Pergamon

Tetrahedron, Vol. 52, No. 31, pp. 10519-10524, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00572-8

Triazolopyridines. 17[1]. N2-Dicyanomethylides: Synthesis, Structure and Reactivity with Acetylenic Dipolarophiles.

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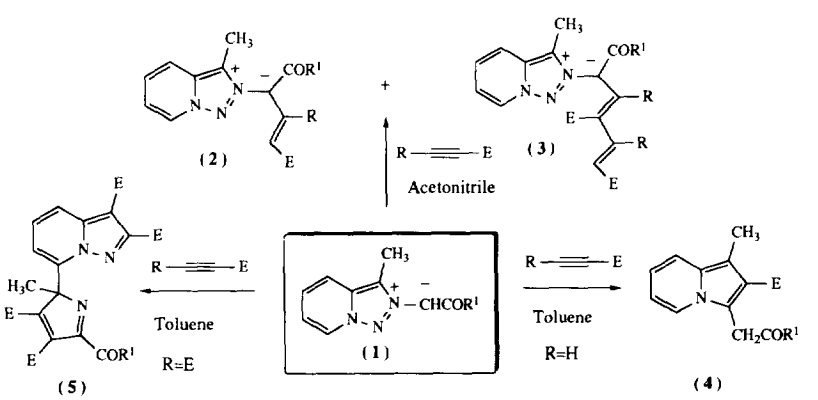
Abstract: Preparation and structure of 1,2,3-triazolo[1,5-a]pyridinium N2-dicyanomethylides **7a,b** are described. Reaction with methyl propiolate gives trisubstituted indolizines **8a,b** in good yield. Reaction of **7b** with dimethyl acetylenedicarboxylate gives a quinolizine **12**. Copyright © 1996 Elsevier Science Ltd

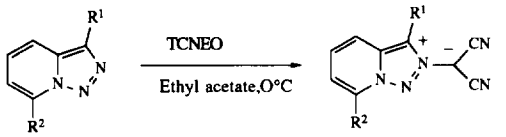
In the course of our work on reactivity of ylides of triazolopyridines and their application in the synthesis of fused heterocycles, we have shown[2-4] that the unstable monosubstituted ylides **1** generated *in situ* from 2-acylmethyl-3-methyl-1,2,3-triazolo[1,5-a]pyridines react with acetylenic esters in acetonitrile to give stable disubstituted ylides of type **2** and **3**.[2] This reaction is influenced by solvent. A change of solvent to toluene produced completely different products; with methyl propiolate (MP)[4] indolizines **4** were formed in high yield and with dimethyl acetylenedicarboxylate (DMAD)[3] pyrroleninylpyrazolo[5,1-a]pyridines **5**. Several mechanistic studies have been made to explain this behaviour.[5,6]



Following these observations, we were interested to study the reactivity of more stable disubstituted ylides of 1,2,3-triazolo[1,5-a]pyridines. In this paper we report the preparation, spectroscopical study, and reactivity with acetylenic esters of the N2-dicyanomethylides of 3 or 7 methyl substituted triazolopyridines **7a, 7b.**

N2-dicyanomethylides **7a** and **7b** were prepared by the method of Linn *et al.* [7] The triazolopyridines **6a, 6b**[8,9] react with tetracyanoethylene oxide (TCNEO) in ethyl acetate from 0°C to room temperature. N2 substitution can be assumed from comparison with experimental and theoretical data about the site of quaternization of triazolopyridines.[10,11] In the case of **6b** the reaction was complete after 3 days giving **7b** in 68% yield; compound **6a**

reacts faster (1 day, 66% yield). No reaction was achieved with **6c**[1] after 7 days. These results can be explained by the difference of N2 basicity. Similar effects are reported in the literature.[12]

