

## The Reaction between Triazolobenzopyridinium and Triazolothiazolium Ylides with Dimethyl Acetylenedicarboxylate

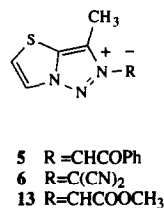
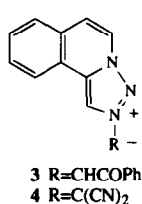
Belén Abarca,\* Rafael Ballesteros, Nadia Houari and Aldelouahid Samadi

Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia,  
Avda. Vicente Andrés Estellés s/n, 46100 Burjassot (Valencia). Spain

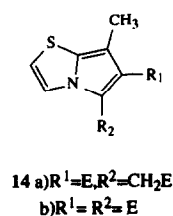
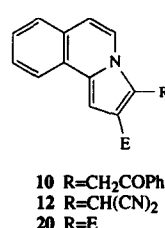
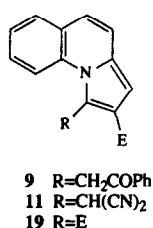
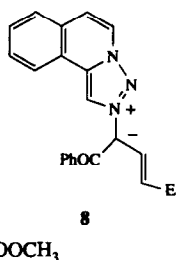
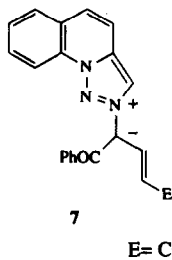
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**Abstract:** The reaction of some [1,2,3]triazolo[1,5-*a*]quinolinium **1,2**, [1,2,3]triazolo[5,1-*a*]isoquinolinium **3,4** and [1,2,3]triazolo[5,1-*b*]thiazolium **5,6** ylides with dimethyl acetylenedicarboxylate is described. Compounds as dimethyl pyrrolo[1,2-*a*]quinoline-1,2-dicarboxylate **19**, dimethyl pyrrolo[2,1-*a*]isoquinoline-2,3-dicarboxylate **20**, 1,1-dicyano-2,3-dimethoxycarbonyl-1*H*-pyrido[1,2-*a*]quinoline **24**, 4,4-dicyano-2,3-dimethoxycarbonyl-4*H*-pyrido[2,1-*a*]isoquinoline **25**, and 7-methyl-5,6-dimethoxy-carbonylpyrrolo[2,1-*a*]thiazole **14b**, are formed. © 1998 Elsevier Science Ltd. All rights reserved.

As an extension of our work on triazolobenzopyridines<sup>1</sup> and triazolothiazoles,<sup>2</sup> we report here the results of the reaction between [1,2,3]triazolo[1,5-*a*]quinolinium **1,2**, [1,2,3]triazolo[5,1-*a*]isoquinolinium **3,4**, and [1,2,3]triazolo[5,1-*b*]thiazolium **5,6** ylides with dimethyl acetylenedicarboxylate (DMAD).



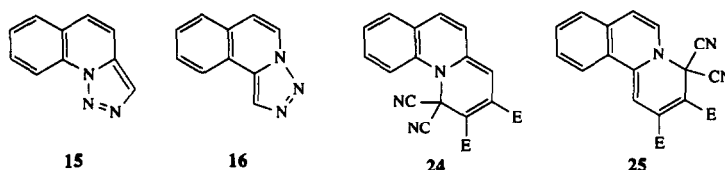
We have reported<sup>1</sup> that compounds **1–4** react with methyl propiolate (MP), giving different results depending on the solvent and the type of ylide. In a polar solvent **1** and **3** gave ylide compounds **7** and **8**; when the solvent was non polar pyrrolo[1,2-*a*]quinoline **9** and pyrrolo[2,1-*a*]isoquinoline **10** were formed. In similar conditions, the ylides **2** and **4** gave the compounds **11** and **12** respectively. We have also reported<sup>2</sup> that the ylide **13** reacted with acetylenic dipolarophiles to give, in very poor yields, pyrrolothiazoles **14**.



