

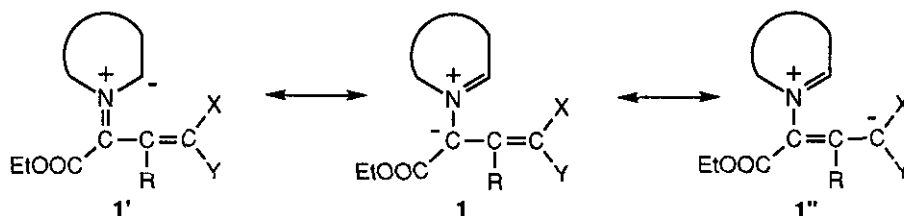
**THERMAL REACTION OF 1,2,4-TRIAZOLIUM *N*-ALLYLIDES:  
FORMATION OF MESOMERIC BETAINES, 1,2,4-TRIAZOLO[4,3-*a*]  
PYRIDINIUMIDES, VIA BACK-DONATED 1,6-CYCLIZATION**

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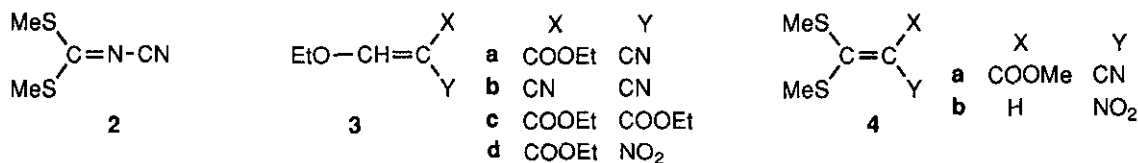
**Abstract** — The reaction of 1,2,4-triazolium salt (**7**) with polarized olefins (**2**, **3a,b**) in the presence of K<sub>2</sub>CO<sub>3</sub> in CHCl<sub>3</sub>-EtOH gave the corresponding triazolium *N*-allylides (**8a-c**). Thermolyses of the *N*-allylides (**8a,c**) afforded the mesomeric betaine (**9a**) and the 8-amino-1,2,4-triazolo[4,3-*a*]pyridine derivative (**10**). Similar treatment of the salt (**7**) with polarized olefins (**3c,d**, **4a**) directly yielded mesomeric betaines (**9c-e**), while the reaction of the salt (**7**) with polarized olefin (**4b**) gave the pyrrolo[1,2-*d*]-1,2,4-triazine derivative (**11**). The formation of mesomeric betaines is suggested to proceed *via* back-donated 1,6-cyclization.

