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Triazolopyridines. Part 11.[1] Ylides Derived from 2-Acylmethyltriazolopyridinium Salts.

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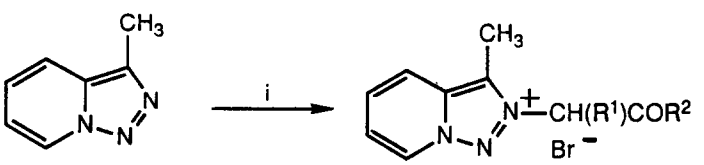
Abstract. *Ylides derived from 2-acylmethyltriazolopyridinium salts (2a) -(2c) react with methyl or ethyl propiolate and with dimethyl acetylenedicarboxylate to give ylides (3a)-(3e) , (6) or (7). In some cases 1.2 adducts are formed, shown to be the novel ylides (8a)-(8d), an X-ray diffraction confirms structure (8a).*

Keywords: Triazolopyridinium ylides; acetylenic esters; Michael addition; X-ray structure; n.m.r. and DIFNOE.

There are a number of reports in the literature of interesting and novel syntheses based on 1,3-dipolar addition to nitrogen ylides. We have reported the preparation of a number of quaternary salts from 1,2,3-triazolo[1,5-a] pyridines, and have established that the general site of alkylation is N2. With a range of quaternary salts (2a)-(2f) from 3-methyltriazolopyridine (1) we hoped, by generating an intermediate ylide, to form new tricyclic compounds, using acetylenic esters as 1,3 dipolarophiles. The results of these experiments are described in this paper.



1

(i) $BrCH(R^1)COR^2$

2a R^1=H, R^2=OMe
2b R^1=H, R^2=OEt
2c R^1=H, R^2=Ph
2d R^1=CH_3, R^2=OMe
2e R^1=CH_3, R^2=OEt
2f R^1=CH_3, R^2=Ph

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Dedicated to Professor Francisco Gaviña

We first established that acetonitrile was a suitable solvent, and that treatment of such solutions with anhydrous potassium carbonate at room temperature generated a yellow colour indicative of ylide formation. Addition of methyl propiolate to the ylides from salts (2a)-(2c) gave adducts. All gave 1:1 adducts and salts (2a) and (2b) also gave 1:2 adducts (salt: methyl propiolate). Structure elucidation is described for the 1:1 adduct from salt (2c) since this salt, for reasons discussed later, gave only a 1:1 adduct. Chromatographic separation of the crude mixture from the reaction gave 3-methyltriazolopyridine (1) and an orange adduct, shown by microanalysis and mass spectral data to have formula $C_{19}H_{17}N_3O_3$ and the ^1H n.m.r. spectrum showed signals at δ2.7(3H,s),3.6(3H,s), 4.25(1H,d,J=14.4Hz), 7.4-7.45(3H,m), 7.45-7.55(2H,m), 7.6(1H,dd,J=7.and 7.1Hz), 7.65-7.75(1H,m), 7.95(1H,d,J=8Hz), 8.05(1H,d,J=14.4Hz), and 8.8(1H,d,J=7Hz). The aromatic region showed the characteristic four proton pattern of a triazolopyridine, but with chemical shifts intermediate between those observed for a triazolopyridine and those (further deshielded) characteristic of salts such as (2a) - (2c). The position of the signal for the methyl group, present at C3 in the original salts (2) was also intermediate between that of compound (1) and those of the salts. The most interesting signals were an AB pair of doublets at δ4.25 and δ8.05, with a large (14.4Hz) coupling. The evidence of n.m.r. shifts and of the orange colour of the adducts suggested an ylide structure, (3c) <---->(4c) rather than the tricyclic product (5). A DIFNOE experiment with irradiation of the C-methyl signal at δ2.7 showed enhancement of the doublet at δ7.45 (H4 in the original triazolopyridine) and of the doublet (J = 14.4Hz) at δ4.25. The ^{13}C n.m.r. spectrum showed the expected 17 signals; here the outstanding features were signals at δ91.29 (CH) and at δ106.2 (quaternary). Both of these,if due to sp^2 hybridized carbon atoms, require considerable shielding, which would be provided in an ylide structure such as (3c)<---- >(4c); we prefer structure (3c) where the charge is localized on C1' because of similarity with the 1:2 adducts, discussed next. A search of the literature revealed that Boekelheide and Nottke prepared a 1:1 adduct from a pyrazolium ylide and methyl propiolate whose structure was very similar to that of compounds (3). The ^1H n.m.r. spectrum was characterized by an AB pair of doublets at δ4.03 and 7.71. We have prepared 1:1 adducts (3a)and (3b) from salts (2a) and (2b) with methyl propiolate, and similar adducts (3d) and (3e) from salts (2a) and (2c) with ethyl propiolate. Finally, in this series, the ylides from salts (2a)-(2c) reacted with dimethyl acetylenedicarboxylate to give adducts (6) or (7). An inspection of the chemical shifts for C5' and for C1' (Table 3) show that in the compound from salt (2c) the shifts are similar to those for compounds (3) leading to formula (6). The shifts for the compounds from salts (2a) and (2b) are quite different, the C1' signal being well downfield. We therefore assign structures (7a) and (7b) to these adducts with the charge substantially on C3'. N.m.r. spectra of ylidic adducts are grouped in Tables 2 and 3.