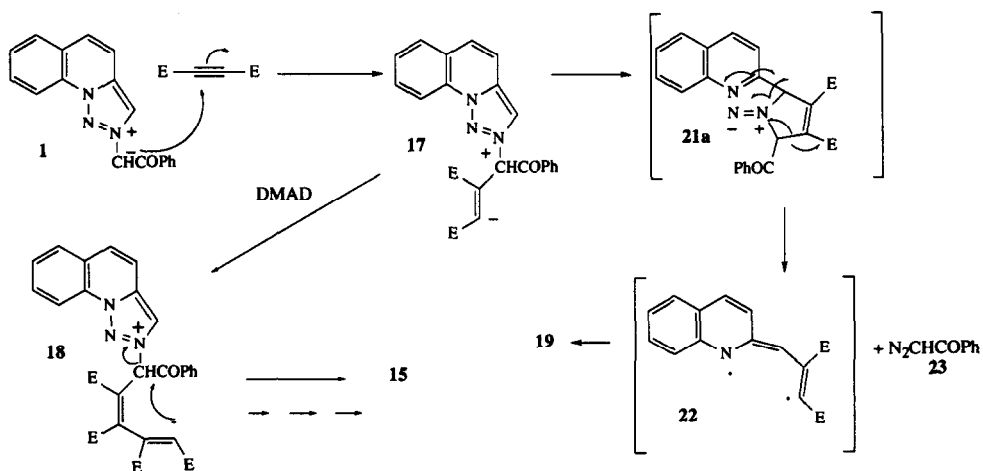
E= COOCH<sub>3</sub>

Previous work on ylides derived from triazolopyridines<sup>3-6</sup> has shown that a change from MP to DMAD alters the course of the reaction. To discover the scope of the influence of the dipolarophile change, we thought it interesting to study the reaction between the ylides **1-6** and DMAD. The results of these experiments are described in this paper.

Ylides **1** and **3** were obtained *in situ* from the corresponding salt.<sup>1</sup> When acetonitrile was the solvent they reacted with DMAD at room temperature with unexpected results. [1,2,3]Triazolo[1,5-*a*]quinoline **15** and [1,2,3]triazolo[5,1-*a*]isoquinoline **16** were isolated respectively in 54% and 61% yield. No other compounds could be identified in the intractable gums also formed.



To account for these results we believe that the reaction starts, as in the reaction with MP,<sup>1</sup> with a nucleophilic Michael addition; the ylide **1** reacts with DMAD giving the betaine **17**. This intermediate could react with another DMAD molecule to give **18** which could produce directly the triazoloquinoline **15** by an intramolecular nucleophilic attack, or could react with more DMAD forming a longer side chain which finally gives **15** by an inter or intramolecular nucleophilic attack. (Scheme 1). The formation of **16** could be explained in a similar manner. No analogous results were found in our work with triazolopyridine ylides and acetylenic dipolarophiles,<sup>3-6</sup> but a triazolopyridine was isolated in a reaction with ethyl methacrylate<sup>7</sup> and there are examples in the literature<sup>8</sup> in which a free heterocyclic base is formed in reactions with a cycloimmonium ylide and diethyl azodicarboxylate.