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

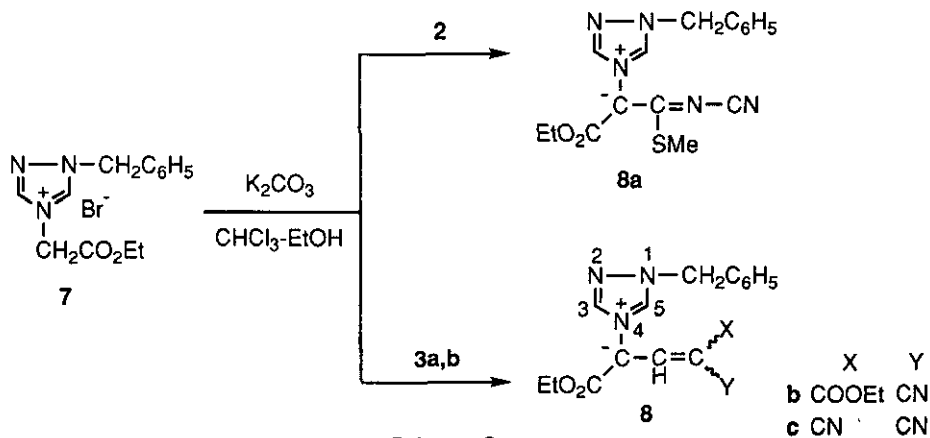


Scheme 1

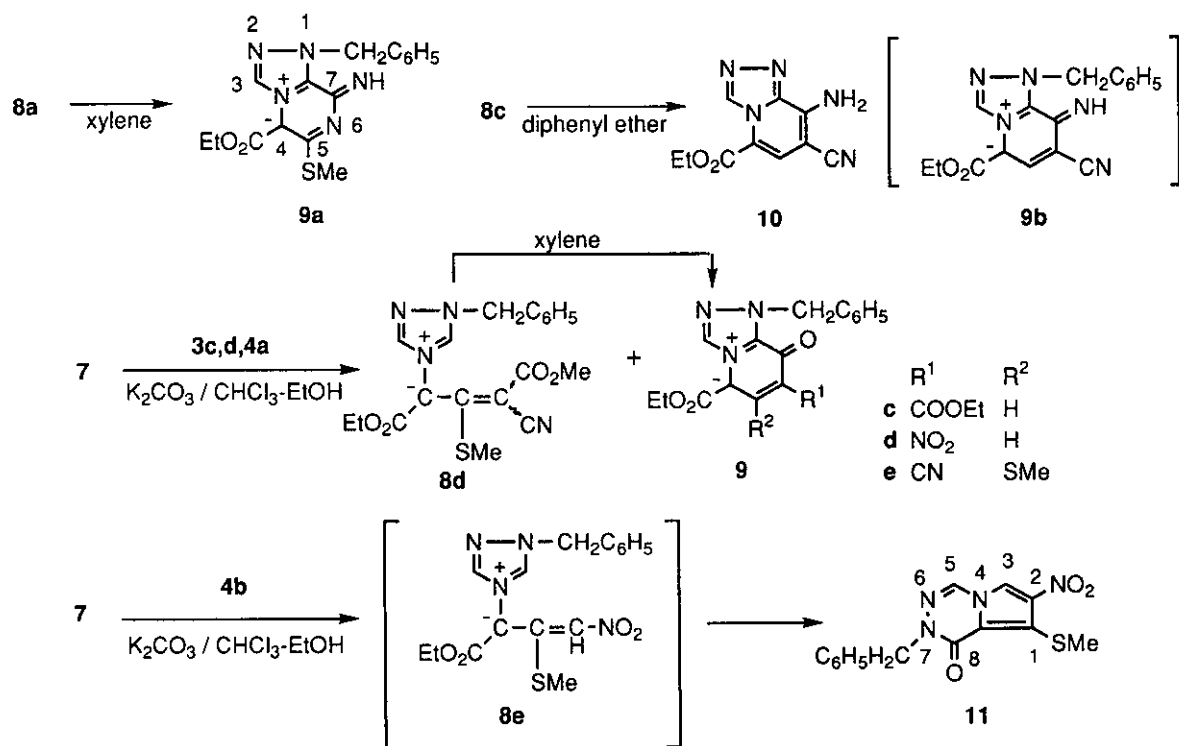
However, a number of previous studies on *N*-allylides (**1**) have been mainly concerned with the synthesis of bicyclic compounds with bridgehead nitrogen, indolizines by 1,5-dipolar cyclization due to the resonance structure (**1''**). We have taken advantage of an alternative *N*-allylide form (resonance structure **1'**) to realize a novel reaction which we have termed a 'back-donated 1,6-cyclization'. Our preliminary studies<sup>4</sup> on the thermolyses of imidazolium *N*-allylides and *N*-vinylimino ylides 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*]pyridiniumimides or imidazo[1,2-*b*]pyridaziniumimides. The purpose of the present investigation was to extend this back-donated 1,6-cyclization to the synthesis of 1,2,4-triazolo[4,3-*a*]pyraziniumimide (**9a**) and 1,2,4-triazolo[4,3-*a*]pyridiniumimide (**9c-e**). The polarized olefins (**2-4**)<sup>5</sup> used in the present work are shown in Scheme 2.