TABLE 1 Analytical Data and Preparative Yields for Ylides (3), (6), (7) and (8)

Compound	Yield(%)	M.p.(°C)	Found			Required			Formula
			C	H	N	C	H	N	
3a	65	80-82[a]	55 75	5 05	13 7	56 37	5 4	14.1	$2C_{14}H_{15}N_3O_4\ H_2O$
3b	82	95-96[a]	58 3	5 85	13 2	58 3	6 0	13.16	$2C_{15}H_{17}N_3O_4\ CH_3OH$
3c	43	170-173[b]	67 7	5 0	12 0	68 05	5 05	12.5	$C_{19}H_{17}N_3O_3$
3d	63	144-145[c]	59 95	5 35	13 85	59 4	5 6	13 85	$C_{15}H_{17}N_3O_4$
3e	80	210-211[c]	68 4	5 1	11.75	68 75	5 45	12 05	$C_{20}H_{19}N_3O_3$
6	70	188-189[d]	64.45	4 85	10 6	64 1	4 85	10 7	$C_{21}H_{19}N_3O_5$
7a	52	147-148[d]	53 0	4 5	11 25	52.6	5.2	11.5	$C_{16}H_{17}N_3O_6.H_2O$
7b	61	184-185[d]	56 2	5 3	11 3	56.5	5 3	11 6	$C_{17}H_{19}N_3O_6$
8a	16(100)	194-195[a]	57 75	4.95	11 2	57 9	5 1	11 25	$C_{18}H_{19}N_3O_6$
8b	6(100)	153-155[e]	58 95	5 5	10 8	58 9	5 4	10 85	$C_{19}H_{21}N_3O_6$
8c	30(100)	154-155[c]	59 7	5 5	10 4	59 85	5 75	10 45	$C_{20}H_{23}N_3O_6$
8d	(100)	156-158[c]	57 75	5 25	10 55	57 55	5.55	10.6	$2C_{19}H_{21}N_3O_6\ H_2O$

[a] Methanol-dichloromethane [b]Benzene-petrol [c]Ethyl acetate [d]Ethanol [e]Ethanol-hexane

TABLE 2 ^{1}H N.M.R. Data for Ylides (3), (6), (7), and (8)[a]