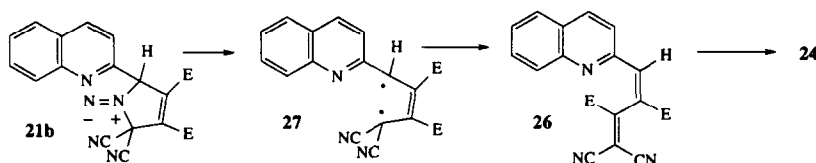


Scheme 1

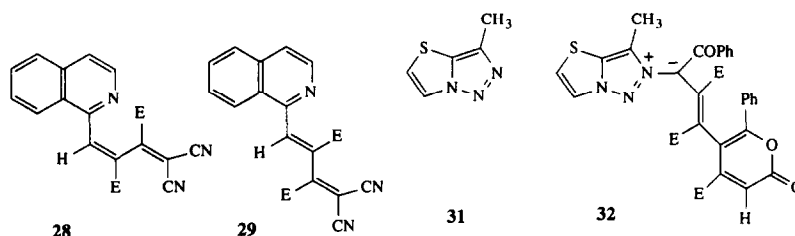
When the solvent was toluene, the reactions of **1** and **3** with DMAD have also produced **15** (59%) and **16** (63%) as major products. Minor products could be identified in these cases. A pyrrolo[1,2-*a*]quinoline **19** (9%) and a pyrrolo[2,1-*a*]isoquinoline **20** (8%) were formed respectively. The structure of them is proposed based on HRMS, <sup>1</sup>H, <sup>13</sup>C and IR spectral data, and analogy with compounds **9-12**. The formation of the adduct **19** could be explained from the betaine **17**; a competitive intramolecular attack on the C3 position gives a 1,1-diazene **21a**, as we have reported previously.<sup>1</sup> In this case the fragmentation of the diazene involves the loss of the diazoderivative **23** followed by cyclisation of the diradical so formed, giving the pyrroloquinoline **19** (scheme1). The formation of the adduct **20** could also be explained by a similar mechanism.

The stable ylides **2** and **4** reacted with DMAD, and now the reaction followed a different course to that in the case in which the MP is the co-reactive. Compounds **24** and **25** were formed as yellow and orange solids respectively. The formation of **24** could be explained from an analogous diazene intermediate **21b** which can lose nitrogen to give a diene **26**, through a 1,4-diradical **27**. The diene gives the benzoquinolizine system by a concerted electrocyclic process or an intramolecular addition. A similar mechanism can explain the formation

of **25**. Also in the reaction with ylide **4** compound **20** was formed as a minor product, the formation of which could be explained if the diazene intermediate fragments with loss of  $N_2C(CN)_2$ . Compound **25** was not a stable one, and by heat or by UV irradiation, can be transformed into **28** probably through the diene **29**.

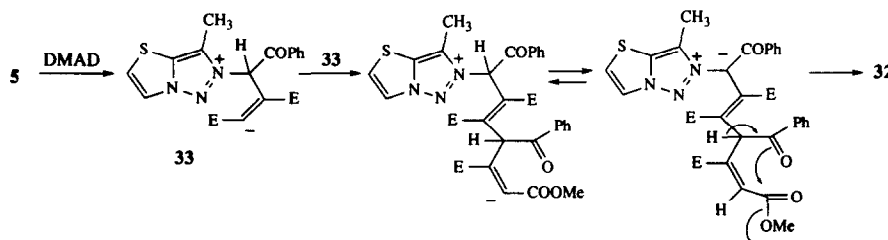


Ylides **5** and **6** are new compounds. To synthesize **5** we first made the corresponding salt from 3-methyl-[1,2,3]triazolo[5,1-*b*]thiazole **31**. Ylide **6** was prepared by the method of Linn *et al.*,<sup>9</sup> the reaction was very slow and the stable compound **6** was isolated in low yield. We have studied the reaction of both with DMAD. The ylide **5** gives different results depending of the solvent. When the solvent is toluene three products were isolated, the aminomaleate **30** resulting from the reaction of triethylamine with DMAD,<sup>12</sup> 3-methyl-[1,2,3]triazolo[5,1-*b*]thiazole **31** and an oil identified as **14b**. The formation of both compounds **31** and **14b** is comparable to the manner of formation of **15** and **19**.



When the solvent was acetonitrile, in addition to the formation of **31**, we found an amazing red solid, with molecular weight 627.1328, consistent with a molecular formula of  $C_{32}H_{25}N_3O_9S$ . We have assigned to it tentatively the structure **32**. It is significant that an ethanol solution of the compound changes from red colour to pale yellow in acid medium. The  $^1H$ nmr spectrum showed the presence of thirteen protons in the aromatic region as a singlet at  $\delta$  7.80(1H), and three multiplets centered at  $\delta$  7.55, 7.40, and 7.27, four protons in each, only three methoxy groups at  $\delta$  4.05, 3.80, 5.50 and another methyl group at  $\delta$  2.49. The more interesting feature in the  $^{13}C$  nmr spectrum is the presence of a CO group at 192.77 $\delta$  and four carbonyl carbons in the region of esters but only three methoxy groups. Also significant is the presence of nine CHs in the aromatic region, indicating the presence of two non equivalent phenyl, and a triazolothiazole groups and an isolated CH. The formation of that compound could be explained as is reflected in scheme 2. With our wide experience in triazolo derivative ylide chemistry, to our knowledge, this represents the first example in which a 1:1 adduct with DMAD undergoes an intermolecular  $S_N$  type reaction with itself. Loss of the free triazoloderivative base results.