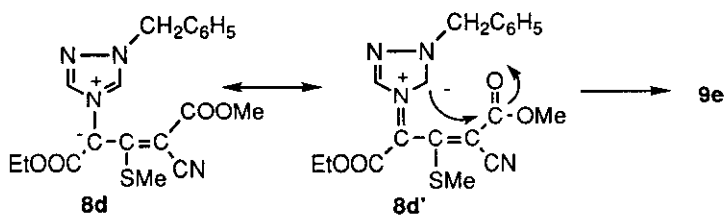
Scheme 2



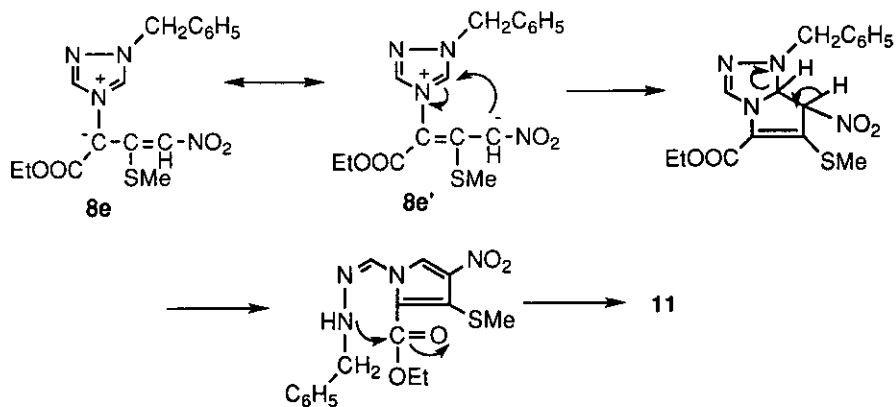
Scheme 3



Scheme 4



Scheme 5



Scheme 6

By Couture's method<sup>6</sup> the starting material, 1,2,4-triazolium salt (7), was prepared from the reaction of ethyl bromoacetate with 1-benzyl-1,2,4-triazole (6), which was obtained by the reaction of 1,2,4-triazole (5) with benzyl bromide in the presence of sodium hydride in THF. The reaction of the salt (7) with polarized olefins (2, 3a,b) in the presence of K<sub>2</sub>CO<sub>3</sub> gave triazolium *N*-allylides (8a-c) (Scheme 3).

A solution of 8a in xylene was refluxed to afford the desired mesomeric betaine, 7-imino-1,2,4-triazolo[4,3-*a*]pyraziniumide (9a). Attempts to obtain the mesomeric betaine from 8b,c by thermolysis in refluxing xylene, trimethylbenzene or acetic acid were fruitless. After much investigation, we found that refluxing of 8c in diphenyl ether did not give the mesomeric betaine (9b), but gave 8-amino-1,2,4-triazolo[4,3-*a*]pyridine (10) with debenylation. In addition, the reaction of the salt (7) with polarized olefins (3c,d, 4a) in the presence of K<sub>2</sub>CO<sub>3</sub> directly afforded the back-donated 1,6-cyclization products (9c-e) together with the *N*-allylide (8d). The compound (9e) was also obtained by the thermolysis of 8d in refluxing xylene. On the other hand, similar treatment of 7 with 2,2-bis(methylthio)-1-nitroethylene (4b) afforded the 1,5-dipolar cyclization product, pyrrolo[1,2-*d*]-1,2,4-triazine (11) without 1,2,4-triazolium *N*-allylide (8e) (Scheme 4).

As pointed out in our previous paper,<sup>4</sup> a reasonable mechanism for the formation of the back-donated 1,6-cyclization product (9e) involves the resonance structure (8d'), as outlined in Scheme 5. As pointed out by Acheson and Elmore<sup>3k</sup> and Meth-Cohn,<sup>3e</sup> the formation of 11 may be rationalized as outlined in Scheme 6.

In conclusion the 1,2,4-triazolium *N*-allylide (8) which had two electron-withdrawing groups at the 3-position of the allylide group participated in back-donated 1,6-cyclization to produce the mesomeric betaine (9). The high efficiency of the back-donated 1,6-cyclization, due to the resonance structure (1'), in thermolysis of the *N*-allylide of the resulting mesomeric betaine, 1,2,4-triazolo[4,3-*a*]pyridiniumide, 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. Uv spectra were recorded on a Hitachi 323 spectrophotometer. <sup>1</sup>H-Nmr spectra were obtained on JNM-FX-90Q spectrometer 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.

### The preparation of 7

By Couture's method,<sup>6</sup> to a stirred solution of 1,2,4-triazole (5) (34.5 g, 0.5 mol) and Na (23 g, 1 mol) in EtOH (300 ml) at 0 °C was added dropwise benzyl bromide (85.5 g, 0.5 mol) and left to warm up to room temperature. After standing overnight the reaction mixture was poured into ice-water (2 l) and extracted with CHCl<sub>3</sub> (4x100 ml). The organic extracts were combined and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was evaporated and the residue was distilled in vacuum (bp 129-133 °C/ 3 mm Hg) to give 1-benzyl-1,2,4-triazole (6) (38.2 g, 48 %) which solidified, mp 52-54 °C (lit. bp 110 °C/ 0.001 mm Hg,<sup>7</sup> mp 54-55 °C<sup>8</sup>). A mixture of 6 (15.9 g, 0.1 mol) and ethyl bromoacetate (16.7 g, 0.1 mol) in acetone (200 ml) was stirred at room temperature for a week. The precipitate was collected by filtration, washed with acetone, dried and recrystallized from EtOH to give 7.

