Thermal Reaction of Imidazolium *N*-Vinylimino Ylides: Formation of Mesomeric Betaines, Imidazopyridaziniumides, *via* Back-Donated 1,6-Cyclization

Yoshiro MATSUDA,* Makoto YAMASHITA, Kimitoshi TAKAHASHI, Shizuki IDE, Takahiro ITOU, Chieko MOTOKAWA, and Yasushige CHIYOMARU

School of Pharmaceutical Sciences, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852, Japan.

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The reaction of *N*-aminoimidazolium salts (4, 5) with polarized olefins (2a—d, 3a, b) in the presence of K_2CO_3 in EtOH gave the corresponding imidazolium *N*-vinylimino ylides (6, 7). Thermolyses of the *N*-vinylimino ylides (6c—f, 7a—c) afforded mesomeric betaines (8a—d, 9a, b, 10a, b). Treatment of the salt (5) with polarized olefins (2b—d, 3c) in the presence of K_2CO_3 in EtOH directly yielded mesomeric betaines (9c—d, 10c), while in EtOH, the reaction of the salt (5) with polarized olefins (2e, 3d) in the presence of K_2CO_3 gave pyrazoles (11a, b). The formation of mesomeric betaines is suggested to proceed *via* back-donated 1,6-cyclization.

Keywords imidazopyridaziniumide; polarized olefin; imidazolium *N*-vinylimino ylide; 1,5-dipolar cyclization; back-donated 1,6-cyclization; mesomeric betaine

Polarized olefins (ethoxymethylene compounds and ketene dithioacetals) that are appropriately functionalized (cyano, methoxycarbonyl, nitro, sulfonyl, pyridyl, *etc.*) are versatile reagents which have been extensively utilized in heterocyclic synthesis.¹⁾ As a part of our continuing interest in polarized olefins, we carried out extensive studies on the reaction of heteroaromatic compounds with various polarized olefins and their analogues.²⁾ In particular, it is well known that heterocyclic *N*-amino salts react with polarized olefins to produce heterocyclic *N*-vinylimino ylides (1). These ylides (1), acting as extended dipoles, are of interest in heterocyclic chemistry.³⁾ These *N*-vinylimino ylides may be considered to be resonance hybrids of the representative structures (1, 1', 1'') shown in Fig. 1.

However, a number of previous studies on *N*-vinylimino ylides (1) have been mainly concerned with the synthesis of bicyclic compounds with bridgehead nitrogen (azain-

dolizine, pyrazoloimidazole, *etc.*) by 1,5-dipolar cyclization due to the resonance structure (1''). We have taken advantage of an alternative *N*-vinylimino ylide form (resonance structure 1') to realize a novel reaction which we have termed a "back-donated 1,6-cyclization." Our preliminary studies on the thermolyses of imidazolium *N*-allylides and the reaction of imidazolium *N*-amino salt with ketene dithioacetal have led to a new heterocyclic ring closure proceeding by back-donated 1,6-cyclization onto carbonyl or cyano carbon at X to produce the mesomeric betaines, imidazo[1,2-*a*]pyridiniumides⁴⁾ or imidazo[1,2-*b*]pyridaziniumides.^{4a)} The purpose of the present investigation was to extend back-donated 1,6-cyclization to the synthesis of 7-oxoimidazopyridaziniumides (8) and benzimidazopyridaziniumides (9, 10), and to examine the decarboxylation of 8a. Consequently, we obtained the hydrobromide (12) and the parent compound (13) by the decarboxylation of 8a. The polarized olefins (2, 3)⁵⁾ used in the present work are shown in Fig. 2.

Results and Discussion

The starting materials, *N*-amino salts (4, 5) were prepared by amination of *N*-alkylimidazoles or *N*-methylbenzimidazole with *O*-mesitylsulfonylhydroxylamine in CH_2Cl_2 .⁶⁾ The reaction of *N*-amino salts (4, 5) with polarized olefins (2a—d, 3a, b) in the presence of K_2CO_3 gave *N*-vinylimino ylides (6, 7) in good yields (Chart 1).