Compound **6** gives, under several conditions, intractable gums.



Scheme 2

**Acknowledgements:** Our thanks are due to the Comision Interministerial de Ciencia y Tecnologia (CICYT, project PB94-0959) for financial support.

## EXPERIMENTAL

Mps were determined on a Kofler heated stage and are uncorrected. NMR spectra were determined on a Bruker 250MHz spectrometer. HRMS (EI) determinations were made using a VG Autospec Trio 1000 (Fisons).

### Preparation of the Ylides 1-4.

The compounds 1-4 were prepared as described.<sup>1</sup>

### 2-Benzoylmethyl-3-methyl-[1,2,3]triazolo[5,1-b]thiazolium ylide 5.

The precursor salt was synthesised as follow. To a solution of 3-methyl-[1,2,3]triazolo[5,1-b]thiazole<sup>10</sup> (500mg, 3.6mmol) in dry acetonitrile (20ml) phenacyl bromide (716mg, 3.6mmol) was added. The mixture was refluxed for 24 h, then was filtered, washed with chloroform to give a white solid (740mg, 80%). mp 202°C. nmr <sup>1</sup>H (DMSO-d<sub>6</sub>) (250MHz) δ 9.05(1H, d, J=3.65 Hz), 8.49(1H, d, J=3.65Hz), 8.14(2H, d, J=7.3Hz), 7.78-7.76(1H, m), 7.66-7.64(2H, m), 6.87(2H, s), 2.73(3H, s). nmr <sup>13</sup>C (DMSO-d<sub>6</sub>) δ 190.14(C), 138.70(C), 135.08(C), 134.53(CH), 133.34(CH), 130.93(C), 129.17(CH), 128.88(CH), 120.96(CH), 58.47(CH<sub>2</sub>), 9.36(CH<sub>3</sub>). IR (KBr) ν<sub>max</sub>(cm<sup>-1</sup>) 1697. Found: C, 46.11; H, 3.48; N, 12.39; S, 9.48; Br, 23.39 %. C<sub>13</sub>H<sub>12</sub>BrN<sub>3</sub>OS requires: C, 46.16; H, 3.57; N, 12.42; S, 9.48; Br, 23.62 %. The ylide 5 was prepared in two different solvents. In one case a solution of the precursor salt in anhydrous acetonitrile was vigorously stirred at room temperature with equimolecular amount of anhydrous potassium carbonate during 4h, a yellow paste formed. In a second experiment the ylide was formed in toluene using a mixture of triethylamine and potassium carbonate as base.

### 3-Methyl-[1,2,3]triazolo[1,5-b]thiazolium-2-dicyanomethylide 6.

To a solution of TCNEO (260mg, 1.8mmol) in ethyl acetate (30ml) cooled at 0 °C, an equimolecular amount of 3-methyl-[1,2,3]triazolo[5,1-b]thiazole (250mg, 1.8mmol) in ethyl acetate (10ml) was added slowly with stirring. The reaction was kept at these conditions for one week. A yellow solid was formed, filtered and identified as 6. (107mg, 29%). mp 191-193 °C. nmr <sup>1</sup>H (DMSO-d<sub>6</sub>) (250MHz) δ 8.78(1H, d, J=3.3Hz), 8.16(1H, d, J=3.3Hz), 2.61(3H, s). nmr <sup>13</sup>C (DMSO-d<sub>6</sub>) δ 137.59(C), 130.54(C), 126.52(CH), 120.32(CH), 119.88(CN), 45.00(Ci), 9.67(CH<sub>3</sub>). IR (KBr) ν<sub>max</sub>(cm<sup>-1</sup>) 2183, 2143. HRMS (EI) Calcd. for C<sub>8</sub>H<sub>5</sub>N<sub>5</sub>S, 203.0265, Obt.: 203.0266.