7 : mp 187-190 °C (17.9 g, 55 %). Ir (KBr) cm<sup>-1</sup> : 1725 (CO). <sup>1</sup>H-Nmr (CDCl<sub>3</sub>) : 1.27 (3H, t, *J*=7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 4.23 (2H, q, *J*=7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 5.65 (2H, s, CH<sub>2</sub>Ar), 5.71 (2H, s, CH<sub>2</sub>CO), 7.33-7.50 (5H, m, Ar-H), 9.23 (1H, s, C<sub>3</sub>-H), 11.32 (1H, s, C<sub>5</sub>-H). *Anal.* Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub>Br : C, 47.87; H, 4.94; N, 12.88. Found : C, 47.78; H, 4.96; N, 12.66.

### General procedure for the preparation of 8

A mixture of the salt (7) (1.30 g, 4 mmol), a polarized olefin (2, 3a,b) (4 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.21 g, 8 mmol) in CHCl<sub>3</sub>-EtOH(1:1, 50 ml) was stirred at room temperature for a week and the mixture was then poured into ice-water (100 ml). The mixture was extracted with CHCl<sub>3</sub> (4x30 ml) and the combined extracts were washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure. The residue was recrystallized from CHCl<sub>3</sub>-MeOH to give 8a-c, respectively.

8a : mp 173-176 °C (0.75 g, 55 %). Ir (KBr) cm<sup>-1</sup> : 2140 (CN), 1650 (CO). Uv (EtOH) λ<sub>max</sub> (log ε) nm : 202 (4.41), 268 (4.11), 305 (4.34). <sup>1</sup>H-Nmr (CDCl<sub>3</sub>) : 1.14 (3H, t, *J*=7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.33 (3H, s, SCH<sub>3</sub>), 4.07 (2H, q, *J*=7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 5.52 (2H, s, CH<sub>2</sub>Ar), 7.48 (5H, s, Ar-H), 8.26 (1H, s, C<sub>3</sub>-H), 8.27 (1H, s, C<sub>5</sub>-H). *Anal.* Calcd for C<sub>16</sub>H<sub>17</sub>N<sub>5</sub>O<sub>2</sub>S : C, 55.96; H, 4.99; N, 20.39. Found : C, 56.04; H, 4.96; N, 20.43.

8b : mp 168-170 °C (0.29 g, 20 %). Ir (KBr) cm<sup>-1</sup> : 2180 (CN), 1680 (CO), 1660 (CO). Uv (EtOH) λ<sub>max</sub> (log ε) nm : 340 (4.62), 239 (4.04) sh. <sup>1</sup>H-Nmr (CDCl<sub>3</sub>) : 1.26 (3H, t, *J*=7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 4.16 (2H, q, *J*=7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 5.50 (2H, s, CH<sub>2</sub>Ar), 7.49 (5H, s, Ar-H), 8.23 (1H, s, CH=), 8.30 (1H, s, C<sub>3</sub>-H), 8.31 (1H, s, C<sub>5</sub>-H). *Anal.* Calcd for C<sub>19</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub> : C, 61.95; H, 5.47; N, 15.21. Found : C, 61.66; H, 5.47; N, 15.15.

8c : mp 199-201 °C (1.03 g, 80 %). Ir (KBr) cm<sup>-1</sup> : 2200 (CN), 1665 (CO). Uv (EtOH) λ<sub>max</sub> (log ε) nm : 278 (3.70), 355 (4.47), 405 (4.10). <sup>1</sup>H-Nmr (CDCl<sub>3</sub>) : 1.43 (3H, t, *J*=7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 4.30 (2H, q, *J*=7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 6.41 (2H, s, CH<sub>2</sub>Ar), 7.28-7.30 (5H, m, Ar-H), 7.37 (1H, s, CH=), 8.30 (1H, s, C<sub>3</sub>-H), 8.31

(1H, s, C<sub>5</sub>-H). *Anal.* Calcd for C<sub>17</sub>H<sub>15</sub>N<sub>5</sub>O<sub>2</sub> : C, 63.54; H, 4.71; N, 21.79. Found : C, 63.47; H, 4.73; N, 21.67.

**4,7-Dihydro-1-benzyl-4-ethoxycarbonyl-7-imino-5-methylthio-1,2,4-triazolo[4,3-*a*]pyrazin-3*a*-ium-4-ide (9a)**

A solution of *N*-allylide (**8a**) (0.69 g, 2 mmol) in xylene (60 ml) was refluxed for 24 h and the solution was then evaporated under reduced pressure. To the residue was added ice-water (50 ml) and the mixture was extracted with CHCl<sub>3</sub> (4x30 ml). The combined extracts were washed with water (50 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a benzene-CHCl<sub>3</sub> (20:1) fraction, **9a** was obtained.

