Pergamon

Tetrahedron, Vol. 53, No. 37, pp. 12765-12770, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00796-5

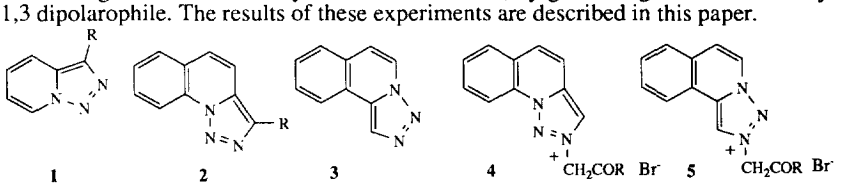
Triazolopyridines. 19.[1] Synthesis and Reactions of Ylides Derived from [1,2,3]Triazolo[1,5-*a*]quinoline and [1,2,3]Triazolo[5,1-*a*]isoquinoline with Methyl Propiolate.

Belén Abarca,* Rafael Ballesteros and Nadia Houari

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

Abstract: Preparation and structure of salts and ylides derived from triazolo[1,5-*a*]quinoline **2** and triazolo[5,1-*a*]isoquinoline **3** are described. Reactions with methyl propiolate of ylides **6-9** give pyrrolo[1,2-*a*]quinolines **13, 18** and pyrrolo[2,1-*a*]isoquinolines **12, 19**.

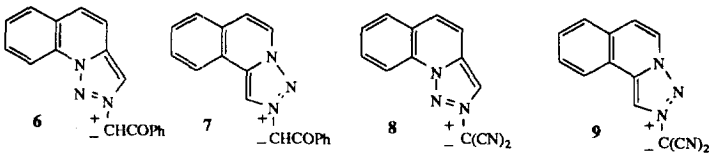
In previous parts of this series, we have reported studies of reactivity of triazolopyridines **1**, triazoloquinolines **2** and triazoloisoquinoline **3** with electrophiles,[2-4] under directed lithiation conditions,[3-5] the preparation of halo-derivatives,[1,6] nucleophilic substitution reactions of bromo derivatives,[1,7,8] and, only from triazolopyridines, the preparation of quaternary salts,[9] the formation of ylides and their reactions with acetylenic and olefinic esters.[10-14] The interesting results found in these last reactions led us to investigate the behaviour of the benzologues **2** and **3** in alkylation reactions, and, by generating an intermediate ylide, in the reaction with a 1,3 dipolarophile. The results of these experiments are described in this paper.



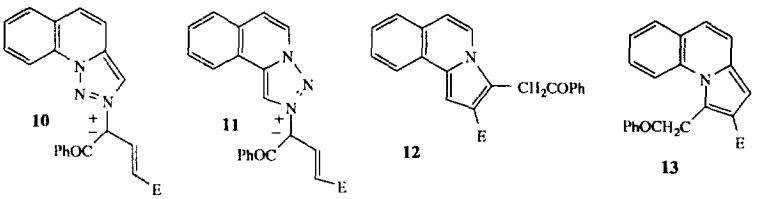
1 a) R = H, b) R = Me; **2** a) R = H, b) R = $CONEt_2$; **3**; **4** a) R = OMe, b) R = Ph; **5** a) R = OMe, b) R = Ph

Of the three nitrogen atoms in [1,2,3]triazolo[1,5-*a*]quinoline **2** and in [1,2,3]triazolo[5,1-*a*]isoquinoline **3**, two would appear to be available sites for quaternization. We have obtained the simple quaternary salts **4a,b** and **5a,b** crystalline and in general high yield. We have shown that all the salts carry the quaternary substituent at N2 by performing DIFNOE experiments (see experimental). We also have done molecular orbital calculations involving full optimizations of the geometry at the RHF/3-21G and RHF/6-31G* levels. Energy calculations at the MP2 level of theory were also done by single-point calculations on RHF/6-31G*-optimized geometries, using the GAUSSIAN 94 package,[15] which provide explanations for the preferred site of alkylation in compounds **2** and **3**. The underlying assumption was that S_N2 attack on the halide was related to atomic charges at the nitrogen atoms. The calculated values using the Mulliken method are given in Table 1; it can be seen that the alkylation of compounds **2** and **3** is in accord with the *ab initio* calculations. We also know that the compound **2** acts as a nitrogen-donor ligand forming a copper(II) complex by the N2.[16]