### Reaction between the ylide 1 and dimethyl acetylenedicarboxylate in acetonitrile.

To the ylide 1 (from the corresponding salt, 300mg, 0.8mmol) was added a solution of dimethyl acetylenedicarboxylate (127mg, 0.89mmol) in dry acetonitrile. A colour change was observed from yellow to red. The mixture was stirred overnight at room temperature, then was filtered and the filtrate was evaporated. Alumina (IV) column chromatography, using ethyl acetate/ hexane (1:9) as eluent gave [1,2,3]triazolo[1,5-a]quinoline 15<sup>11</sup> (54%).

### Reaction between the ylide 3 and dimethyl acetylenedicarboxylate in acetonitrile.

To the ylide 3 (from the corresponding salt, 250mg, 0.68mmol) was added a solution of dimethyl acetylenedicarboxylate (106mg, 0.74mmol) in dry acetonitrile. A colour change was observed from yellow to red. The mixture was stirred overnight at room temperature, then was filtered and the filtrate was evaporated. Alumina (IV) column chromatography using ethyl acetate/ hexane (1:9) as eluent gave [1,2,3]triazolo[5,1-a]isoquinoline 16<sup>11</sup> (61%).

### Reaction between the ylide 1 and dimethyl acetylenedicarboxylate in toluene

To the ylide 1 (from the corresponding salt, 200mg, 0.5mmol) was added a solution of dimethyl acetylenedicarboxylate (50mg, 0.6mmol) in dry toluene. A colour change was observed from yellow to red. The mixture was stirred overnight at room temperature. Chromatography on the chromatotron using 2mm plates of silica (Merck PF254) and hexane/ethyl acetate as eluent and then HPLC gave [1,2,3]triazolo[1,5-a]quinoline 15 (59%) and dimethyl pyrrolo[1,2-a]quinoline-1,2-dicarboxylate 19(13%). nmr <sup>1</sup>H (CDCl<sub>3</sub>) (250MHz) δ 8.59(1H, d, J=8.44Hz), 7.98(1H, d, J=9.42Hz), 7.78(1H, d, J=7.8Hz), 7.67(1H, d, J=9.1Hz), 7.68(1H, m), 7.51(1H, d, J=8Hz), 7.50(1H, s), 3.99(3H, s), 3.88(3H, s). nmr <sup>13</sup>C (CDCl<sub>3</sub>) δ 163.57(CO), 162.76(CO), 146.25(C), 139.66(C), 133.92(C), 130.43(CH), 129.06(CH), 128.54(CH), 126.43(CH), 124.50(C), 123.97(CH), 122.72(C), 116.70(CH), 116.38(CH), 53.02(CH<sub>3</sub>), 51.84(CH<sub>3</sub>). HRMS (EI) Calcd. for C<sub>16</sub>H<sub>13</sub>NO<sub>4</sub>, 283.0844, Obt.: 283.0792.

### Reaction between the ylide 3 and dimethyl acetylenedicarboxylate in toluene

To the ylide 3 (from the corresponding salt, 100mg, 0.27mmol) was added a solution of dimethyl acetylenedicarboxylate (42mg, 0.29mmol) in dry toluene. A colour change was observed from yellow to red.

