MeO), 6.88 (1H, d, J = 6.9 Hz; H6), 7.30 (1H, dd, J = 9.0 and 6.9 Hz; H7), 7.97 (1H, s; H2), 8.16 (1H, d, J = 9.0 Hz; H8); ^{13}C NMR δ 26.5 (C5), 33.5 (C4), 51.3 (MeO), 107.5 (C5a), 112.1 (C6), 117.8 (C8), 120.4 (C2), 122.9, 127.0 (C7), 134.6, 137.6, 164.6 (CO$_2$), 184.7 (C3). Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 67.72; H, 4.82; N, 6.08.

3-(*tert*-Butoxycarbonyl)-1-(methoxycarbonyl)-5-indolizinepropionic Acid (10). Yield 71 mg (14%); dark oil; ^{1}H NMR δ 1.60 (9H, s; *t*-BuO), 2.70 (2H, t, J = 7.5 Hz; CH$_2$CO$_2$), 3.55 (2H, t, J = 7.5 Hz; CH$_2$CH$_2$CO$_2$), 3.91 (3H, s; MeO), 6.82 (1H, d, J = 7 Hz; H6), 7.27 (1H, t, J = 7 Hz; H7), 7.88 (1H, s; H2), 8.31 (1H, d, J = 7 Hz; H8); ^{13}C NMR δ 28.2, 29.4, 30.6, 51.2, 81.6, 104.5, 115.0, 118.0, 119.2, 125.7, 126.5, 140.3, 141.1, 160.4, 164.6, 177.4; MS m/z (relative intensity) 347 (M$^+$, 18), 291 (100), 247 (20), 228 (21), 200 (13), 142 (9), 126 (6), 69 (9), 57 (4); HRMS calcd for $C_{16}H_{19}NO_4$ 347.1369, found 347.1377.

Analogously, **9a** was prepared from the reactions of **3d** and **3i** with methyl propynoate (1.5 equiv) in DMSO in 68% and 40% yield, respectively.

***tert*-Butyl 1-Methoxycarbonyl-3-oxo-3*H*-2a,8a-dihydropyrrolo[2,1,5-*de*]quinolizine-2a-carboxylate (12).** A solution of ylide **4b** (29 mg, 0.12 mmol) and methyl propynoate (0.033 mL, 0.36 mmol) in $CDCl_3$ (0.5 mL) was kept at 60 °C for 45 min. ^{1}H NMR showed a formation of **12** as a sole product, which decomposed upon attempted isolation: ^{1}H NMR δ 1.45 (9H, s; *t*-BuO), 3.83 (3H, s; MeO), 5.42 (1H, d, J = 6.0 Hz; H6), 5.63 (1H, q, J = 2.5 Hz; H8a), 5.99 (1H, dd, J = 10.0 and 2.5 Hz; H8), 6.16 (1H, d, J = 9.8 Hz; H4), 6.18 (1H, ddd, J = 10.0, 6.0 and 2.5 Hz; H7), 7.10 (1H, d, J = 2.5 Hz; H2), 7.24 (1H, d, J = 9.8 Hz; H5); ^{13}C NMR δ 27.0 ((Me)$_3$C), 51.5 (MeO), 64.4 (C8a), 81.9 (C2a), 83.6 (C(Me)$_3$), 103.7 (C6), 116.8 (C8), 121.0 (C4), 123.7 (C7), 134.9, 137.0 (C5), 139.6, 141.2 (C8), 163.1 (CO$_2$), 165.8 (CO$_2$), 184.6 (C3).

Analogously, **12** was generated from **4b** in DMSO-d_6 at 75 °C within 30 min.

Methyl 3-Oxo-3*H*-pyrrolo[2,1,5-*de*]quinolizine-1-carboxylate (13).[4] A solution of ylide **4b** (0.5 g, 2 mmol) and methyl propynoate (0.275 mL, 3 mmol) in DMSO (15 mL) was stirred at 75 °C for 1 h. Compound **13** (0.27 g, 1.2 mmol) was isolated from the reaction mixture as described above for **9**: yellow needles (benzene); mp 207−208 °C; ^{1}H NMR (DMSO-d_6) δ 3.93 (3H, s), 7.29 (1H, d, J = 9.9 Hz), 8.00 (1H, dd, J = 8.4 and 7.4 Hz), 8.15 (1H, s), 8.19 (1H, d, J = 7.4 Hz), 8.33 (1H, d, J = 9.9 Hz), 8.70 (1H, d, J = 8.4 Hz); ^{13}C NMR δ 51.8, 112.7, 119.3, 121.7, 122.3, 125.6, 127.1, 128.7, 130.4, 134.7, 135.2, 164.1, 172.7. Anal. Calcd for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.17. Found: C, 69.08; H, 4.18; N, 5.83.