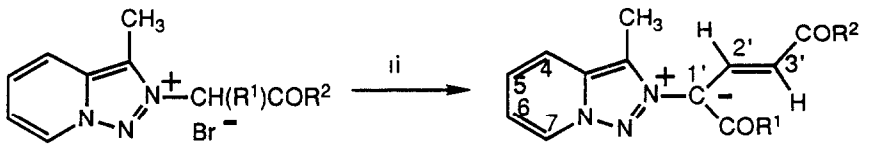
	3-CH_3	H4	H5	H6	H7	H2'	H3'	H4'	H5'	Other	J Values (Hz)
3a	2.63(s)	7 9(d)	< 7.5 - 7 65(m) >		8.9(d)	8.2(d)	4 05(d)	-	-	3.63(3H,s), 3 75(3H,s)	$J_{6,7}$=7 08; $J_{2',3'}$=14.6
3b	2 6(s)	7 9(d)	7.65(t)	7.52(t)	8 7(d)	8.3(d)	4.2(d)	-	-	1.35(3H,t), 3.65(3H,s),4.2(2H,q)	$J_{6,7}$=7 08; $J_{2',3'}$=15 65
3c	2 7(s)	7 95(d)	7 65(t)	7.5(t)	8 8(d)	8 05(d)	4.25(d)	-	-	3 6(3H,s),7.75 (2H,m),7 45(3H,m)	$J_{6,7}$=7; $H_{2'3'}$=14 4
3d	2 6(s)	7 88(d)	7 6(t)	7 48(t)	8.7(d)	8 26(d)	4.1(d)	-	-	1.21(3H,t), 3.73(3H,s), 4 05(2H,q)	$J_{4,5}$=8 9, $J_{6,7}$=6 9, $J_{2',3'}$=13.78
3e	2 68(s)	7 93(d)	7.6(t)	7 5(t)	8 75(d)	8.04(d)	4.24(d)	-	-	1.16(3H,t),4.05(2H, q),7.41-7 44 (3H,m), 7.67-7.71 (2H,m)	$J_{4,5}$=8.79; $J_{6,7}$=6.85; J2',3'=14 4
6‡	2 54(s)	8 26(d)	< 7.5-7.8(m) >		9 1(d)	-	4.15(s)	-	-	6 8-7.2(6H,m), 3 4(3H,s),3 75(3H,s)	
7a‡	2 6(s)	8 4(d)	< 7.7-7 9(m) >		9 3(d)	-	3 7(s)	-	-	3 75(3H,s),3.4(6H,s)	
7b‡	2 49	8.0(m)	< 7.6-7.9(m) >		8 8(m)	-	4 09(s)	-	-	1.23(3H,t),4.15(2H, q),3.57(3H,s), 4 03(3H,s)	
8a*†	2.56(s)	7 96(d)	7.7(t)	7.59(t)	8 8(d)	8 38(s)	-	5 88(d)	5.62(d)	3.2(3H,s),3.69(3H, s),3.72(3H,s)	$J_{4,5}$=9 0; $J_{6,7}$=7.1, $J_{4',5'}$=15 2
8b*	2.55(s)	7 90(d)	7 65(t)	7.5(t)	8 75(d)	8 45(s)	-	6 0(d)	5 6(d)	1 3(3H,t),3.25(3H, s),3 7(3H,s),4.2 (2H,q)	$J_{4,5}$=9.0; $J_{6,7}$=9 0; $J_{4',5'}$=15 1
8c*†	2 55(s)	7 94(d)	7.73(t)	7.55(t)	8.77(d)	8 38(s)	-	5.95(d)	5.51(d)	0 98(3H,t),1.29(3H, t),3 71-3.87(2H,m), 3 71(3H,s),4 14 (2H,q)	$J_{4,5}$=8.8; $J_{6,7}$=6.8; $J_{4',5'}$=15 1
8d*	2 55(s)	7.9(d)	< 7.7-7 5(m) >		8.75(brs)	8 5(brs)	-	6 0(d)	5.65(d)	1.3(3H,t),3.25(3H, s),3 77(3H,s),4.2 (2H,q)	$J_{4,5}$=8 8, $J_{4',5'}$=14

[a] Numbering is given on the formulae Solvent is $CDCl_3$ unless otherwise specified *At -50°C unless otherwise specified ‡ DMSO-d_6 † CD_2Cl_2.

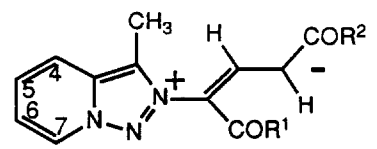
TABLE 3 ^{13}C N.M.R. Shifts and Off-resonance Multiplicities for Ylides (3), (6), (7) and (8)[a]