Attempts to obtain the mesomeric betaine from 3-methylimidazolium *N*-vinylimino ylides (6a—c) by thermolysis in refluxing xylene, trimethylbenzene or diphenyl ether, *etc.*, were fruitless. Thus, only unreacted material and/or unidentified decomposition products could be detected by ¹H-NMR spectroscopy and TLC, and these were not further studied. After much investigation, we found that heating of 3-benzylimidazolium *N*-vinylimino ylides (6d, e) in refluxing xylene resulted in back-donated 1,6-cyclization, giving rise to the mesomeric betaines, 7-oxoimidazo[1,2-*b*]pyridaziniumides (8a, b), in moder-

Fig. 1

Fig. 2

Chart 1

Chart 2

Chart 3

Chart 4

ate yields. On the other hand, thermolysis of **6f** in a variety of refluxing solvents did not proceed. In our previous paper we reported the synthesis of the mesomeric betaine **8d** by the reaction of the salt (**4b**) with ketene dithioacetal (**3a**) in the presence of K_2CO_3 in dimethylsulfoxide (DMSO) at room temperature for a week. Therefore we treated **6f** under similar conditions to give **8d** in good yield. Similar treatment of **6c** gave **8c** in good yield. However, other *N*-vinylimino ylides (**6a, b**, **6d, e**) did not afford the expected mesomeric betaines under the same conditions. The reasons for failure of the cyclization of **6a, b** are unclear at the present time (Chart 2).

Reactions of benzimidazolium *N*-vinylimino ylides (**7a, c**) were investigated under a variety of conditions. Thermolysis of **7a** in refluxing trimethylbenzene (TMB) proceeded, with formation of 4-oxobenzimidazopyridaziniumide (**9a**) together with 4-iminobenzimidazopyridaziniumide (**10a**). The mesomeric betaine (**10b**) was obtained by heating of **7c** in refluxing EtOH. Under conditions similar to those used in the formation of **8c** and

8d, the mesomeric betaine (**9b**) was obtained by the reaction of **7b** in the presence of K_2CO_3 . The reaction of the benzimidazolium *N*-amino salt (**5**) with polarized olefins (**2b—d**, **3c**) in the presence of K_2CO_3 did not give *N*-vinylimino ylide but directly afforded the back-donated 1,6-cyclization products, benzimidazopyridaziniumides (**9c—e**, **10c**, respectively) (Chart 3).

Similar treatment of **5** with the polarized olefins (**2e, 3d**) afforded the 1,5-dipolar cyclization products (pyrazoles **11a, b**) (Chart 4).

In order to obtain the parent base of the imidazo[1,2-*b*]-pyridaziniumide derivative, we examined various conditions for removal of the methoxycarbonyl or cyano groups, and succeeded in isolation of 1-benzylimidazo[1,2-*b*]-pyridaziniumide (**13**). The methoxycarbonyl group of **8a** could be easily removed upon treatment with 47% hydrobromic acid under reflux to give the hydrobromide

(12), which was converted to the free base (13) by the use of K_2CO_3 . However, attempts to produce the parent base of the benzo analogue were fruitless (Chart 5).

Physical Properties of Mesomeric Betaines The thermal stability of most of the mesomeric betaines (8, 9, 10) is shown by the fact that the mesomeric betaines melt over $159^\circ C$, except for the parent free base (13). The parent base (13) was so unstable and hygroscopic that it decomposed within a week on exposure to air at room temperature.

Infrared (IR) Absorption Spectra The 7-carbonyl absorption maxima for the mesomeric betaines (8a—d, 13) vary from 1575 to 1620 cm^{-1} . This result indicates that, in certain cases, the carbonyl absorption maxima for the mesomeric betaines are influenced by the electronic properties of the substituent group at the 6-position. The mesomeric betaines (8a—d, 13) can be described to a first approximation by the resonance structures A and B as shown below. Comparison of the 7-carbonyl absorption maximum (1575 cm^{-1}) of the parent base (13) with those (1575 — 1620 cm^{-1}) of the other mesomeric betaines (8a—d) left no doubt that at least the parent base (13) has the dipolar form B (Fig. 3).

NMR Spectra of Mesomeric Betaines The chemical shifts (7.91 — 8.27 ppm) of the C_2 - and C_3 -protons in the 1H -NMR spectra of the mesomeric betaines (8a—d, 13) are little influenced by the electronic properties of the substituent groups on the pyridazine moiety.