Reaction of Ylide 3b with DMAD. A mixture of **3b** (0.500g, 2 mmol) and DMAD (0.522 mL, 4.2 mmol) in acetone (30 mL) was kept at 55 °C for 20 min without stirring. Removal of the solvent under reduced pressure followed by silica gel chromatography gave azocine **15**.

***tert*-Butyl (2aa,10aa)-3-Oxo-1,2,6,7-tetramethoxycarbonyl-2a,4,5,10a-tetrahydro-3*H*-azocino[2,1,8-*cd*]-indolizine-2a-carboxylate (15).** Yield 0.54 g (50%); yellow prisms (MeOH); mp 164.5−165.5 °C; IR (KBr) 1763, 1745, 1737, 1716, 1699 cm^{-1}; ^{1}H NMR δ 1.48 (9H, s; *t*-BuO), 2.41 (1H, m; H4), 2.53 (1H, m; H5), 2.64 (1H, brd, J = 16.5 Hz; H4), 3.47, 3.75, 3.78, 3.87 (each 3H, s; MeO), 4.62 (1H, brd, J = 18 Hz; H5), 5.95 (1H, t, J = 8 Hz; H10), 6.12 (1H, d, J = 7.8 Hz; H10a), 6.72 (1H, dd, J = 8 and 2.3 Hz; H9), 7.21 (1H, d, J = 2.3 Hz; H8); ^{13}C NMR δ 24.5, 27.4, 34.2, 51.3, 52.1, 52.6, 52.7, 65.3, 82.8, 84.9, 100.8, 131.3, 133.9, 134.1, 135.1, 137.2, 138.2, 152.5, 161.7, 162.2, 164.6, 167.5, 167.9, 201.2. Anal. Calcd for $C_{26}H_{29}NO_{11}$: C, 58.75; H, 5.50; N, 2.64. Found: C, 58.74; H, 5.51; N, 2.58.

Stepwise Reaction of Ylide 3b with Methyl Propynoate and DMAD. A mixture of **3b** (0.500 g, 2 mmol) and methyl propynoate (0.356 mL, 2 mmol) in acetone (30 mL) was kept without stirring at 55 °C for 12 min, and then DMAD (0.249 mL, 2 mmol) was added. The reaction mixture was kept for 15 min at the same conditions. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded **16**.

***tert*-Butyl (2aa,10aa)-3-Oxo-2a,4,5,10a-tetrahydro-1,6,7-trimethoxycarbonyl-3*H*-azocino[2,1,8-*cd*]-indolizine-2a-carboxylate (16).** Yield 0.67 g (70%); light yellow prisms (MeOH); mp 164.5−165.5 °C; IR (KBr) 1755, 1724, 1716, 1708, 1691 cm^{-1}; ^{1}H NMR δ 1.46 (9H, s; *t*-BuO), 2.44 (2H, m; H4, H5), 2.60 (1H, brd, J = 18 Hz), 3.58, 3.75, 3.77 (each 3H, s; MeO), 4.65 (1H, brd, J = 18.0 Hz), 5.79 (1H, dd, J = 10.0 and 7.4 Hz; H10), 6.05 (1H, d, J = 7.4 Hz; H10a), 6.70 (1H, dd, J = 10.0 and 3.0 Hz; H9), 6.88 (1H, d, J = 2.0 Hz; H2), 7.25 (1H, d, J = 3.0 Hz; H8); ^{13}C NMR δ 24.8 (C5), 27.6 ((Me)$_3$C), 34.7 (C4), 51.3, 52.1, 52.2 (MeO), 64.8 (C10a), 83.6 (C(Me)$_3$),

(15) Preparations of cycloadducts were performed without stirring unless otherwise mentioned.

85.1 (C2a), 100.3 (C7a), 132.1, 134.0, 134.1, 134.9, 136.8, 138.8, 153.7 (C6a), 162.2, 165.0, 167.7, 168.2 (CO_2), 201.8 (C3). Anal. Calcd for $C_{24}H_{27}NO_9$: C, 60.88; H, 5.75; N, 2.96. Found: C, 60.65; H, 5.82; N, 2.92.

Reaction of Quinolizinium-olate 4b with DMAD. A solution of **4b** (1.00 g, 4 mmol) and DMAD (1.51 mL, 12 mmol) in chloroform (50 ml) was refluxed for 5 h. The reaction mixture was concentrated under reduced pressure and subjected to silica gel chromatography. The first fraction was identified as **18**. The second fraction was isolated as a pale yellow oil and assigned as **19.** The third fraction was identified as **20**.