	C3	C3a	C4	C5	C6	C7	C1'	C2'	C3'	C4'	C5'	Other
3a	134 92(s)	133 4(s)	118.95(d)	125 39(d)	121 59(d)	127.63(d)	90 96(s)	140.57(d)	85.86(d)			9 17(q),50.3(q),50 55(q),164.04 (s),169.85(s)
3b	134 91(s)	133 49(s)	118.86(d)	125 39(d)	121 35(d)	127 46(d)	91.38(s)	140 6(s)	85.56(d)			9 22(q),15.01(q),50 32(q),59.13 (t),163.79(s),169 9(s)
3c	134 75(s)	133 37(s)	118.85(d)	125 29(d)	121 31(d)	127 29(d)	106.2(s)	142 34(d)	91.29(d)			8.78(q),50.24(q),128.19(d), 129.04(d),140.79(s),169 09(s), 179.84(s)
3d	134 92(s)	133.43(s)	118.93(d)	125.4(d)	121 5(d)	127 59(d)	90 87(s)	140.47(d)	86 33(d)			9.21(q),14 77(q),50 59(q),58.6 (t),164.04(s),169.49(s)
3e	135 02(s)	133.56(s)	119 05(d)	125 48(d)	121.31(d)	127.34(d)	106 43(s)	142.67(d)	91 8(d)			9 13(q),14 57(q),59 0(t),128 14 (d),128 46(d),129 32(d),140 68 (s),142 67(s),169 0(s),180 15(s)
6 *	135 24(s)	133 4(s)	119.79(d)	125 81(d)	122.51(d)	127 61(d)	100.76(s)	141 32(s)	91 44(d)			8.85(q),49 87(q),51 43(q),128 31 (d),126.66(d),166 51(s),167 63 (s),177 29(s)
7a*	135,76(s)	133.7(s)	120 3(d)	126 3(d)	122.81(d)	128.11(d)	147.9(s)	149 2(s)	84 53(d)			8.66(q),49 73(q),50.04(q),51 86 (q),160.7(s),166.64(s),167 9(s)
7b*	135,14	133.33	119.95	125.95	122 42	128 0	147 8(s)	148.92	79.06			8.3(q),14 6(q),49 33(q),51 35,(q) ,57 44(t),160 3(s),166 21(s),167 .47(s)
8a	134 9(s)	133 75(s)	119.03(d)	115 52(d)	121 6(d)	127 85(d)	96 02(s)	140.0(s)	95 42(s)	108 81(d)		9 3(q),50 43(q),50 83(q),50.78 (q),164 79(s),168 67(s),169 04 (s)
8b	134 91(s)	133 69(s)	119.00(d)	125 5(d)	121 58(d)	127.85(d)	96 56(s)	140 02(d)	95 15(s)	139 46(d)	108.52(d)	9 31(q),14 77(q),50 48(q),50 78 (q),60.19(t),164.41(s),165 77 (s),167.05(s)
8c	134 85(s)	132.73(s)	118.98(d)	125.5(d)	121.62(d)	127 86(d)	95 87(s)	139.87(d)	95 87(s)	139.31(d)	109.34(d)	9.33(q),14.44(q),14.70(q),51 40 (q),58.95(t),59 40(t),164 78(s), 168.4(s),168.65(s)
8d	134 88(s)	132 73(s)	119 00(d)	125 5(d)	121 54(d)	127.78(d)	95.92(s)	139 96(d)	95.79(s)	139 47(d)	108 73(d)	9.33(q),14.71(q),50.43(q),51 41 (q),59.44(t),164 82(s),163.37 (s),169.08(s)

[a] Solvent is $CDCl_3$ unless otherwise stated *DMSO-d_6

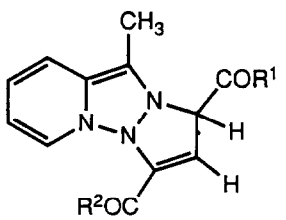


3a $R^1=R^2=OMe$
3b $R^1=OEt$, $R^2=OMe$
3c $R^1=Ph$, $R^2=OMe$
3d $R^1=OMe$, $R^2=OEt$
3e $R^1=Ph$, $R^2=OEt$