Chart 5

Fig. 3

Chart 6

Chart 7

^{13}C -NMR spectra of mesomeric betaines (8a, 12, 13) were measured in $DMSO-d_6$. The C-7 signal appears at 160.3 ppm in 8a, 154.4 ppm in 12, and 161.2 ppm in the free base (13). Those values are similar to the chemical shifts^{3k)} (159.5 , 157.8 ppm) of the carbonyl carbons in the mesomeric betaines, triazolopyridazines.

Mechanistic Overview As pointed out in our previous paper,⁴⁾ a reasonable mechanism for the formation of the back-donated 1,6-cyclization product (8a) involves the resonance structure (6d'), as outlined in Chart 6.

As pointed out by Acheson and Elmore^{3d)} and Meth-Cohn,^{3m)} the formation of 11 may be rationalized as outlined in Chart 7.

In conclusion, the *N*-vinylimino ylides (15) with hydrogen at the 3-position of the vinylimino group underwent 1,5-dipolar cyclization to give the pyrazole derivatives (11), whereas the other *N*-vinylimino ylides (6, 7) which had two electron-withdrawing groups at the 3-position of the vinylimino group participated in back-donated 1,6-cyclization to produce the mesomeric betaines (8, 9, 10). The high efficiency of the back-donated 1,6-cyclization, due to the resonance structure 1', in thermolysis of the *N*-vinylimino ylide of the resulting mesomeric betaine, imidazo[1,2-*b*]pyridaziniumide, presents interesting synthetic possibilities.

Experimental

Melting points were determined with a Mitamura Mel-Temp and are uncorrected. IR spectra were recorded in KBr pellets on a JASCO IRA-2 spectrophotometer. Ultraviolet (UV) spectra were recorded on a Hitachi 323 spectrophotometer. 1H - and ^{13}C -NMR spectra were obtained on JNM-FX-90Q and JNM-GX400 spectrometers with tetramethylsilane as an internal standard. Chemical shifts are reported in parts per million (δ). Elemental analyses (C, H, N) of all compounds described here were performed on a Yanagimoto MT-2 CHN recorder. Mass spectra (MS) were measured on a JMS-DX-303G spectrometer.

General Procedure for the Preparation of 6 and 7 A mixture of a salt (4, 5) (4 mmol), a polarized olefin (2a—d, 3a, b) (4 mmol) and K_2CO_3 (8 mmol) in EtOH (50 ml) was stirred at room temperature for a week and the mixture was then evaporated under reduced pressure. The residue was taken up in ice-water (100 ml). The precipitate was collected by filtration, washed with water, dried and recrystallized from $CHCl_3$ -MeOH to give the corresponding product (6a—f, 7a—c, respectively).

6a: mp 188 — $190^\circ C$ (36%). IR (KBr) cm^{-1} : 2180 (CN), 1645 (CO). UV λ_{max}^{EtOH} nm (log ϵ): 222 (4.14), 311 (4.32). 1H -NMR ($DMSO-d_6$) δ : 1.16 (3H, t, $J=7\text{ Hz}$, OCH_2CH_3), 3.79 (3H, s, NMe), 4.02 (2H, q, $J=7\text{ Hz}$, OCH_2CH_3), 7.58 (1H, t, $J=2\text{ Hz}$, C_4-H), 7.83 (1H, t, $J=2\text{ Hz}$,

C₅-H), 8.33 (1H, s, -CH=), 9.10 (1H, t, $J=2$ Hz, C₂-H). *Anal.* Calcd for C₁₀H₁₂N₄O₂: C, 54.54; H, 5.49; N, 25.44. Found: C, 54.48; H, 5.54; N, 25.13.

6b: mp 223–225 °C (10%). IR (KBr) cm⁻¹: 2200 (CN), 2180 (CN). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 312 (3.82). ¹H-NMR (DMSO-*d*₆) δ : 3.79 (3H, s, NMe), 7.58 (1H, t, $J=2$ Hz, C₅-H), 7.90 (1H, t, $J=2$ Hz, C₄-H), 8.09 (1H, s, -CH=), 9.10 (1H, t, $J=2$ Hz, C₂-H). *Anal.* Calcd for C₈H₇N₅: C, 55.48; H, 4.07; N, 40.44. Found: C, 55.34; H, 4.14; N, 40.40.