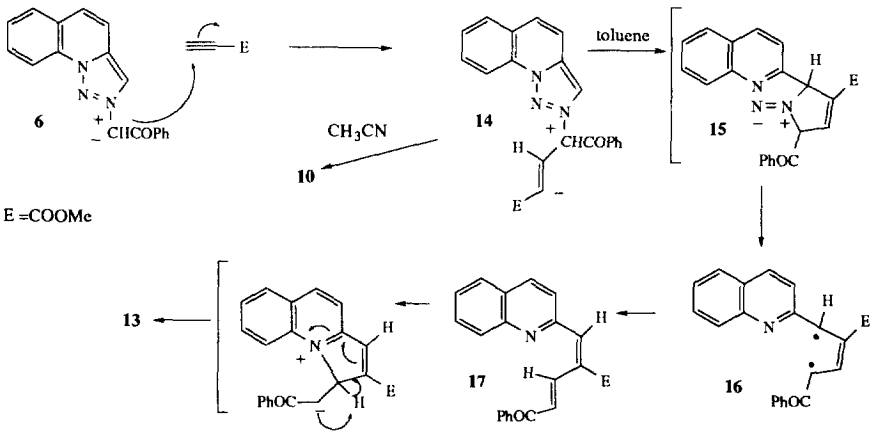
Ylides **6** and **7** were obtained *in situ* from the corresponding salt, using acetonitrile as solvent. On treating the solutions with anhydrous potassium carbonate at room temperature, a yellow colour was generated indicative of ylide formation. Ylides **8** and **9** are stable yellow compounds and were prepared by the method of Linn *et al.*[17] N2 substitution can be assumed from comparison with experimental and theoretical data about the site of quaternization of triazoloquinoline and triazoloisoquinoline related above. Both compounds showed the characteristic two strong bands in the IR at 2190-2150 cm^{-1} for these type of compounds. EI mass, ^1H, and ^{13}C NMR spectra are in accord with those of the other similar ylides previously described by us.[14]



All the ylides **6-9** react with methyl propiolate, giving different results depending on the solvent and the type of ylide. In acetonitrile the ylide **6** gave an orange adduct in 52% yield, shown by HRMS to have formula $C_{22}H_{17}N_3O_3$. The ^1H nmr spectrum showed the characteristic pattern of a triazoloquinoline, but with chemical shifts deshielded like the salts and ylide derivatives. The most interesting signals were an AB pair of doublets at δ7.95 and δ5.80 with a large (14.9Hz) coupling. The ^{13}C nmr spectrum showed the expected 20 signals; here the outstanding features were signals at δ 95.89 (CH) and at δ 109.69 (C). Both of these, if due to sp^2 hybridized carbon atoms, require considerable shielding, which would be present in an ylide structure such as **10**. Similar compounds were prepared from triazolopyridinium ylides and methyl propiolate.[10] The reaction with ylide **7**, under the same conditions, gave two products, the major one (48%) was also an orange 1:1 adduct, to which could be attributed the structure **11** on the basis of its analytical and spectral data. The minor one (11%), a yellow compound was shown to have formula $C_{22}H_{17}NO_3$, that is a 1:1 adduct with loss of N_2. We propose the structure of a pyrrolo[2,1-*a*]isoquinoline **12** based on HRMS, ^1H, ^{13}C NMR and IR spectral data, and analogy with the indolizines found in the reactions with triazolopyridines.[12]



A change of solvent to toluene required a mixture of potassium carbonate and triethylamine as base to form the ylides **6** and **7**. Further reaction with methyl propiolate under these conditions gave different results. 1-Benzoylmethyl-2-methoxycarbonylpyrrolo[1,2-*a*]quinoline **13** and 3-benzoylmethyl-2-methoxycarbonylpyrrolo [2,1-*a*]isoquinoline **12**, respectively, were formed as the only compounds in good yields.