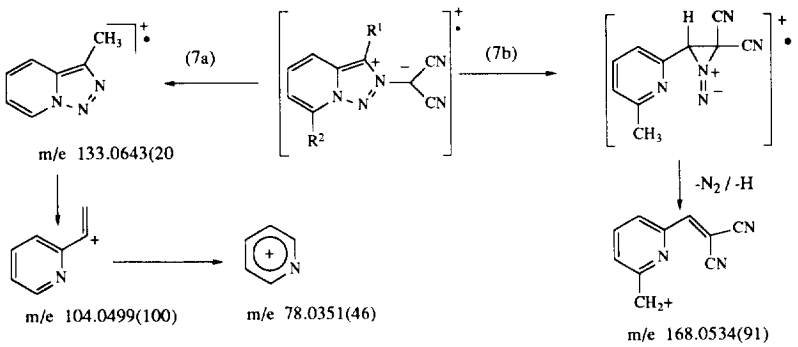


(6) a) $R^1 = CH_3$, $R^2 = H$
b) $R^1 = H$, $R^2 = CH_3$
c) $R^1 = CN$, $R^2 = H$

(7) a) $R^1 = CH_3$, $R^2 = H$
b) $R^1 = H$, $R^2 = CH_3$

Formation of ylides was easily established by the observation in the IR spectra of two characteristic strong bands at 2188-2158 cm^{-1} associated with the high degree of ionic character.[12,13] The UV spectra (in ethanol) showed the normal charge transfer band for these type of compounds at 362 and 361 nm for **7a** and **7b** respectively.

Ylides **7a,b** are stable compounds with high melting points, and have very interesting EI mass spectra. To the best of our knowledge this is the first report on the mass spectrum data of cycloimonium ylides. Both ylides show a great abundance of molecular ions, at m/e 197.0701 (57%) for **7a** and m/e 197.0709 (100%) for **7b**. The major fragmentation pathway of ylide **7a** involves the loss of the dicyanomethyl group from the molecular ion, and subsequent loss of nitrogen gives the vinylpyridine ion [m/e 104.0499 (100%)]. In ylide **7b** the major abundance ion was at m/e 168.0534 (91%). This fragment could be explained by an intramolecular rearrangement and further loss of nitrogen as described in Scheme 1. Some minor fragments in the mass spectrum of **7a** could be interpreted by a similar behaviour.



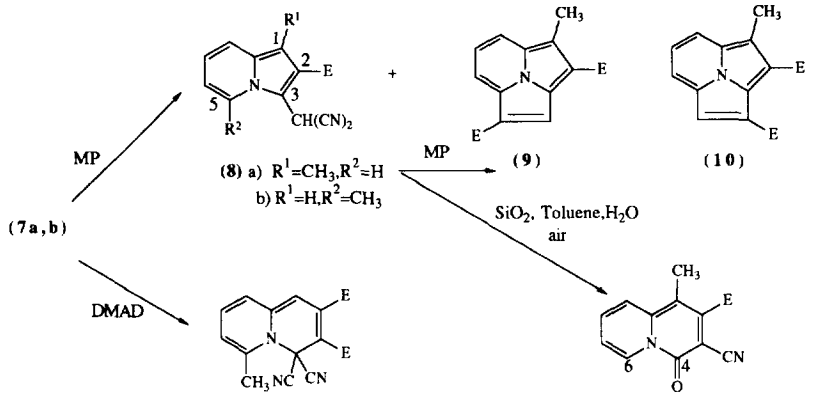
Scheme 1

The ^{1}Hnmr spectra of the ylides showed methyl substituents and aromatic protons with chemical shifts similar to those of the other ylides previously described.[2] Assignment of signals has been made from a study of coupling constant (see experimental).