6c: mp 142–143 °C (52%). IR (KBr) cm⁻¹: 2180 (CN), 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 217 (3.89), 263 (3.70). ¹H-NMR (DMSO-*d*₆) δ : 2.29 (3H, s, SMe), 3.36 (3H, s, OMe), 3.78 (3H, s, NMe), 7.49 (1H, brs, C₄-H or C₅-H), 7.51 (1H, brs, C₄-H or C₅-H), 8.94 (1H, brs, C₂-H). *Anal.* Calcd for C₁₀H₁₂N₄O₂S: C, 47.61; H, 4.79; N, 22.21; S, 12.71. Found: C, 47.44; H, 4.73; N, 22.11; S, 12.76.

6d: mp 157–158 °C (83%). IR (KBr) cm⁻¹: 1650 (CO), 1630 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 202 (4.20), 236 (4.11), 310 (4.34). ¹H-NMR (CDCl₃) δ : 1.26 (6H, t, $J=7$ Hz, 2 × OCH₂CH₃), 4.15 (4H, q, $J=7$ Hz, 2 × OCH₂CH₃), 5.32 (2H, s, CH₂Ph), 6.96 (1H, t, $J=2$ Hz, C₄-H), 7.20–7.45 (6H, m, C₅-H and ArH), 8.64 (1H, s, -CH=), 9.16 (1H, t, $J=2$ Hz, C₂-H). *Anal.* Calcd for C₁₈H₂₁N₃O₄: C, 62.96; H, 6.16; N, 12.24. Found: C, 62.75; H, 6.10; N, 12.24.

6e: mp 176–178 °C (47%). IR (KBr) cm⁻¹: 1675 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 276 (4.34), 360 (4.56). ¹H-NMR (CDCl₃) δ : 1.32 (3H, t, $J=7$ Hz, OCH₂CH₃), 4.29 (2H, q, $J=7$ Hz, OCH₂CH₃), 5.42 (2H, s, CH₂Ph), 7.04 (1H, brs, C₄-H), 7.27–7.41 (5H, m, Ar-H), 7.49 (1H, brs, C₅-H), 9.07 (1H, s, -CH=), 9.29 (1H, brs, C₂-H). *Anal.* Calcd for C₁₅H₁₆N₄O₄: C, 56.96; H, 5.10; N, 17.71. Found: C, 56.70; H, 5.04; N, 17.41.

6f: mp 154–155 °C (50%). IR (KBr) cm⁻¹: 2180 (CN), 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 207 (4.02), 236 (3.77) sh, 256 (3.77) sh, 307 (3.63). ¹H-NMR (CDCl₃) δ : 2.35 (3H, s, SMe), 3.57 (3H, s, OMe), 5.24 (2H, s, -CH₂Ph), 7.03 (1H, t, $J=2$ Hz, C₄-H), 7.26 (1H, t, $J=2$ Hz, C₅-H), 7.40–7.50 (5H, m, Ar-H), 8.14 (1H, t, $J=2$ Hz, C₂-H). *Anal.* Calcd for C₁₆H₁₆N₄O₂S: C, 58.52; H, 4.91; N, 17.06. Found: C, 58.43; H, 4.91; N, 17.11.

7a: mp 191–193 °C (62%). IR (KBr) cm⁻¹: 2190 (CN), 1635 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 216 (4.28), 274 (4.22), 281 (4.30), 289 (4.27), 318 (4.05). ¹H-NMR (DMSO-*d*₆) δ : 1.17 (3H, t, $J=7$ Hz, OCH₂CH₃), 4.02 (3H, s, NMe), 4.04 (2H, q, $J=7$ Hz, OCH₂CH₃), 7.55–7.99 (4H, m, C_{4,5,6,7}-H), 8.51 (1H, s, -CH=), 9.74 (1H, s, C₂-H). *Anal.* Calcd for C₁₄H₁₄N₄O₂: C, 62.21; H, 5.22; N, 20.73. Found: C, 62.22; H, 5.26; N, 20.77.

7b: mp 131–132 °C (52%). IR (KBr) cm⁻¹: 2170 (CN), 1675 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 274 (4.26), 280 (4.27), 320 (3.74). ¹H-NMR (CDCl₃) δ : 2.48 (3H, s, SMe), 3.52 (3H, s, OMe), 4.07 (3H, s, NMe), 7.34–7.77 (4H, m, C_{4,5,6,7}-H), 8.57 (1H, s, C₂-H). *Anal.* Calcd for C₁₄H₁₄N₂O₂S: C, 55.61; H, 4.67; N, 18.53. Found: C, 55.49; H, 4.65; N, 18.47.