***tert*-Butyl (2aa,10aa)-2a,10a-Dihydro-3-oxo-1,2,6,7-tetramethoxycarbonyl-3*H*-azocino[2,1,8-*cd*]indolizine-2a-carboxylate (18).** Yield 0.44 g (21%); orange prisms (MeOH); mp 160.5−161.5 °C; IR (KBr) 1759, 1738, 1724, 1703, 1687 cm^{-1}; ^1H NMR δ 1.43 (9H, s; *t*-BuO), 3.65, 3.76, 3.78, 3.90 (each 3H, s; MeO), 5.94 (1H, dd, J = 9.9 and 7.8 Hz; H10), 6.01 (1H, d, J = 7.8 Hz; H10a), 6.21 (1H, d, J = 10.6 Hz; H5), 6.70 (1H, dd, J = 9.9 and 2.8 Hz; H9), 7.35 (1H, d, J = 2.8 Hz; H8), 8.64 (1H, d, J = 10.6 Hz; H4); ^{13}C NMR δ 27.4, 52.1, 52.2, 52.6, 52.7, 66.8, 81.4, 84.6, 111.4 126.2, 130.3, 133.7, 134.0, 136.7, 137.0, 138.4, 141.0, 143.2, 161.7, 162.8, 165.3, 166.2, 166.5, 188.4; MS *m*/*z* (relative intensity) 529 (M^+, 1.2), 498 (0.5), 470 (1), 429 (21), 397 (100), 365 (35), 338 (41), 306 (7), 278 (13), 254 (6), 220 (6), 193 (6), 57 (15). Anal. Calcd for $C_{26}H_{27}NO_{11}$: C, 58.98; H, 5.14; N, 2.65. Found: C, 58.92; H, 5.08; N, 2.52.

***tert*-Butyl 3,4-Di(methoxycarbonyl)-2-[2,3-di(methoxycarbonyl)cinnamoyl]pyrrol-2-carboxylate (19).** Yield 0.39 g (19%); ^1H NMR δ 1.55 (9H, s; *t*-BuO), 3.78, 3.88, 3.89, 3.93 (each 3H, s; MeO), 6.46 (1H, d, J = 12.2 Hz; CH=C<u>H</u>CO), 7.34 (1H, d, J = 12.2 Hz; C<u>H</u>=CHCO), 7.42 (1H, t, J = 7.8 Hz; Ph-H5), 7.60 (1H, s; H5), 7.65 (1H, d, J = 7.8 Hz; Ph-H6), 7.90 (1H, d, J = 7.8 Hz; Ph-H4); ^{13}C NMR δ 27.6, 51.6, 52.2, 52.4, 52.6, 83.2, 115.6, 123.2, 124.2, 125.3, 127.7, 128.5, 129.3, 130.3, 132.5, 132.8, 133.5, 142.2, 158.2, 161.8, 163.0, 163.6, 165.6, 168.1; MS (CI^+) *m*/*z* (relative intensity) 530 (M^+, 25), 474 (100), 428 (10), 284 (12), 228 (83), 196 (8); HRMS calcd for $C_{26}H_{27}NO_{11}$ ($M^+ + 1$) 530.1662, found 530.1636.

Dimethyl 3-Oxo-3*H*-pyrrolo[2,1,5-*de*]quinolizine-1,2-dicarboxylate (20). Yield 0.114 g (10%); ^1H NMR δ 3.97 (3H, s), 4.08 (3H, s), 7.29 (1H, d, J = 10 Hz), 7.81 (2H, m), 7.92 (1H, d, J = 10 Hz), 8.75 (1H, dd, J = 1.8 and 7.6 Hz); ^{13}C NMR δ 55.2, 53.4, 109.3, 119.9, 122.3, 123.9, 126.5, 128.4, 128.9, 130.6, 134.0, 134.9, 163.1, 165.2, 172.1.

Hydrolysis of 19. A mixture of **19** (0.39 g, 0.74 mmol) and 0.01 mL of 10% KOH/MeOH in 15 mL of methanol was stirred at room temperature for 30 min. After removal of the solvent under reduced pressure, the residue was acidified with 1% HCl and extracted with methylene chloride. Combined extracts were washed with brine and dried over anhydrous magnesium sulfate; the residue after removal of solvent was subjected to silica gel chromatography. The first fraction, a clear oil, 0.195 g (95%), was identified as **22**. The second fraction was identified as **21**.