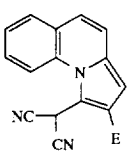


Scheme 1

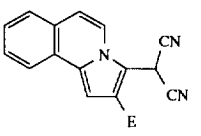
To account for the differing modes of reaction between ylides **6**, **7** and methyl propiolate in polar or non-polar solvent we assume a mechanism resembling that reported previously,[12] which is described here for the reaction with ylide **6** since this ylide gave simpler results, (scheme 1). The first stage is the same whether the solvent is polar or non-polar, a nucleophilic Michael addition giving the betaine **14**. In polar solvent a hydrogen transfer rapidly stabilizes the system to give the ylide **10**, but in non-polar medium this process is slowed and attack on the C3 carbon allows cleavage of the N_1-N_{10} bond giving the diazene **15**. This type of

intermediate can lose nitrogen to give a 1,4-diradical **16**, which gives a diene **17**, recyclization of which could produce the pyrroloquinoline skeleton.

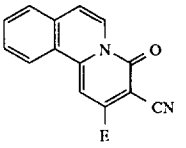
The reaction with ylides **8, 9** and methyl propiolate were also investigated. Compounds **18** and **19** respectively were obtained as yellow solids. The formation of such compounds can be explained in the same way as that of **12** and **13**. In the purification process of **19** by column chromatography a new compound was formed, identified as **20**. There is one precedent in the literature for this type of transformation helped by silica gel.[14]



18



19



20

Acknowledgements: Our thanks are due to Comisión Interministerial de Ciencia y Tecnología (CICYT, Project PB94-0959) for financial support, and Dr. Amparo Asensio for helpful assistance in molecular orbital calculations.

EXPERIMENTAL

Mps were determined on a Kofler heated stage and are uncorrected. Chromatography on the Chromatotron used 2mm plates of silica (Merck PF254) with hexane/ ethyl acetate as eluent. N.M.R. spectra were determined on a Bruker 250MHz spectrometer. HRMS (EI) determinations were made using a VG Autospec Trio 1000 (Fisons).

Table 1. Total Atomic Charges

Compound	Atom	RHF/3-21G	RHF/6-31G*	[a]MP2/6-31G*
2	N1	-0.02	-0.04	-0.04
	N2	-0.33	-0.27	-0.57
3	N2	-0.33	-0.28	-0.28
	N3	-0.02	-0.04	-0.04

a) Single point calculations

Quaternary Salt Preparation

Salts were prepared by boiling a solution of triazoloquinoline **2a** or triazoloisoquinoline **3** with equimolar amount of methyl bromoacetate or phenacyl bromide in dry acetonitrile (three days). Purification was by recrystallization.

2-Methoxycarbonylmethyl-[1,2,3]triazolo[1,5-a]quinolinium bromide **4a.** Yield 66%. m.p. 143-145°C ($CHCl_3$/Toluene). ^1H n.m.r. (DMSO-d_6) δ 9.55(s,1H), 8.66(d,J=8.02Hz,1H), 8.39-8.31(m,2H), 8.27-8.21(m,1H), 8.15-7.90(m,2H), 6.14(s,CH_2), 3.81(s,CH_3). ^{13}C n.m.r. (DMSO-d_6) δ166.09 (C=O), 134.52(C), 132.48(CH), 131.81(CH), 131.12(CH), 130.28(CH), 129.52(C), 127.27(CH), 126.07(C), 116.66(CH), 115.34(CH), 54.53(CH_2), 53.58(CH_3). IR (KBr) ν_{max}(cm^{-1}) 1759.

2-Benzoylmethyl-[1,2,3]triazolo[1,5-a]quinolinium bromide **4b.** Yield 94%. m.p. 195-197°C (2-propanol). ^1H n.m.r. (DMSO-d_6) δ 9.55(s,1H), 8.65(d,J=8.05Hz,1H), 8.38(d,J=9.5Hz,1H), 8.37(m,1H), 8.29(d,J=9.5Hz,1H), 8.18(d,J=7.3Hz,2H), 8.10-8.09(m,2H), 7.82(t,J=7.3Hz,1H), 7.68(t,J=7.3,2H), 6.9(s,2H). DIFNOE irradiation at δ6.9 produce enhancement at δ9.55 (H3) and 8.18 (2H *ortho*). ^{13}C n.m.r. (DMSO-d_6) δ 190.10(C=O), 135.10(CH), 134.48(C), 133.39(CH), 131.60(CH), 130.95(CH), 130.23(CH), 129.49(C), 129.35(CH), 128.73(CH), 127.42(CH), 125.93(C), 116.55(CH), 115.36(CH), 60.57(CH_2). IR (KBr) ν_{max}(cm^{-1}) 1700. Found: C, 58.64; H, 3.77; N, 11.48; Br, 21.69 %. $C_{18}H_{14}BrN_3O$ requires: C, 58.71; H, 3.80; N, 11.42; Br, 21.72 %.