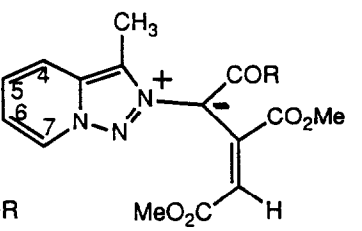


4c $R^1=Ph$, $R^2=OMe$

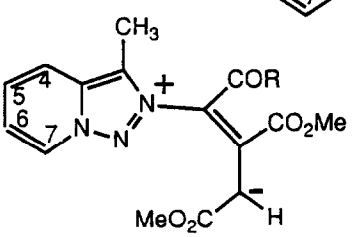
(ii) $HC\equiv C\text{-}COR^2$



5 $R^1=Ph$, $R^2=OMe$



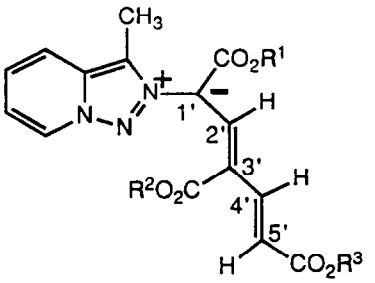
6, R=Ph



7a, R=OMe
7b, R=OEt

From the reaction between propiolate esters and the ylides from salts (2a) and (2b) a second series of adducts was obtained, in which one molecule of ylide had combined with two of acetylenic ester. The adducts, shown to have general structure (8), were orange, and showed fluxional behaviour in their n.m.r. spectra, the sharpest peaks being observed at -50°C. The general fluxional behaviour is still being studied, but the low temperature ^1H n.m.r. spectrum of compound (8a) (the adduct from salt (2a) and methyl propiolate) showed the four triazolopyridine protons, three methyl ester absorptions at δ3.69, 3.67, and 3.2, a singlet (1H) at δ8.39, and an AB pair of doublets at δ5.62 and 5.85 (J=14Hz). The formulae (8a)-(8c) were confirmed by an X-ray analysis of compound (8a) which gave the structure shown in Figure 1. This X-ray structure shows very clearly the ylide carbanionic carbon next to the triazolopyridinium ring, and the orientation of the side chain relative to the heterocyclic ring, with the five coplanar side chain carbon atoms. The angle between the planes of ring and side chain is 93.4°. To confirm that adducts (8) could be derived from adducts (3) we have reacted solutions of adducts (3a), (3b), and (3d) in acetonitrile with equimolar amounts of propiolate ester at room temperature, giving

virtually quantitative yields of the corresponding 1:2 adducts. The preparation of a new adduct (8d), by reaction between ylide (3d) and methyl propiolate allowed the identification of the single upfield ester signal in the 1:2 adducts (δ3.2 as against δ3.7 for the "normal" signal) as due to the terminal ester group on C5'. Inspection of a model and of the X-ray structure of compound (8a) indicate that this shielding is caused by the placing of the terminal ester above the plane of the heteroaromatic ring, as is the upfield shift of H4'.



8a $R^1=R^2=R^3=Me$

8b $R^1=Et, R^2=R^3=Me$

8c $R^1=Me, R^2=R^3=Et$

8d $R^1=R^3=Me, R^2=Et$

The phenacyltriazolopyridinium salt (2c) did not form 1:2 adducts, nor could the ylides (3c) or (3e) be induced to react with a further molecule of propiolate. An explanation of this lack of reactivity appears on study of the ^{13}C n.m.r. shifts of the ylides (3) (Table 3). The reactive ylides show shifts for C1' in the narrow range δ90.87 to 91.38 and for C3' in the range δ85.56 to 86.33. In contrast the unreactive ylides show shifts for C1' at δ106.2 and 106.43 and for C3' at δ91.3 and 91.8. The decreased degree of shielding in the signals for the unreactive ylides (3c) and (3e) can be attributed to the greater degree of delocalisation of negative charge on to the carbonyl group in the benzoyl derivatives, and a smaller but still consistent difference is shown in the chemical shift of the carbonyl carbon atoms measured as Δδ which is the difference between salt (2) and ylide (3) in each case. Thus Δδ for reactive ylides is between 0.2 and 2.49 ppm, while that for the unreactive ylides is 8.21 and 8.6 ppm, indicating a considerably larger transfer of charge in the latter. Our further studies in this area are concerned with solvent effects on ylide formation, and with the chemical transformations of the ylides.

X-ray Structure Determination.