7c: mp 180–182 °C (70%). IR (KBr) cm⁻¹: 2190 (CN), 2150 (CN). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 273 (4.35), 279 (4.34). ¹H-NMR (DMSO-*d*₆) δ : 2.53 (3H, s, SMe), 4.04 (3H, s, NMe), 7.71–8.04 (4H, m, C_{4,5,6,7}-H), 9.68 (1H, s, C₂-H). *Anal.* Calcd for C₁₃H₁₁N₅S: C, 57.97; H, 4.12; N, 26.00. Found: C, 57.86; H, 4.14; N, 25.94.

General Procedure for the Preparation of 8a,b A solution of an *N*-vinylimino ylide (**6d,e**) (2 mmol) in xylene (60 ml) was refluxed for 24 h and the solution was then evaporated under reduced pressure. The residue was taken up in ice-water (50 ml) and the mixture was extracted with CHCl₃ (4 × 30 ml). The combined extracts were washed with water (50 ml), dried (Na₂SO₄), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a benzene-CHCl₃ (1:20) fraction, the corresponding product (**8a,b**) was obtained.

8a: mp 181–182 °C (58%). IR (KBr) cm⁻¹: 1705 (CO), 1580 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 205 (4.32), 237 (4.29), 244 (4.23) sh, 273 (3.80) sh, 283 (3.85) sh, 315 (4.24), 323 (4.21). ¹H-NMR (DMSO-*d*₆) δ : 1.26 (3H, t, $J=7$ Hz, OCH₂CH₃), 4.19 (2H, q, $J=7$ Hz, OCH₂CH₃), 6.00 (2H, s, CH₂Ph), 7.32–7.41 (5H, m, Ar-H), 8.08 (1H, d, $J=2$ Hz, C₂-H), 8.19 (1H, d, $J=2$ Hz, C₃-H), 8.48 (1H, s, C₅-H). ¹³C-NMR (DMSO-*d*₆) δ : 14.3, 51.4, 59.1, 106.3, 117.6, 123.8, 127.7, 128.0, 128.7, 135.2, 136.5, 150.5, 160.3, 164.7. *Anal.* Calcd for C₁₆H₁₅N₃O₃: C, 64.64; H, 5.09; N, 14.13. Found: C, 64.52; H, 5.16; N, 14.02.

8b: mp 208–210 °C (50%). IR (KBr) cm⁻¹: 1620 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 204 (4.23), 246 (4.16), 276 (3.69), 286 (3.64) sh, 355 (4.13). ¹H-NMR (DMSO-*d*₆) δ : 5.98 (2H, s, CH₂Ph), 7.29–7.38 (5H, m, Ar-H), 8.12 (1H, d, $J=2$ Hz, C₂-H), 8.27 (1H, d, $J=2$ Hz, C₃-H), 8.89 (1H, s, C₅-H). *Anal.* Calcd for C₁₃H₁₀N₄O₃: C, 57.78; H, 3.73; N, 20.73. Found:

C, 57.77; H, 3.86; N, 20.77.

General Procedure for the Preparation of 8c,d A mixture of an *N*-vinylimino ylide (**6c,f**) (4 mmol) and K₂CO₃ (8 mmol) in DMSO (30 ml) was stirred at room temperature for a week and then evaporated under reduced pressure. The residue was taken up in ice-water (100 ml). The precipitate was filtered, washed with water, dried and recrystallized from CHCl₃-MeOH to give the corresponding product (**8c,d**, respectively).

8c: mp 288–290 °C (95%). IR (KBr) cm⁻¹: 2200 (CN), 1595 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 242 (3.97), 309 (3.66), 322 (3.60) sh. ¹H-NMR (DMSO-*d*₆) δ : 2.52 (3H, s, SMe), 4.19 (3H, s, NMe), 7.91 (1H, d, $J=2$ Hz, C₂-H), 8.08 (1H, d, $J=2$ Hz, C₃-H). *Anal.* Calcd for C₉H₈N₄OS: C, 49.08; H, 3.66; N, 25.44. Found: C, 49.00; H, 3.47; N, 25.63.