**9a** : mp 160-163 °C (0.27 g, 40 %). Ir (KBr) cm<sup>-1</sup> : 3130 (=NH), 1650 (CO). Uv (EtOH) λ<sub>max</sub> (log ε) nm : 254 (4.24), 282 (3.98), 327 (4.14), 369 (4.09). <sup>1</sup>H-Nmr (CDCl<sub>3</sub>) : 1.41 (3H, t, *J*=7Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.43 (3H, s, SCH<sub>3</sub>), 4.36 (2H, q, *J*=7Hz, CH<sub>2</sub>CH<sub>3</sub>), 6.27 (2H, s, CH<sub>2</sub>Ar), 7.51-7.26 (5H, m, Ar-H), 9.69 (1H, s, C<sub>3</sub>-H). *Anal.* Calcd for C<sub>16</sub>H<sub>17</sub>N<sub>5</sub>O<sub>2</sub>S : C, 55.96; H, 4.99; N, 20.39. Found : C, 55.90; H, 5.00; N, 20.34.

**8-Amino-7-cyano-5-ethoxycarbonyl-1,2,4-triazolo[4,3-*a*]pyridine (10)**

A solution of *N*-allylide (**8c**) (0.64 g, 2 mmol) in diphenyl ether (60 ml) was refluxed for 4 h and hexane was then added to the solution. The precipitate was collected by filtration, washed with hexane, dried, and recrystallized from CHCl<sub>3</sub>-MeOH to give **10**.

**10**: mp 230-231 °C (0.09 g, 20 %). Ir (KBr) cm<sup>-1</sup> : 2215 (CN), 1640 (CO). Uv (EtOH) λ<sub>max</sub> (log ε) nm : 227 (4.36), 251 (4.15), 312 (4.08), 341 (4.30), 352 (4.25). <sup>1</sup>H-Nmr (DMSO-d<sub>6</sub>) : 1.36 (3H, t, *J*=7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 4.37 (2H, q, *J*=7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 7.71 (1H, s, C<sub>3</sub>-H), 8.40 (2H, s, NH<sub>2</sub>), 9.69 (1H, s, C<sub>6</sub>-H). *Anal.* Calcd for C<sub>10</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub> : C, 51.95; H, 3.92; N, 30.29. Found : C, 51.92; H, 4.08; N, 29.22.

**General procedure for the preparation of 9c-e**

A mixture of the salt (**7**) (1.30 g, 4 mmol) with a polarized olefin (**3c,d, 4a**) in the presence of K<sub>2</sub>CO<sub>3</sub> (1.21 g, 8 mmol) in CHCl<sub>3</sub>-EtOH (1:1, 30 ml) was stirred at room temperature for a week and the mixture was then poured into ice-water (100 ml). The mixture was extracted with CHCl<sub>3</sub> (4x30 ml) and the combined extracts were washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a benzene-CHCl<sub>3</sub> (20:1) fraction, **8d** was obtained. From a benzene-CHCl<sub>3</sub> (1:1) fraction, **9c-e** were obtained. In addition, thermolysis of **8d** (0.40 g, 1 mmol) in refluxing xylene gave also **9e** (0.16 g, 43%).

**8d** : mp 116-118 °C (1.04 g, 65 %). Ir (KBr)  $\text{cm}^{-1}$  : 2190 (CN), 1690 (CO), 1660 (CO). Uv (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) nm : 205 (4.27), 300 (3.93), 383 (4.24).  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) : 1.24 (3H, t,  $J=7$  Hz,  $\text{CH}_2\text{CH}_3$ ), 2.50 (2H, s,  $\text{SCH}_3$ ), 3.37 (3H, s,  $\text{OCH}_3$ ), 4.17 (2H, q,  $J=7$  Hz,  $\text{CH}_2\text{CH}_3$ ), 5.45 (2H, s,  $\text{CH}_2\text{Ar}$ ), 7.42 (5H, s, Ar-H), 8.18 (1H, s,  $\text{C}_3\text{-H}$ ), 9.21 (1H, s,  $\text{C}_5\text{-H}$ ). *Anal.* Calcd for  $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_4\text{S}$  : C, 56.99; H, 5.03; N, 13.99.

Found : C, 57.22; H, 5.11; N, 13.79.