2-Methoxycarbonylmethyl-[1,2,3]triazolo[5,1-a]isoquinolinium bromide **5a**. Yield 68%. m.p. 154-155°C ($CHCl_3$/petroleum ether). ^1H n.m.r. (DMSO-d_6) δ10.14(s,1H), 9.24 (d,J=7.3Hz,1H), 8.70-8.67(m,1H), 8.27(d,J=7.3Hz,2H), 8.01-7.96(m,2H), 6.16(s,2H), 3.82(s,3H). ^{13}C n.m.r. (DMSO-d_6) δ166.03(C=O),

134.83(C), 132.30(CH), 131.18(CH), 129.10(C), 128.99(CH), 126.11(CH), 125.38(CH), 123.98(CH), 122.77(CH), 121.11(C), 54.46(CH_2), 53.65(CH_3). IR (KBr) ν_{max}(cm^{-1}) 1761. Found: C, 48.43; H, 3.72; N, 13.05 %, $C_{13}H_{12}BrN_3O_2$ requires: C, 48.46; H, 3.73; N, 13.05 %.

2-Benzoylmethyl-[1,2,3]triazolo[5,1-a]isoquinolinium bromide **5b.** Yield 70%. m.p. 165-167°C ($CHCl_3$/petroleum ether). ^1H n.m.r. (DMSO-d_6) δ10.02(s,1H), 9.26(d,J=7.3Hz,1H), 8.73-8.70(m,1H), 8.30-8.25(m,2H), 8.17(d,J=7.3Hz,2H), 8.05-8.01(m,2H), 7.83(t,J=7.3Hz,1H), 7.69(t,J=7.3Hz,2H), 6.96 (s,CH_2). DIFNOE irradiation at δ6.9 produce enhancement at δ10.02 (H1) and 8.17 (2H *ortho*). ^{13}C n.m.r. (DMSO-d_6) δ190.11(C=O), 135.12(CH), 134.73(C), 133.54(C), 132.13(CH), 131.04(CH), 129.34(CH), 129.02(C), 128.89(CH), 128.76 (CH), 126.23(CH), 125.34(CH), 123.64(CH), 122.77(CH); 121.06(C); 60.38(CH_2). IR (KBr) ν_{max}(cm^{-1}) 1694. Found: C, 58.71; H, 3.81; N, 11.41; Br, 21.50 %, $C_{18}H_{14}BrN_3O$ requires: C, 58.71; H, 3.80; N,11.42; Br, 21.72 %.

General procedure for preparation of ylides **6, 7.**

A solution of the appropriate salt **4b,** or **5b**, in anhydrous acetonitrile (15ml) was vigorously stirred at room temperature with equimolar amount of anhydrous potassium carbonate. During four hours a yellow paste formed. When the solvent was anhydrous toluene (10ml) a mixture of equimolar amounts of potassium carbonate and triethylamine was used to generate the yellow ylides.

Preparation of dicyanomethylides **8, 9.**

To a solution of the triazoloquinoline **2a** or triazoloisoquinoline **3** (0.250g,1.4mmol) in ethyl acetate (5ml), cooled at 0 °C, an equimolar amount of TCNEO in ethyl acetate (15ml) was added. The reaction mixture was kept at room temperature for two days, then the crude product was filtered and purified.

[1,2,3]Triazolo[1,5-a]quinolinium-2-dicyanomethylide **8.** Yield 52%. m.p. 302-305°C (chloroform). ^1H n.m.r. (DMSO-d_6) δ 8.92(s,1H), 8.36(d,J=8.3Hz,1H), 8.17(d,J=8.3Hz,1H), 8.12 (d, J=9.75 Hz,1H), 7.94(t,J=8.3Hz,1H), 7.83-7.75(m,2H). ^{13}C (DMSO-d_6) δ134.60(C), 132.05(CH), 131.09(CH), 129.90(CH), 129.43(C), 128.96(CH), 124.37(C), 118.15(CN), 116.22(CH), 115.77(CH), 113.75(CH), 53.15(C). IR (KBr) ν_{max}(cm^{-1}) 2189, 2152. UV (Ethanol) λ_{max}(nm) 385. m/z (%) 233 (100) , 204 (45),178 (16), 154 (46), 141 (27). HRMS (EI) Calcd. for $C_{13}H_7N_5$: 233.0701, Obt.: 233.0698.