8d: mp 226–228 °C (95%) (lit.⁴⁰) mp 227 °C).

Thermolysis of 7a A solution of **7a** (2 mmol) in TMB (60 ml) was refluxed for 24 h and the solution was then evaporated under reduced pressure. The residue was taken up in ice-water (50 ml) and the mixture was extracted with CHCl₃ (4 × 30 ml). The combined extracts were washed with water (50 ml), dried (Na₂SO₄), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a benzene-CHCl₃ (2:1) fraction, **9a** was obtained. From a CHCl₃ fraction, **10a** was obtained.

9a: mp 257–260 °C (6%). IR (KBr) cm⁻¹: 2240 (CN), 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 204 (4.55), 229 (4.41), 257 (4.12), 263 (4.12), 327 (4.21). ¹H-NMR (CDCl₃) δ : 3.77 (3H, s, NMe), 7.27–7.57 (3H, m, C_{6,7,8}-H), 8.20 (1H, s, C₂-H), 8.31–8.42 (1H, m, C₅-H). *Anal.* Calcd for C₁₂H₈N₄O: C, 64.28; H, 3.60; N, 24.99. Found: C, 64.25; H, 3.80; N, 24.80.

10a: mp 159–160 °C (5%). IR (KBr) cm⁻¹: 1700 (CO), 1600 (C=NH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 215 (4.20), 253 (3.81), 358 (3.98). ¹H-NMR (CDCl₃) δ : 1.39 (3H, t, $J=7$ Hz, OCH₂CH₃), 3.81 (3H, s, NMe), 4.34 (2H, q, $J=7$ Hz, OCH₂CH₃), 7.31–7.57 (3H, m, C_{6,7,8}-H), 8.48 (1H, s, C₂-H), 8.95 (1H, m, C₉-H), 9.25 (1H, brs, C=NH). *Anal.* Calcd for C₁₄H₁₄N₄O₂: C, 62.21; H, 5.22; N, 20.73. Found: C, 62.20; H, 5.22; N, 20.72.

3-Cyano-4,5-dihydro-4-imino-5-methyl-2-methylthiobenzimidazo[1,2-*b*]pyridazin-9*b*-ium-1-ide (10b) A solution of **7c** (2 mmol) in EtOH (60 ml) was refluxed for 24 h and the solution was then evaporated under reduced pressure. The residue was taken up in ice-water (50 ml) and the mixture was extracted with CHCl₃ (4 × 30 ml). The combined extracts were washed with water (50 ml), dried (Na₂SO₄), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a CHCl₃ fraction, **10b** was obtained.

10b: mp 267–270 °C (20%). IR (KBr) cm⁻¹: 2180 (CN). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 202, 235 sh, 246, 268 sh, 276, 298 sh, 310 sh, 375, 390. ¹H-NMR (DMSO-*d*₆) δ : 2.60 (3H, s, SMe), 4.54 (3H, s, NMe), 7.33 (1H, brs, C=NH), 7.53–8.14 (4H, m, C_{6,7,8,9}-H). *Anal.* Calcd for C₁₃H₁₁N₅S: C, 57.97; H, 4.12; N, 26.00. Found: C, 57.97; H, 4.20; N, 25.90.

3-Cyano-4,5-dihydro-5-methyl-2-methylthio-4-oxobenzimidazo[1,2-*b*]pyridazin-9*b*-ium-1-ide (9b) A mixture of **7b** (4 mmol) and K₂CO₃ (8 mmol) in DMSO (30 ml) was stirred at room temperature for a week and the mixture was then evaporated under reduced pressure. The residue was taken up in ice-water (100 ml). The precipitate was filtered, washed with water, dried and recrystallized from CHCl₃-MeOH to give **9b**.

9b: mp > 300 °C (95%). IR (KBr) cm⁻¹: 2200 (CN), 1590 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 236 (3.76), 253 (3.89), 259 (3.92), 265 (3.89), 297 (2.96), 332 (3.48), 346 (3.61), 364 (3.58). ¹H-NMR (DMSO-*d*₆) δ : 2.69 (3H, s, SMe), 4.41 (3H, s, NMe), 7.67 (4H, m, C_{6,7,8,9}-H). *Anal.* Calcd for C₁₃H₁₀N₄OS: C, 57.76; H, 3.73; N, 20.73. Found: C, 57.94; H, 3.84; N, 20.74.