**9c** : mp 256-259 °C (0.14 g, 10 %). Ir (KBr)  $\text{cm}^{-1}$  : 1675 (CO), 1605(CO). Uv (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) nm : 321 (4.36), 355 (4.30).  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) : 1.40 (3H, t,  $J=7$ Hz,  $\text{CH}_2\text{CH}_3$ ), 1.42 (3H, t,  $J=7$  Hz,  $\text{CH}_2\text{CH}_3$ ), 4.39 (2H, q,  $J=7$ Hz,  $\text{CH}_2\text{CH}_3$ ), 4.42 (2H, q,  $J=7$  Hz,  $\text{CH}_2\text{CH}_3$ ), 6.29 (2H, s,  $\text{CH}_2\text{Ar}$ ), 7.22-7.62 (5H, m, Ar-H), 8.59 (1H, s,  $\text{C}_3\text{-H}$ ), 9.84 (1H, s,  $\text{C}_5\text{-H}$ ). *Anal.* Calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_5$  : C, 61.78; H, 5.18; N, 11.38.

Found : C, 61.58; H, 5.10; N, 11.49.

**9d** : mp 154-155 °C (0.27 g, 20 %). Ir (KBr)  $\text{cm}^{-1}$  : 1700 (CO), 1625 (CO). Uv (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) nm : 225 (4.17), 329 (4.35), 390 (4.12).  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) : 1.42 (3H, t,  $J=7$  Hz,  $\text{CH}_2\text{CH}_3$ ), 4.42 (2H, q,  $J=7$  Hz,  $\text{CH}_2\text{CH}_3$ ), 6.72 (2H, s,  $\text{CH}_2\text{Ar}$ ), 7.39-7.57 (5H, m, Ar-H), 8.83 (1H, s,  $\text{C}_3\text{-H}$ ), 9.91 (1H, s,  $\text{C}_5\text{-H}$ ). *Anal.* Calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_5$  : C, 56.14; H, 4.12; N, 16.37. Found : C, 55.93; H, 4.18; N, 16.32.

**9e** : mp 143-146 °C (0.12 g, 8 %). Ir (KBr)  $\text{cm}^{-1}$  : 2200 (CN), 1680 (CO), 1590 (CO). Uv (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) nm : 207 (4.04), 345 (3.95).  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) : 1.45 (3H, t,  $J=7$  Hz,  $\text{CH}_2\text{CH}_3$ ), 2.63 (3H, s,  $\text{SCH}_3$ ), 4.47 (2H, q,  $J=7$  Hz,  $\text{CH}_2\text{CH}_3$ ), 6.18 (2H, s,  $\text{CH}_2\text{Ar}$ ), 7.29-7.64 (5H, m, Ar-H), 9.54 (1H, s, H). *Anal.* Calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_3\text{S}$  : C, 58.68; H, 4.38; N, 15.21. Found : C, 58.56; H, 4.41; N, 15.17.

### 7,8-Dihydro-7-benzyl-1-methylthio-2-nitro-8-oxopyrrolo[1,2-d]-1,2,4-triazine (11)

A mixture of the salt (7) (1.30 g, 4 mmol) with polarized olefin (4b) (0.53 g, 4 mmol) in the presence of  $\text{K}_2\text{CO}_3$  (1.21 g, 8 mmol) in  $\text{CHCl}_3\text{-EtOH}$  (1:1, 30 ml) was stirred at room temperature for a week and the mixture was poured into ice-water (100 ml). The mixture was extracted with  $\text{CHCl}_3$  (4x30 ml) and the combined extracts were washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a benzene- $\text{CHCl}_3$  (20:1) fraction, **11** was obtained.

**11** : mp 203-205 °C (0.43 g, 34 %). Ir (KBr)  $\text{cm}^{-1}$  : 1650 (CO). Uv (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) nm : 209 (4.36), 240 (4.18), 277 (4.20).  $^1\text{H-Nmr}$  ( $\text{CDCl}_3$ ) : 2.64 (3H, s,  $\text{SCH}_3$ ), 5.17 (2H, s,  $\text{CH}_2\text{Ar}$ ), 7.26-7.39 (5H, m, Ar-H), 7.90 (1H, s,  $\text{C}_3\text{-H}$ ), 7.91 (1H, s,  $\text{C}_5\text{-H}$ ). *Anal.* Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_3\text{S}$  : C, 53.16; H, 3.82; N, 17.71.

Found : C, 53.22; H, 3.83; N, 17.79.

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