[1,2,3]Triazolo[5,1-a]isoquinolinium-2-dicyanomethylide **9**. Yield 66%. m.p. 295-297°C (chloroform). ^1H n.m.r. (DMSO-d_6) δ9.62(s,1H), 8.90(d,J=7.3Hz,1H), 8.66-8.62(m,1H), 8.11-8.08(m,1H), 7.89-7.87(m,2H), 7.83(d,J=7.3Hz,1H). ^{13}C n.m.r. (DMSO-d_6) δ134.95(C), 131.48(CH), 130.10(CH), 129.29(C), 128.27(CH), 125.43(CH), 122.30(CH), 120.19(C), 119.21(CH), 118.29 (CN), 115.55(CH), 52.98(C). IR (KBr) ν_{max}(cm^{-1}) 2190, 2150. UV (Ethanol) λ_{max}(nm) 378. m/z (%) 233(100), 204(58), 178(14), 154(51), 141(31). HRMS (EI) Calcd. for $C_{13}H_7N_5$: 233.0701, Obt.: 233.0706.

Reaction between the ylide 6 and methyl propiolate in acetonitrile.

To the ylide **6** (generated from salt **4b** (0.2g,0.5mmol) in acetonitrile as described in the general procedure) was added a solution of methyl propiolate (0.05g,0.6mmol) in dry acetonitrile (5ml). The mixture was stirred overnight at room temperature, and then was filtered and evaporated. The crude product was recrystallized in chloroform-hexane to give an orange solid identified as 2-benzoyl-(E)2-methoxycarbonylvinylmethyl-[1,2,3]triazolo[1,5-*a*] quinolinium ylide **10** (0.105g, 52%). m.p. 221-223°C. ^1H n.m.r. ($CDCl_3$) δ 9.78(s,1H), 8.57(d,J=8.4Hz,1H), 7.95(d,J=14.9Hz,1H), 7.92(d,J=8.02Hz,1H), 7.90-7.71(m,4H), 7.65-7.54(m,3H), 7.38-7.35(m,2H), 5.80(d,J=14.9Hz,1H), 3.58(s,3H). ^{13}C n.m.r. ($CDCl_3$) δ 181.60(C=O), 170.06(C=O), 141.29(C), 139.85(CH), 131.98(C), 131.80(CH), 130.06(CH), 129.85(C), 129.45(CH), 129.38(CH), 129.19(CH), 128.34(CH), 128.07(CH), 124.69(C), 122.76(CH), 116.61(CH), 113.48(CH), 109.69(C), 95.89(CH), 50.77(CH_3). IR (KBr) ν_{max}(cm^{-1}) 1671, 1585. UV (Ethanol) λ_{max}(nm) (log ε) 430(3.3), 247(4.2), 257(4.4), 205(4.2). m/z (%) 371(43), 342(35), 312(100), 169(26), 141(58), 105(48), 77(25). HRMS (EI) Calcd. for: $C_{22}H_{17}N_3O_3$, 371.1269, Obt.: 371.1268

Reaction between the ylide 7 and methyl propiolate in acetonitrile

To the ylide **7** (generated from salt **5b** (0.2g,05mmol) in acetonitrile as described in the general procedure) was added a solution of methyl propiolate (0.05g,0.6mmol) in dry acetonitrile (5ml). The mixture was stirred overnight at room temperature, and then was filtered and evaporated. The crude mixture was purified by column chromatography (silica gel, hexane-ethyl acetate) giving two compounds. The first compound eluted was identified as methyl 3-benzoylmethylpyrrolo[2,1-*a*]isoquinoline-2-carboxylate **12** (0.020g,11%). m.p. 174-176°C (hexane). ^1H n.m.r. ($CDCl_3$). δ8.10(d,J=7.3Hz,2H), 7.98(d,J=7.6Hz,1H), 7.55(dd,J=7.3Hz,2H), 7.50-7.42(m,4H), 7.37-7.31(m,2H), 6.74(d,J=7.6Hz,1H), 5.03(s,CH_2), 3.85(s,CH_3). ^{13}C n.m.r. ($CDCl_3$) δ195.64(C=O), 166.00(C=O), 136.26(C), 133.67(C), 133.51(CH), 130.16(C), 129.72(C), 128.71(CH), 128.59(CH), 127.93(CH), 126.96(CH), 126.34(CH), 124.52(C), 122.08(CH), 121.51(CH),