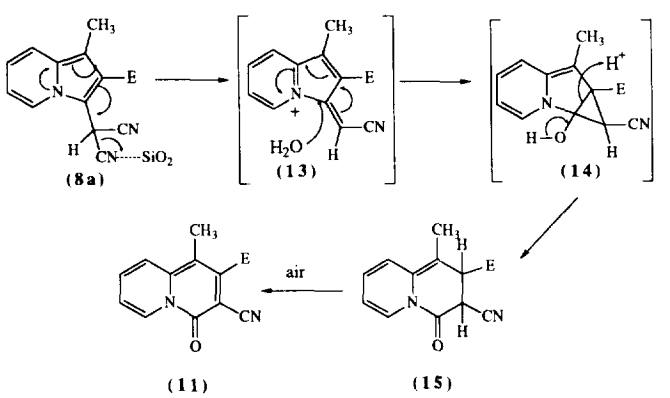
The more interesting feature in the ^{13}Cnmr spectra of these compounds is the chemical shift of the ylide carbons (Ci). The shielding observed is consistent with its electron density. The assignment of the aromatic carbons signals is based on the ^{1}H -^{13}C correlated spectrum. A great difference of chemical shift values has been observed for the methyl groups in the ylides **7a** and **7b**. The deshielding of the methyl group in **7b** can be related to the interaction between the methyl group and the nitrogen N1.

Ylide **7a** reacts with methyl propiolate at reflux in dry acetonitrile, and the reaction was completed in four days. Two compounds were formed. One was identified as the indolizine **8a**, obtained in a good yield (73%). The most significant feature in the ^{1}Hnmr spectrum is the shielding of the aromatic protons in contrast with those of starting ylide **7a**. The presence of a singlet at δ7.50 is due to the proton of the dicyanomethyl group. The methyl substituent at δ2.52 and the methoxy group at δ3.98 are consistent with the structure. The ^{13}C nmr spectra (Cl_3CD) showed twelve signals but in DMSO-d_6 fourteen signals appear as required by the molecular formula. The second compound isolated, a yellow solid, has molecular formula $C_{15}H_{13}NO_4$ (molecular ion in HRMS (EI) at 241.0853). The examination of the ^{1}H nmr spectrum showed the presence of three aromatic protons in a ABC system at δ8.5 (d, J=8.3Hz), δ8.07 (d, J=7.8Hz) and δ7.87 (dd). One singlet at δ8.19, two methoxy groups (δ4.04 and 4.02) and one methyl group at δ2.94 suggest the structure of a [2,2,3]cyclazine **9** or **10**. The distinction between these two possibilities had been made by DIFNOE experiments. When the methoxy signal at δ4,02 was irradiated, a positive NOE was observed for the

doublet at δ8,50 and for the singlet at δ8.19. By contrast, irradiation of the methoxy group signal at δ4,04 showed methyl signal and δ8.19 singlet enhancement. These results are only compatible with the [2,2,3]cyclazine **9**. The formation of this product can be explained by classical [8π +2π] reaction between indolizine **8a** and MP,[14] with further loss of the dicyanomethyl group.[15]



In order to confirm this, we studied the reaction between the indolizine **8a** and methyl propiolate in dry acetonitrile. The crude mixture showed by t.l.c. and ^{1}Hnmr the presence of the cyclazine **9** and starting material, but on further purification by column chromatography we obtained the cyclazine **9** in 73% yield and a new product. The HRMS (EI) analysis revealed a molecular formula of $C_{13}H_{10}N_2O_3$. The IR spectrum showed a cyano absorption at 2216 cm^{-1} and two carbonyl absorption at 1718 and 1590 cm^{-1}. The ^{1}H nmr spectrum of the new compound showed four protons in the aromatic region (δ9.80, 7.70, 7.52 and 7.22). The multiplicity and the coupling constants suggest a ABCD system. The surprising deshielding of the signal at δ9.80 can be explained by an anisotropic effect of a carbonyl group near this proton. Two singlets at δ4.02 and 2.43 indicated the presence of methoxy and methyl groups. The ^{13}Cnmr showed the expected thirteen peaks. The carbonyl ester appears at δ164.34 and a signal at δ151.09 can be assigned to an amide-lactam carbonyl. The combined spectral evidence was best accommodated by the 4H- quinolizinone structure **11**.[16] The isolation of compound **11** in the purification process suggests that this compound could be obtained by rearrangement of the initial indolizine **8a** during silica gel column chromatography. To clarify this, a mixture of indolizine **8a** in dry toluene and silica gel, in an argon atmosphere was boiled for several hours, but the presence of 4H-quinolizinone **11** could not be observed. By contrast, the same reaction in wet toluene, with an air atmosphere gives a quantitative yield of compound **11** in a few minutes. A possible explanation of these results could be that the silica gel helps the elimination of CN^- from the indolizine **8a** to give an unstable indolizinium ion **13**, which by reaction with water and further cyclopropyl ring opening gives an dihydro compound **15**. Air oxidation could generate the 4H-quinolizinone **11**.