The mixture was stirred overnight at room temperature. Chromatography on the chromatotron using 2mm plates of silica (Merck PF254) and hexane/ethyl acetate as eluent and then HPLC gave [1,2,3]triazolo[5,1-*a*]isoquinoline **16** (63%) and dimethyl pyrrolo[2,1-*a*]isoquinoline-2,3-dicarboxylate **20** (9%). m.p. 157–159°C. nmr  $^1\text{H}$  ( $\text{CDCl}_3$ ), (250MHz)  $\delta$  8.93(1H, d,  $J=7.6\text{Hz}$ ), 7.99(1H, dd,  $J=7.8$ ,  $J_2=1.8\text{Hz}$ ), 7.57(1H, dd,  $J=7.8$ ,  $J_2=1.8\text{Hz}$ ), 7.48–7.41(2H, m), 7.16(1H, s), 6.96(1H, d,  $J=7.6\text{Hz}$ ), 3.87(3H, s), 3.86(3H, s). nmr  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  166.01(CO), 161.24(CO), 133.32(C), 128.07(CH), 127.84(CH), 127.67(C), 126.94(CH), 125.13(C), 124.86(C), 124.23(CH), 123.00(CH), 114.87(C), 114.35(CH), 102.60(CH), 52.33( $\text{CH}_3$ ), 51.84( $\text{CH}_3$ ). IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 1736, 1699. UV  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ) (chloroform) 365.0(1.37), 348.0(1.36), 266.5(1.74). HRMS (EI) Calcd. for  $\text{C}_{16}\text{H}_{13}\text{NO}_4$ , 283.0844, Obt.: 283.0793.

*Reaction between the ylide 2 and dimethyl acetylenedicarboxylate.*

The ylide **2** (200mg, 0.85mmol.) was heated in dry acetonitrile 7h, then dimethyl acetylenedicarboxylate was added (113mg, 0.93mmol) and boiled 48h. The solvent was evaporated and the reaction crude was purified by column chromatography (silica gel, hexane-ethyl acetate 9:1). A yellow product was identified as 1,1-dicyano-2,3-dimethoxycarbonyl-1H-pyrido[1,2-*a*]quinoline **24**. (61%). mp 144–146°C (hexane). nmr  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  8.24(1H, d,  $J=8.4\text{Hz}$ ), 8.06(1H, d,  $J=7.6\text{Hz}$ ), 8.05(1H, s), 7.82(1H, d,  $J=8.4\text{Hz}$ ), 7.75(1H, m), 7.60(1H, m), 7.57(1H, d,  $J=8.4\text{Hz}$ ), 3.93(3H, s), 3.74(3H, s). nmr  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  163.34(CO), 161.87(CO), 160.37(C), 150.00(C), 147.57(C), 143.25(CH), 137.62(CH), 130.94(CH), 128.81(CH), 128.57(CH), 127.75(C), 127.53(CH), 127.36(C), 123.58(CH), 111.38(CN), 91.80(C), 53.59( $\text{CH}_3$ ), 53.36( $\text{CH}_3$ ). IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2228, 1724, 1628. UV  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ) (ethanol) 338.0(3.98), 269.5(4.44), 232.5(4.10). HRMS (EI) Calcd. for  $\text{C}_{19}\text{H}_{13}\text{N}_3\text{O}_4$ , 347.0906, Obt.: 347.0895.

*Reaction between the ylide 4 and dimethyl acetylenedicarboxylate.*

The ylide **4** (200mg, 0.85mmol.) was heated in dry acetonitrile 3h, then dimethyl acetylenedicarboxylate was added (113mg, 0.93mmol) (a change of colour to red was observed) and boiled 42h. The solvent was evaporated and the reaction crude was purified by column chromatography (alumina, hexane-ethyl acetate 9:1). The first product eluted was compound **20** (12%). The second one was 4,4-dicyano-2,3-dimethoxycarbonyl-4H-pyrido[2,1-*a*]isoquinoline **25** (59%). nmr  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  9.43(1H, d,  $J=8.57\text{Hz}$ ), 7.80–7.62(3H, m), 7.13(1H, d,  $J=7.2\text{Hz}$ ), 7.05(1H, d,  $J=7.2\text{Hz}$ ), 6.34(1H, s), 4.00(3H, s), 3.85(3H, s). nmr  $^{13}\text{C}$  ( $\text{DMSO}-d_6$ )  $\delta$  165.40(CO), 161.24(CO), 146.91(C), 143.87(C), 134.50(CH), 134.09(C), 132.22(CH), 129.27(CH), 128.06(CH), 125.65(CH), 122.66(C), 119.15(CH), 116.38(CH), 115.68(CN), 98.04(C), 73.63(C), 53.28( $\text{CH}_3$ ), 52.65( $\text{CH}_3$ ). IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2190, 1740, 1712. UV  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ) (chloroform) 474.0(2.6), 316.5(2.7), 240.5(3.0). HRMS (EI) Calcd. for  $\text{C}_{19}\text{H}_{13}\text{N}_3\text{O}_4$ , 347.0906, Obt.: 347.0908. A solution of **25** in chloroform was heated to reflux. The reaction was monitored by nmr, a new compound was formed and identified as **28**. nmr  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  9.69(1H, d,  $J=8.5\text{Hz}$ ), 9.13(1H, d,  $J=7.6\text{Hz}$ ), 7.93–7.80(3H, m), 7.6(1H, s), 7.55(1H, d,  $J=7.6\text{Hz}$ ), 4.08(3H, s), 3.97(3H, s). nmr  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  165.15(CO), 163.74(CO), 154.56(C), 148.09(C), 146.69(C), 134.33(CH), 133.93(CH), 131.26(CH), 129.12(CH), 128.83(CH), 128.66(C), 127.55(CH), 126.31(CH), 123.55(CH), 117.82(CN), 80.84(C), 53.72( $\text{CH}_3$ ), 52.65( $\text{CH}_3$ ). The same compound was formed when the solution of **25** was irradiated with a lamp of medium pressure mercury, pyrex filter.