115.65(C), 113.24(CH), 101.20(CH), 51.31(CH_3), 35.33(CH_2). IR (KBr) $\nu_{max}(cm^{-1})$ 1693, 1676. UV ($CHCl_3$) λ_{max}(nm) (log ε) 403(3.5), 378(3.5), 357(3.5) 328(3.7), 269(1.7). m/z (%) 343(10), 252(11), 238(100), 178(10), 77(5). HRMS (EI) Calcd. for $C_{22}H_{17}NO_3$, 343.1208, Obt.: 343.1207. Further elution gave the 2-benzoyl-(E)-2-methoxycarbonylvinylmethyl-[1,2,3]triazolo[5,1-*a*]isoquinolinium ylide **11** (0.097g,48%). m.p. 177-179°C (2-propanol). ^1H n.m.r. ($CDCl_3$) δ10.00(s,1H), 8.34(d,J=7.3Hz,1H), 7.92(d,J=8.02Hz,1H), 7.88(d,J=14.9Hz,1H), 7.84-7.71(m,3H), 7.53-7.49(m,3H), 7.32-7.29(m,3H), 5.55(d,J=14.9Hz,1H), 3.53(s,3H). ^{13}C n.m.r. ($CDCl_3$) δ 179.78(C=O), 168.90(C=O), 139.94(C), 139.21(CH), 130.42(CH), 129.71(CH), 128.51(CH), 128.26(CH), 127.92(C), 127.42(CH), 127.10(CH), 126.78(CH), 123.73(CH), 121.91(CH), 120.12(CH), 115.13(C), 108.67(C), 95.13(CH), 49.79(CH_3). IR (KBr) $\nu_{max}(cm^{-1})$ 1677, 1585. m/z (%) 371(43), 342(41), 312(100), 169(11), 141(55), 105(50), 77(28). HRMS (EI) Calcd. for $C_{22}H_{17}N_3O_3$, 371.1269, Obt.: 371.1269.

Reaction between the ylide **6** *and methyl propiolate in toluene.*

To the ylide **6** (generated from salt **4b** (0.15g,0.41mmol) in toluene (10ml) as described in the general procedure) was added a solution of methyl propiolate (0.04g,0.44mmol) in dry toluene (5ml). The mixture was stirred overnight at room temperature, and then was filtered and evaporated. The crude product was purified by column chromatography (silica gel, hexane-ethyl acetate) to give a yellow solid identified as methyl 1-benzoylmethylpyrrolo[1,2-*a*]quinoline-2-carboxylate **13** (0.09g,64%). m.p. 170-172°C (hexane). ^1H n.m.r. ($CDCl_3$) δ8.35(d,J=6.9Hz,2H), 7.98(d,J=8.05Hz,1H), 7.90-7.72(m,4H), 7.53-7.41(m,3H), 7.20(s,1H), 7.19(d,J=8.05,1H), 5.82(s,2H), 4.03(s,3H). ^{13}C n.m.r. ($CDCl_3$) δ 196.34(C=O), 166.10(C=O), 136.62(C), 134.73(C), 133.57(CH), 131.97(C), 128.90(CH), 128.87(CH), 128.42(CH), 128.29(C), 127.28(CH), 126.25(C), 124.55(CH), 120.35(CH), 119.55(CH), 117.71(C), 116.37(CH), 104.46(CH), 51.32(CH_3), 39.46(CH_2). IR (KBr) $\nu_{max}(cm^{-1})$ 1696, 1679. m/z (%), 343(16), 311(12), 238(100), 178(14), 77(3). UV ($CHCl_3$) λ_{max}(nm) (log ε), 341(3.9), 248(4.7). HRMS (EI) Calcd. for $C_{22}H_{17}NO_3$, 343.1208, Obt.: 343.1203.