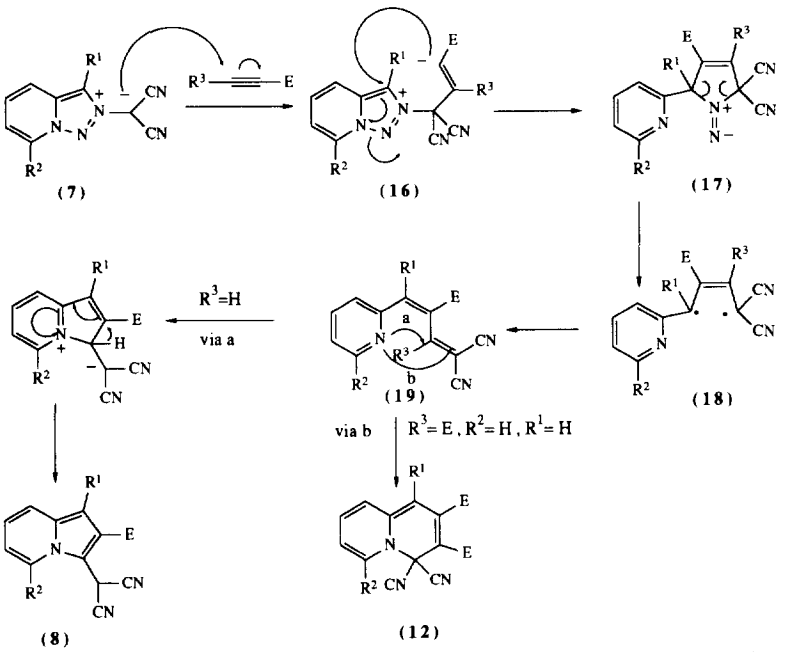


Reaction of the ylide **7b** with methyl propiolate afforded in a 60% yield the indolizine **8b** as single product. The methyl substitution in C5 of the indolizine hindered the formation of the corresponding cyclazine. The indolizine

8b showed in the ^{1}Hnmr spectrum a broad singlet for the proton of the dicyanomethyl group. The observation of this coalescence effect is in accord with the sterical interaction between the methyl group in C5 and the dicyanomethyl group in C3. The mass spectra of indolizines **8a, 8b** are similar and show substantial peaks for the loss of the ester and the methyl groups. The indolizine **8b** was decomposed in presence of silica gel only when boiled in toluene, but we obtained complicated mixtures, which were not investigated further.

We have studied also the reaction between the ylides **7a** and **7b** with DMAD. Compound **7a** gives under several conditions intractable gums, but with the ylide **7b** we have obtained a new type of compound, the 4H-quinolizine **12**. The assignment of this structure is based on HRMS (EI) and spectroscopic analysis. Although quinolizines can be obtained by different methods from substituted pyridines and DMAD,[13] the formation of this type of compound has no precedent in triazolopyridine ylide chemistry.

To explain the formation of indolizines **8** and quinolizines **12**, we propose that the ylides **7** react with acetylenic dipolarophiles as we have reported previously,[4] a nucleophilic Michael addition giving the betaine **16**. Intramolecular attack to the C3 position gives a 1,1-diazene. This type of intermediate can lose nitrogen to give an 1.4-diradical **18**.[17] The 1,4-diradical gives a diene **19** (this type of compound has been observed when the heterocycle base is thiazole).[6] The diene gives, *via* route a the indolizine skeleton, or *via* route b the quinolizine system by a intramolecular addition or by a concerted electrocyclic process. In neither case, have we obtained products derived from reaction of the cyano group as is frequent in reactions of N-heterocyclic dicyanomethylides with MP or DMAD.[18]



From these results it can be concluded that the dicyanomethylides **7a, 7b** are more stable and less reactive than the monosubtituted ylides **1** but, are excellent synthons for 1,2,3 and 2,3,5-trisubstituted indolizines with funtional groups suitable for further transformation, and for the production of 4-H quinolizine ring system.