General Procedure for the Preparation of 9c–d and 10c A mixture of the salt **5** (4 mmol), a polarized olefin (**2b–d, 3c**) (4 mmol) and K₂CO₃ (8 mmol) in EtOH (50 ml) was stirred at room temperature for a week and the mixture was then evaporated under reduced pressure. The residue was taken up in ice-water (100 ml). The precipitate was collected by filtration, washed with water, dried and recrystallized from CHCl₃-MeOH to give the corresponding product (**9c–e, 10c**, respectively).

9c: mp 270–272 °C (10%). IR (KBr) cm⁻¹: 1710 (CO), 1690 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 232 (4.34), 259 (4.40), 264 (4.45), 295 (3.59), 306 (3.65), 328 (3.95), 344 (4.21), 361 (4.21). ¹H-NMR (CDCl₃) δ : 1.44 (3H, t, $J=7$ Hz, OCH₂CH₃), 4.43 (2H, q, $J=7$ Hz, OCH₂CH₃), 4.63 (3H, s, NMe), 7.60–7.75 (4H, m, C_{6,7,8,9}-H), 8.83 (1H, s, C₂-H). *Anal.* Calcd for C₁₄H₁₃N₃O₃: C, 61.99; H, 4.83; N, 15.49. Found: C, 61.92; H, 4.97; N, 15.35.

9d: mp 297—300 °C (11%). IR (KBr) cm^{-1} : 1635 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 228, 238, 270, 277, 301, 313, 372, 382. $^1\text{H-NMR}$ (DMSO- d_6) δ : 3.83 (3H, s, NMe), 7.07—7.84 (4H, m, $\text{C}_{6,7,8,9}\text{-H}$), 8.11 (1H, s, $\text{C}_2\text{-H}$). *Anal.* Calcd for $\text{C}_{11}\text{H}_8\text{N}_4\text{O}_3$: C, 54.10; H, 3.30; N, 22.94. Found: C, 53.90; H, 3.43; N, 22.82.

9e: mp 182—184 °C (7%). IR (KBr) cm^{-1} : 1735 (CO), 1670 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 212 (4.41), 220 (4.41), 251 (4.51), 273 (3.88), 345 (4.19), 360 (4.05). $^1\text{H-NMR}$ (CDCl_3) δ : 2.69 (3H, s, SMe), 3.73 (3H, s, OMe), 3.98 (3H, s, NMe), 7.27—8.38 (4H, m, $\text{C}_{6,7,8,9}\text{-H}$). *Anal.* Calcd for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$: C, 55.43; H, 4.32; N, 13.85. Found: C, 55.35; H, 4.45; N, 13.64.

10c: mp 247—249 °C (23%). IR (KBr) cm^{-1} : 2200 (CN). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 234 (4.32), 237 (4.32), 264 (4.28), 273 (4.42), 290 (4.14), 306 (3.93), 310 (3.88), 318 (3.74), 382 (3.99), 392 (3.97). $^1\text{H-NMR}$ (DMSO- d_6) δ : 4.58 (3H, s, NMe), 7.42 (1H, br s, $\text{C}=\text{NH}$), 7.45—8.20 (4H, m, $\text{C}_{6,7,8,9}\text{-H}$), 9.75 (1H, s, $\text{C}_2\text{-H}$). *Anal.* Calcd for $\text{C}_{12}\text{H}_9\text{N}_5$: C, 64.56; H, 4.06; N, 31.37. Found: C, 64.40; H, 4.19; N, 31.35.

General Procedure for the Preparation of 11 A mixture of the salt **5** (4 mmol), a polarized olefin (**2e**, **3d**) (4 mmol) and K_2CO_3 (8 mmol) in EtOH (50 ml) was stirred at room temperature for a week and the mixture was then evaporated under reduced pressure. The residue was taken up in ice-water (100 ml). The precipitate was collected by filtration, washed with water, dried and recrystallized from CHCl_3 –MeOH to give the corresponding product (**11a**, **b**).