Reaction between the ylide **7** *and methyl propiolate in toluene.*

To the ylide **7** (generated from salt **5b** (0.14g,0.41mmol) in toluene (10ml) as described in the general procedure) was added a solution of methyl propiolate (0.035g,0.42mmol) in dry toluene(5ml). The mixture was stirred overnight at room temperature, and then was filtered and evaporated. The crude product was purified by column chromatography (silica gel, hexane-ethyl acetate) to give a yellow solid identified as methyl 3-benzoylmethylpyrrolo[2,1-*a*]isoquinoline-2-carboxylate **12** (0.070g, 54%) (described above).

Reaction of the dicyanomethylide **8** *and methyl propiolate.*

To a heated solution of [1,2,3]triazolo[1,5-*a*]quinolinium-2-dicyanomethylide **8** (0.2g, 0.85 mmol) in dry acetonitrile (15ml) was added a solution of methyl propiolate (0.08g,0.95mmol) in acetonitrile (5ml). The mixture was refluxed (two days). The reaction crude was purified by column chromatography (silica gel, hexane-ethyl acetate 9:1). A pure compound eluted was identified as the methyl 1-dicyanomethylpyrrolo[1,2-*a*]quinoline-2-carboxylate **18** (0.150g,56%). m.p. 210-212°C (hexane). ^1H n.m.r. ($CDCl_3$) δ 8.37 (d,J=8.4Hz,1H), 8.17(s,1H), 7.70 (t,J=7.6Hz,2H), 7.49(m,1H), 7.29(d,J=9.3Hz,1H), 7.18(d,J=9.27Hz,1H), 6.98(s,1H), 3.93(s,3H). ^{13}C n.m.r. ($CDCl_3$) δ165.72(C=O), 134.04(C), 132.99(C), 129.50(CH), 128.30(CH), 126.12(CH), 125.99(C), 123.20(CH), 118.74(CH), 118.29(C), 117.45(CH), 114.15(C), 111.01(CN), 101.00(CH), 52.31(CH_3), 20.68(CH). IR (KBr) $\nu_{max}(cm^{-1})$ 2120, 1687. m/z (%) 289 (51), 274 (100) 258 (19), 229 (30), 203 (37), 78 (11). UV ($CHCl_3$) λ_{max}(nm) (log ε) 346(3.6), 329(3.7), 249(4.2). HRMS (EI) Calcd. for $C_{17}H_{11}N_3O_2$, 289.0851, Obt.: 289.0849. Starting material **8** (0.040g,26%) was recovered.

Reaction of the dicyanomethylide **9** *with methyl propiolate.*

To a heated solution of [1,2,3]triazolo[5,1-*a*]isoquinolinium-2-dicyanomethylide **9** (0.15g, 0.64 mmol) in dry acetonitrile (15ml) was added a solution of methyl propiolate (0.06g,0.7mmol) in acetonitrile (5ml). The mixture was refluxed (two days). The crude mixture was purified by column chromatography (silica gel, hexane-ethyl acetate 9:1) to give two products. The first compound eluted, an oil which was not present in the crude, was identified as methyl 3-cyano-4-oxo-4H-pyrido[2,1-*a*]isoquinoline-2-carboxylate **20** (0.009g,6%). ^1H n.m.r. ($CDCl_3$) δ9.32(d,J=7.8Hz,1H), 8.19-8.14(m,1H), 7.78-7.74(m,1H), 7.67-7.63(m,2H), 7.49(s,1H), 7.31(d,J=7.8Hz,1H), 3.97(s,3H). m/z (%)278 (100), 252 (31), 247 (40), 222 (7), 192 (16), 164 (21). UV ($CHCl_3$) λ_{max} (nm) (log ε), 405(2.7), 380(2.8). HRMS (EI) Calcd. for $C_{16}H_{10}N_2O_3$, 278.0691, Obt.: 278.0694. The second product was identified as the methyl 3-dicyanomethylpyrrolo[2,1-*a*]isoquinoline-2-carboxylate **19** (0.09g,48%). m.p. 170-172°C (hexane). ^1H n.m.r. ($CDCl_3$) 8.01(d,J=7.8Hz,1H), 7.90(d,J=7.3Hz,1H), 7.61 (d,J=7.3Hz,1H), 7.56-7.42(m,2H), 7.36(s,1H), 7.34(s,1H), 7.10(d,J=7.3Hz,1H), 3.90(s,3H). ^{13}C n.m.r. ($CDCl_3$) δ164.18(C=O), 131.27(C), 127.88(CH), 126.89(CH), 126.58(CH), 125.60(C), 124.52(C), 121.54(CH), 118.92(CH), 115.60(C), 114.86(CH), 109.84(CN), 108.84(C), 100.82(CH), 51.22(CH_3), 16.96(CH). IR (KBr) $\nu_{max}(cm^{-1})$ 2150, 1688. m/z (%)289 (30) 274 (100), 258 (9), 229 (34), 203 (10).UV ($CHCl_3$) λ_{max} (nm) (log ε) 406 (2.8), 363 (2.9), 346 (3.0), 265 (4.2). HRMS (EI) Calcd. for $C_{17}H_{11}N_3O_2$, 289.0851, Obt.: 289.0852.