Methyl 2′,3′-Di(methoxycarbonyl)cinnamate (22). ^1H NMR δ 3.63 (3H, s; MeO), 3.90 (6H, s; 2MeO), 6.10 (1H, d, J = 12.6 Hz; CH=C<u>H</u>CO), 7.11 (1H, d, J = 12.6 Hz; C<u>H</u>=CHCO), 7.47 (1H, t, J = 7.8 Hz; Ph-H5), 7.66 (1H, d, J = 7.8 Hz; Ph-H6), 7.94 (1H, d, J = 7.8 Hz; Ph-H4); ^{13}C NMR δ 51.5, 52.6, 52.7, 123.0, 128.2, 128.7, 129.7, 133.2, 133.9, 134.0, 140.2, 165.5, 166.1, 168.8; MS *m*/*z* (relative intensity) 278 (M^+, 2), 263 (0.5), 247 (15), 231 (5), 219 (100), 203 (4), 187 (6), 173 (6), 157 (9), 129 (5), 94 (6), 75 (5), 57(5); HRMS calcd for $C_{14}H_{14}O_6$ 278.0790, found 278.0780.

***tert*-Butyl 3,4-Di(methoxycarbonyl)pyrrol-2-carboxylate (21).** Yield 0.198 g (97%); colorless oil; ^1H NMR δ 1.55 (9H, s; *t*-BuO), 3.82, 3.94 (each 3H, s; MeO), 7.44 (1H, d, J = 2.7 Hz; H5), 9.98 (1H, brs; H1); ^{13}C NMR δ 28.1, 51.6, 52.6, 82.8, 115.7, 122.3, 122.5, 125.7, 159.2, 163.2, 165.9; MS *m*/*z* (relative intensity) 283 (M^+, 12), 247 (7), 227 (61), 219 (50) 196 (100), 178 (49), 152 (36), 93 (15), 57 (15); HRMS calcd for $C_{13}H_{17}NO_6$ 283.1056, found 283.1034.

Reactions of 3-Oxo-1,2,3,4-tetrahydroquinolizinium Bromides 6 with Methyl Propynoate. To a stirred suspension of salt **6a** (0.50 g, 2.2 mmol) in acetonitrile (20 mL) were added ethyldiisopropylamine (0.42 mL, 2.4 mmol) and methyl propynoate (0.4 mL, 4.4 mmol). The reaction mixture was stirred at 60 °C for 0.5 h and then concentrated under reduced pressure. The residue was distributed between methylene chloride and water, and water layer was extracted with methylene chloride. Combined methylene chloride solutions were washed with brine and dried over anhydrous magnesium sulfate. The residue after removal of the solvent was purified by silica gel chromatography to give **9a** (0.30 g, 65%). Further elution with 6% water−ethanol mixture gave a second fraction as an orange oil, which was identified as **24a** (90 mg, 20%).

4-(2-Methoxycarbonylethenyl)-3-oxo-1,2,3,4-tetrahydroquinolizinium-4-ide (24a). ^1H NMR δ 2.51 (2H, t, J = 7.2 Hz), 3.12 (2H, t, J = 7.2 Hz), 3.73 (3H, s), 6.67 (1H, d, J = 15.0 Hz), 7.43 (1H, d, J = 7.6 Hz), 7.47 (1H, dd, J = 6.4 and 7.2 Hz), 7.55 (1H, dd, J = 7.2 and 7.6 Hz), 7.72 (1H, d, J = 15.0 Hz), 8.34 (1H, d, J = 6.4 Hz); ^{13}C NMR δ 28.3, 31.5, 51.0, 103.2, 115.0, 124.8, 125.3, 132.7, 134.1, 134.7, 146.4, 171.1, 181.0.

Similarly, **9e** was obtained from **6e**.

Methyl 4,5-Dihydro-4-methyl-3-oxo-3*H*-pyrrolo[2,1,5-*de*]quinolizine-1-carboxylate (9e). Light yellow needles (*i*-PrOH); mp 127−128 °C; IR (KBr) 1701, 1643 cm^{-1}; ^1H NMR δ 1.30 (3H, d, J = 6.3 Hz; Me), 2.84 (1H, m; H4), 3.14 (1H, dd, J = 16.3 and 11.1 Hz; H5), 3.44 (1H, dd, J = 16.3, and 5.7 Hz; H5), 3.91 (3H, s; MeO), 6.88 (1H, d, J = 6.9 Hz; H6), 7.32 (1H, dd, J = 6.9 and 8.9 Hz; H7), 7.96 (1H, brs; H2), 8.16 (1H, d, J = 8.9 Hz; H8); ^{13}C NMR δ 14.9 (Me), 34.2 (C5), 37.6 (C4), 51.3 (MeO), 107.5 (C5a), 112.2 (C6), 117.8 (C8), 120.5 (C2), 122.2, 126.8 (C7), 134.4, 137.2, 164.6 (CO_2), 187.5 (C3). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.38; N, 5.76. Found: C, 69.05; H, 5.40; N, 5.64.

Supporting Information Available: ^1H and ^{13}C NMR spectra of **3a**−**i**, **4a,b**, **5a**, **6a**−**c**, **9a,e**, **12**, **13**, **15**, **16**,and **18**−**22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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