11a: mp 81—82 °C (10%). IR (KBr) cm^{-1} : 3400 (NH), 2250 (CN). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 235 (4.30), 315 (3.66). $^1\text{H-NMR}$ (CDCl_3) δ : 2.86 (3H, d, $J=5\text{ Hz}$, NMe), 5.20 (1H, br s, NH), 6.65—7.44 (4H, m, Ar-H), 8.02 (1H, d, $J=2\text{ Hz}$, $\text{C}_3\text{-H}$ or $\text{C}_5\text{-H}$), 8.06 (1H, d, $J=2\text{ Hz}$, $\text{C}_3\text{-H}$ or $\text{C}_5\text{-H}$). *Anal.* Calcd for $\text{C}_{11}\text{H}_{10}\text{N}_4$: C, 66.65; H, 5.09; N, 28.26. Found: C, 66.62; H, 5.12; N, 28.11.

11b: mp 178—180 °C (57%). IR (KBr) cm^{-1} : 3400 (NH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 242 (3.99). $^1\text{H-NMR}$ (CDCl_3) δ : 2.58 (3H, s, SMe), 2.88 (3H, d, $J=5\text{ Hz}$, NMe), 5.20 (1H, br s, NH), 6.65—7.45 (4H, m, Ar-H), 8.37 (1H, s, $\text{C}_5\text{-H}$). *Anal.* Calcd for $\text{C}_{11}\text{H}_{12}\text{N}_4\text{O}_2\text{S}$: C, 49.99; H, 4.58; N, 21.20. Found: C, 50.13; H, 4.55; N, 21.28.

1,7-Dihydro-1-benzyl-7-oxoimidazo[1,2-*b*]pyridazin-3a-ium-4-ide Hydrobromide (12) A solution of **8a** (4 mmol) in 47% HBr (20 ml) was refluxed for 1 h. The reaction mixture was evaporated under reduced pressure. The residue was recrystallized from MeOH to give **12**.

12: mp 278—280 °C (82%). IR (KBr) cm^{-1} : 1575 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 203 (4.35), 233 (4.16), 240 (4.14) sh, 297 (4.11). $^1\text{H-NMR}$ (DMSO- d_6) δ : 5.90 (2H, s, CH_2Ph), 6.68 (1H, d, $J=6\text{ Hz}$, $\text{C}_6\text{-H}$), 7.36 (5H, br s, Ar-H), 8.26 (1H, d, $J=2\text{ Hz}$, $\text{C}_2\text{-H}$), 8.43 (1H, d, $J=6\text{ Hz}$, $\text{C}_5\text{-H}$), 8.45 (1H, d, $J=2\text{ Hz}$, $\text{C}_3\text{-H}$). $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 52.1, 95.3, 106.0, 118.4, 124.9, 127.6, 128.2, 128.7, 132.3, 135.9, 148.9, 154.4. *Anal.* Calcd for $\text{C}_{14}\text{H}_{11}\text{BrN}_3\text{O}$: C, 51.00; H, 3.95; Br, 26.10; N, 13.72. Found: C, 50.69; H, 3.98; Br, 26.05; N, 13.65.

1,7-Dihydro-1-benzyl-7-oxoimidazo[1,2-*b*]pyridazin-3a-ium-4-ide (13) A solution of **12** (2 mmol) in water (20 ml) was made basic to

litmus with K_2CO_3 and immediately extracted with CHCl_3 ($3 \times 10\text{ ml}$). The extract was dried (Na_2SO_4) and evaporated under reduced pressure. The residue was dried under vacuum in a desiccator (2 mmHg) for 10 min. The NMR, IR, UV, HRMS spectra of the crude free base (**13**) were recorded.

13: mp 117—120 °C (95%), (hygroscopic). IR (KBr) cm^{-1} : 1575 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 234, 240, 298. $^1\text{H-NMR}$ (DMSO- d_6) δ : 5.98 (2H, s, CH_2Ph), 6.00 (1H, d, $J=6\text{ Hz}$, $\text{C}_6\text{-H}$), 7.29—7.42 (5H, m, Ar-H), 7.99 (1H, d, $J=6\text{ Hz}$, $\text{C}_5\text{-H}$), 8.00 (1H, d, $J=2\text{ Hz}$, $\text{C}_2\text{-H}$), 8.10 (1H, d, $J=2\text{ Hz}$, $\text{C}_3\text{-H}$). $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 51.0, 106.2, 116.9, 122.4, 127.9, 128.1, 128.7, 135.9, 136.9, 148.5, 161.2. HRMS Calcd for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}$: 225.0902. Found: 225.0911.

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