*Reaction between the ylide 5 and dimethyl acetylenedicarboxylate in acetonitrile.*

The ylide **5** generated from the salt (150mg, 0.44mmol) in the conditions described above, was reacted with DMAD (63mg, 0.44mmol) at room temperature overnight. The mixture was filtered, the filtrate evaporated under reduced pressure and the residue was separated by a chromatotron, using hexane/ethyl acetate (2:8) as eluent. The first fraction eluted was 3-methyl-[1,2,3]triazolo[5,1-*b*]thiazole **31**.<sup>10</sup> The following fraction was a red solid identified as compound **32** (30%). m.p. 130–132°C ( $\text{CCl}_4$ ). nmr  $^1\text{H}$  (200MHz) ( $\text{Cl}_2\text{CD}$ )  $\delta$  7.8(1H, s), 7.59–7.27(12H, m), 4.06(3H, s), 3.81(3H, s), 3.51(3H, s), 2.49(3H, s). nmr  $^{13}\text{C}$  ( $\text{Cl}_2\text{CD}$ )  $\delta$  192.77(C), 168.48(C), 165.89(C), 165.50(C), 164.59(C), 149.22(C), 147.13(C), 137.12(C), 136.22(C), 135.63(CH), 132.83(CH), 129.73(C), 128.80(CH), 128.60(CH), 128.38(CH), 128.04(CH), 127.76(CH), 125.36(CH), 119.69(CH), 110.69(C), 107.19(C), 53.16( $\text{CH}_3$ ), 51.77( $\text{CH}_3$ ), 51.35( $\text{CH}_3$ ), 10.22( $\text{CH}_3$ ). IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 1697. UV  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ) (EtOH) 507(0.63), 262(0.64). ( $\text{EtOH}+\text{HClO}_4$ ) 433(0.27), 276(0.74). HRMS (EI) Calcd. for  $\text{C}_{32}\text{H}_{25}\text{N}_3\text{O}_9\text{S}$ , 627.1311, Obt.: 627.1328.

*Reaction between the ylide 5 and dimethyl acetylenedicarboxylate in toluene.*

The ylide **5** generated from the salt (150mg, 0.44mmol) in the conditions described above, was reacted with DMAD (63mg, 0.44mmol) at room temperature overnight. The mixture was filtered, the filtrate evaporated under reduced pressure and the residue was separated by a chromatotron, using hexane as eluent. The first fraction eluted was identified as the dimethyl 2-diethylaminomaleate<sup>12</sup> (13mg, 13%). The second fraction eluted was a yellow oil the 7-methyl-5,6-dimethoxycarbonylpyrrolo[2,1-*a*]thiazole **14b**<sup>2</sup> (25mg, 22%). The third compound eluted was 3-methyl-[1,2,3]triazolo[5,1-*b*]thiazole **31**<sup>10</sup> (15mg, 24%).

## REFERENCES

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