Acknowledgements: This research was supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT Project PB94-0959).

EXPERIMENTAL

Mp were determined on a Kofler heated stage and are uncorrected. Chomatography on the Chromatotron used 2 mm plates of silica (Merck PF_{254}) with hexane/ ethyl acetate as eluent. N.M.R. spectra were determined on a Bruker 250 MHz spectrometer. Ms/gc and HRMS (EI) determinations were made using a VG Autospec Fisons.

Preparation of Dicyanomethylides (**7a,7b**).

To a solution of the triazolopyridine[7,8] **6a** or **6b** in the minimum quantity of ethyl acetate cooled at 0°C was added an equimolar amount of TCNEO in ethyl acetate. The reaction mixture was kept at room temperature for variable periods, then the crude product was filtered and purified.

3-Methyl-1,2,3-triazolo[1,5-a]pyridinium-2-dicyanomethylide (**7a**). The compound was prepared with a reaction time of 24h, (66%). mp 175-176°C (sublimed). δH (DMSO-d_6) 2.50(s, 3H), 7.37(dd, J_1=6.9, J_2=7.0, H6), 7,51(dd, J_1=8.8, J_2=7.0, H5), 7.99(d, J=8.8, H4), 8.93(d, J=6.9, H7). δC (DMSO-d_6) 9.54(CH_3), 45.97(Ci), 117.94(C4), 119.65(CN), 120.54(C6), 125.17(C7), 128.12(C3), 128.31(C5), 133.94(C3a). (IR (KBr) ν_{max} (cm^{-1}) 2188, 2158. m/z 197 (M^+,57%), 142 (12), 129 (55), 104 (100), 78 (46). UV (Ethanol) λ_{max} (log ε) 362 (4.0), 261 (4.5), 212 (4.2), 193 (3.3), 192 (3.2), 190 (3.8). HRMS (EI) Calcd. for $C_{10}H_7N_5$: 197.0701, Obt.: 197.0701.

7-Methyl-1,2,3-triazolo[1,5-a]pyridinium-2-dicyanomethylide (**7b**). The compound was prepared with a reaction time of 3 days (68%). mp 265-268°C (chloroform). δH (DMSO-d_6) 2.75(s,3H),7.43(d, J=7.3), 7.72(d, J_1=9.1, J_2=7.3, H5), 7.87(d, J=9.1, H4), 8.90(s, H3). δC (DMSO-d_6) 17.79(CH_3), 52.54(Ci), 114.46(C3), 115.12(C6), 118.26(CN), 118.34(C4), 130.34(C5), 135.75(C7), 136.07(C3a). IR (KBr) ν_{max} (cm^{-1}) 2188, 2151. m/z 197 (M^+, 100%), 168 (91), 141 (8), 78 (6). UV (Ethanol) λ_{max} (log ε) 361 (4.3), 265 (4.0), 203 (4.4). HRMS (EI) Calcd. for $C_{10}H_7N_5$: 197.0701, Obt.: 197.0708.