REFERENCES

1. Part 18. Jones, G.; Pitman, M.A.; Lunt, E.; Lythgoe, D.J.; Abarca, B.; Ballesteros, R.; Elmasnaouy, M. *Tetrahedron*, **1997**, *53*, 8257-8268.
2. Jones, G.; Sliskovic, D. R. *J. Chem. Soc. Perkin Trans. I*, **1981**, 78-81.
3. Jones, G.; Sliskovic, D. R. *J. Chem. Soc. Perkin Trans. I*, **1982**, 967-971.
4. Abarca, B.; Gómez-Aldaraví, E.; Jones, G. *J. Chem. Res.*, **1984**, (*S*) 140; (*M*), 1430.
5. Abarca, B.; Ballesteros, R.; Gómez-Aldaraví, E.; Jones, G. *J. Chem. Soc. Perkin Trans. I*, **1985**, 1897-1901.
6. Abarca, B.; Ballesteros, R.; Mojarrad, F.; Jones, G.; Mouat, D. J. *J. Chem. Soc. Perkin Trans. I*, **1987**, 1865-1868.
7. Abarca, B.; Ballesteros, R.; Jones, G.; Mojarrad, F. *Tetrahedron Lett*, **1986**, *27*, 3543-3546.
8. Abarca, B.; Mojarrad, F.; Jones, G.; Phillips, C. *Tetrahedron*, **1988**, *44*, 3005-3014.
9. Abarca, B.; Asensio, A.; Ballesteros, R.; Bosch, J.; Jones, G.; Mojarrad, F.; Metni, M. R.; Richardson, C. M. *J. Chem. Research (S)*, **1990**, 9, *(M)*, 0347.
10. Abarca, B.; Ballesteros, R.; Mojarrad, F.; Metni, M. R.; García-Granda, S.; Perez-Carreño, E.; Jones, G. *Tetrahedron* **1991**, *47*, 5277-5286.
11. Abarca, B.; Ballesteros, R.; Metni, M. R.; Jones, G.; Ando, D. J.; Hursthouse, M. B.*Tetrahedron Lett.*, **1991**, *32*, 4977-4980.
12. Abarca, B.; Ballesteros, R.; Metni, M. R.; Jones, G. *Heterocycles* , **1992**, *33*, 203-210.
13. Abarca, B.; Ballesteros, R.; Jones, G. *Heterocycles* , **1993**, *35*, 851-862.
14. Abarca, B.; Ballesteros, R.; Muñoz, A.; Jones, G. *Tetrahedron*, **1996**, *52*, 10519-10524.
15. Frisch, M. J.; Schelegel, H. B.; Gill, P. M. W.; Johnson, B.G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgometry, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioloswski, B. B.; Stefanov, B. B.; Nanayakkara, A.;Challacombe, N.; Peng, C.Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andrés, J. L.; Replogle, E. S.; Gomperts, R.; Martín, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Stewart, J. J. P.; Head-Gordon, M.; González, C.; Pople,J. A. *GAUSSIAN 94*, Revision C.3; Gaussian Inc.: Pittsburg, PA, 1995.
16. Escrivá, E.; Server-Carrió, J.; Lezama, L.; Folgado, J.V.; Pizarro, J.L.; Ballesteros, R.; Abarca, B. *J. Chem. Soc. Dalton Trans.*, **1997**, in press.
17. Linn, W. J.; Webster, O. W.; Benson, R. E.*J. Am. Chem. Soc.* **1963**, *85*, 2032. *Ibid* **1965**, *87*, 3651.

(*Received in UK* 19 *June* 1997; *revised* 9 *July* 1997; *accepted* 10 *July* 1997)