Reaction of the dicyanomethylide (**7a**) *with methyl propiolate.*

To a solution of 3-methyl-1,2.3-triazolo[1,5-a]pyridinium-2-dicyanomethylide (**7a**) (0.7g, 3.55mmol) in dry acetonitrile (20ml) was added a solution of methyl propiolate (0.59g, 7,1mmol) in dry acetonitrile (5ml). The mixture was refluxed (four days). The crude mixture was purified by column chromatography (silica gel, chloroform) to give two compounds. The first was identified as the 3-dicyanomethyl-1-methyl-2-methoxycarbonylindolizine (**8a**) (0.61g,73%). mp 190-193°C (chloroform). δH ($CDCl_3$) 2.52(s,3H), 3.98(s,3H), 6.88-6.98(m,2H), 7.50(s,1H), 7.54-7.59(m,1H), 8.02-8.06(m,1H). δC (DMSO-d6) 10.02(CH_3), 20.28(CH), 51.88(CH_3), 104.26(C), 108.42(C), 110.64(C), 111.77(CH), 114.60(CH), 117.01(C), 119.27(CH), 119.48(C), 122.89(CH), 129.80(C), 164.50(CO). IR (KBr) ν_{max} (cm^{-1}) 2249(CN), 1685(C=O). m/z(%) 253(34.1), 238(100), 193(37). UV (acetonitrile) λ_{max} (nm) (log ε) 419.5(4.0), 350.5(3.5), 291.0(4.0), 232.5(4.5). HRMS (EI) Calcd. for $C_{14}H_{11}N_3O_2$: 253.0851 , Obt.: 253.0850. Further elution gave the 1-methyl-2,4-dimethoxycarbonyl[2,2,3]cyclazine (**9**) (0,07g,7%). mp 136°C(chloroform). δH ($CDCl_3$) 2.96(s,3H), 4.02(s,3H), 4.04(s,3H), 7.87(dd, J_1=8.3Hz, J_2=7.8Hz,1H), 8.07(d, J=7.8Hz, 1H), 8.19(s,1H), 8.50(d, J=8.3Hz). δC($CDCl_3$) 11.60(CH_3), 51.52(CH_3), 51.84(CH_3), 114.23(C), 114.57(CH), 117.92(CH), 120.12(CH), 123.46(CH), 125.28(C), 125.94(C), 130.03(C), 130.68(C), 131.11(C), 165.08(C), 165.35(C). IR (KBr) ν_{max} (cm^{-1}) 1700(C=O). m/z(%) 271(100), 256(94.8), 240(53.5), 212(16.4), 153(21.3). UV (Ethanol) λ_{max} (nm) (log ε) 446.5(1.5), 316.0(1.6), 308.5(1.6), 275.0(1.8), 254.5(1.8). HRMS (EI) Calcd. for $C_{15}H_{13}NO_4$: 271.0857, Obt.: 271.0854.

Reaction between the indolizine (**8a**) *and methyl propiolate.* A solution of the indolizine (**8a**) (1.15g, 0.59mmol) and methyl propiolate (0.1g,1.18mmol) in dry acetonitrile (10ml) was heated at reflux temperature for 130h. The nmr analysis of alicuota showed only the presence of the cyclazine (**9**) and starting material. After removal the solvent and purification by chromatography (chromatroton) two fractions were obtained. In the first was the cyclazine (**9**) (0.117g, 73%) and the second fraction gave a yellow solid that has been identified as the 3-cyano-1-methyl-2-methoxycarbonylquinolizin-4-one (**11**) (0.018g, 13%). mp 130-132°C(hexane). δH ($CDCl_3$) 2.43(s,3H), 4.02(s,3H), 7.22(ddd, J_1=J_2=7.8Hz, J_3=1.5Hz,1H), 7.52(ddd, J_1=8.9Hz, J_2=7.8Hz, J_3=0.9Hz,1H), 7.70(dd, J_1=8.9Hz, J_2=1.5Hz,1H), 9.80 (dd, J_1=7.8Hz, J_2=0.9Hz,1H). δC ($CDCl_3$) 9.15(CH_3), 52.75(CH_3), 114.26(C), 117.60(C), 117.99(CH), 118.14(CH), 119.35(C), 128.61(CH), 129.45(C), 129.85(CH), 139.74(C), 151.09(C), 164.34(C). IR (KBr) ν_{max} (cm^{-1}) 2216(CN), 1718(C=O), 1590(C=O). m/z(%) 242(770), 211(37.5), 210(39.7), 183(6.0), 182(6.5), 154(100), 128(12.1), 78(10.6). UV (acetonitrile) λ_{max} (nm) (log ε) 420.5(4.1), 291.0(3.9), 256.5(3.9), 206.0(4.4). HRMS (EI) Calcd. for $C_{13}H_{10}N_2O_3$: 242.0691, Obt.: 242.0692.

Synthesis of 3-cyano-1-methyl-2-methoxycarbonylquinolizin-4-one (**11**) *from 3-dicyanomethyl-1-methyl-2-methoxycarbonylindolizine* (**8a**). To a solution of the indolizine (**8a**) (0.05g,0.2mmol) in commercial toluene (5ml), was added silica gel ($60PF_{254}$)(1g) and the mixture was stirred and refluxed (12h). The crude product was filtered and the solution gives the quinolizinone (**11**) in 90% yield. When this reaction was repeated in an argon atmosphere and with dry toluene only a intractable gum has been observed.

Reaction of the dicyanomethylide (**7b**) *with methyl propiolate.*

To a solution of 7-methyl-1,2.3-triazolo[1,5-a]pyridinium-2-dicyanomethylide (**7b**) (0.39g, 2mmol) in dry acetonitrile (20ml) was added a solution of methyl propiolate (0.34g,4mmol) in dry acetonitrile (5ml). The mixture

was refluxed (seven days). The crude mixture was purified by column chromatography (silica gel, ethyl acetate) to give two compounds. The first was identified as 3-dicyanomethyl-5-methyl-2-methoxycarbonylindolizine **(8b)** (0.29g,58%). mp 146-147°C (chloroform). δH ($CDCl_3$) 3.20(s,3H), 3.96(s,3H), 6.59(d, J=6.8Hz, 1H), 6.84(dd, J_1=6.8Hz, J_2=8.8Hz, 1H), 6.98(s,1H), 7.36(d, J=8.8Hz, 1H), 8.11(s_{br}, 1H). δC ($CDCl_3$) 19.44(CH_3), 21.46(CH), 52.22(CH_3), 103.12(CH), 109.85(C), 112.81(C), 115.26(C), 116.62(CH), 118.95(CN), 120.81(CH), 134.18(C), 136.68(C) 165.97(C). IR (KBr) ν_{max} (cm^{-1}) 2254(CN), 1691(C=O). m/z(%) 253(41.5), 238(100), 222(14.5), 192(30.8), 167(32.7). UV (Acetonitrile) λ_{max} (nm) (log ε) 417.5(3.4), 388.5(3.8), 232.0(4.3), 204.5(4.2). HRMS (EI) Calcd. for $C_{14}H_{11}N_3O_2$: 253.0851, Obt.: 253.0846. Further elution gave only starting ylide **(7b)** (0.112g).

Reaction of the dicyanomethylide **(7b)** *with dimethylacetylene dicarboxylate (DMAD).*

To a solution of 7-methyl-1,2,3-triazolo[1,5-a]pyridinium-2-dicyanomethylide **(7b)** (0.032g, 0.162mmol) in dry acetonitrile (25ml) was added DMAD (0.023g 0.162mmol). The mixture was stirred and refluxed (90 min.) The crude mixture was evaporated and the solid obtained was recrystallized from cyclohexane to give the 4,4-dicyano-2,3-dimethoxycarbonyl-6-methylquinolizine **(12)** (0.031g,62%). mp 144-145°C (cyclohexane). δH ($CDCl_3$) 2.40(s,3H), 3.77(s,3H), 3.90(s,3H), 7.16(d, J=7.8Hz, 1H), 7.33(d, J=7.8Hz, 1H), 7.67(dd, J_1=J_2=7.8Hz, 1H), 7.87(s, 1H). δC ($CDCl_3$) 23.15(CH_3), 53.29(CH_3), 53.41(CH_3), 124.92(CH), 125.71(C), 137.56(CH), 143.55(CH), 149.51 (C), 158.97(C), 163.54(C). IR (KBr) ν_{max} (cm^{-1}) 2205(CN), 1726(C=O). m/z(%) 311(21.6), 280(12.0), 252(100.0), 220(4.2), 193(12.7), 166(11.6). HRMS (EI) Calcd. for $C_{16}H_{13}N_3O_4$: 311.0906, Obt.: 311.0904. A similar reaction with the ylide **(7a)** and DMAD in various conditions gave only polymeric material.

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(*Received in UK* 22 *May* 1996; *accepted* 18 *June* 1996)