The ylide (8a) gave an orange crystal, $C_{18}H_{19}N_3O_6$, 0.23 x 0.13 x 0.10 mm size. M_r = 372.36, triclinic, space group P-1, a = 9.343(3), b = 9.574(4), c = 11.161(5) Å, α = 87.12(4), β = 79.65(3), γ = 66.09(4)°, V= 900. (1) $Å^3$, Z = 2, D_x = 1.37 Mg/m^3. MoKα radiation used with a graphite crystal monochromator on a Enraf-Nonius CAD4 single crystal diffractometer, λ = 0.7103 Å, μ(MoKα) = 0.98 cm^{-1}, F(000) = 390, T = 293K. Unit cell dimensions from the angular settings of 25 reflections with 5° < θ < 20°. Space group P-1 from the systematic absences and structure determination. 6297 reflections measured, hkl range (-11, -11, -13) to (10, 21, 25), theta limits (0° < θ < 25°). ω-2θ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. Intensity checked by monitoring three standard reflections every 60 minutes. Final drift correction factors between 0.98

and 1.00. On all reflections profile analysis performed[4,5]; semiempirical absorption correction was applied, using ψ scans[6], μ(MoKα) = 0.98 cm^{-1} (correction factors in the range 0.88 to 1.00). Symmetry equivalent reflections averaged, $R_{int}=\Sigma(I-\langle I\rangle)/\Sigma I$ = 0.030, resulting in 3150 unique reflections of which only 1323 were observed with $I>3\sigma(I)$. Lorentz and polarization corrections applied and the data reduced to $|F_o|$-values. Structure solved by Direct Methods, using the program SHELX86[7].

Isotropic least-squares refinement, using SHELX76[8], converged to R = 0.17. At this stage additional empirical absorption correction was applied[9]. Maximum and minimum absorption correction factors, respectively, 1.35 and 0.60. Further anisotropic refinements followed by a Difference Fourier synthesis allowed the location of all the hydrogen atoms. During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms were refined. All hydrogen were refined isotropically. The final conventional agreement factors were R = 0.057 and R_w = 0.059 for the 1323 'observed' reflections and 252 variables. The function minimized was $\Sigma w(F_o-F_c)^2$, $w=1/(\sigma^2(F_o) + 0.00080\ F_o^2)$ with $\sigma(F_o)$ from counting statistics. The maximum shift over error ratio in the last full matrix least-squares cycle was less than 0.002. The final Difference Fourier map showed no peaks higher than 0.25 e/Å^3 and deeper than -0.26 e/Å^3. Atomic scattering factors were taken from the International tables for X-ray Crystallography (1974)[10]. The plot was made with PLUTO program[11] Geometrical calculations were made with PARST[12]. Distances and angles are normal. All supplementary crystallographic data are available on request from the Cambridge Crystallographic Data Centre.[13]

The structure is shown in Figure 1 (see above for comments).

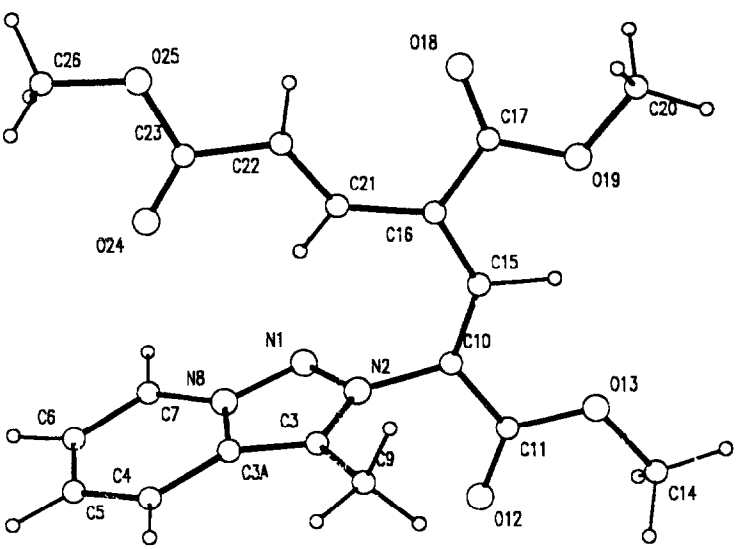


Figure 1. X-Ray diffraction structure of ylide (8a)

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EXPERIMENTAL

M.p.s were performed on a hot stage microscope and are uncorrected. Chromatographic separations were on alumina (activity 4) or Chromatotron plates (Merck Silica PF_{254}) with mixtures of ethyl acetate and petroleum ether (60-80°C b.p.). N.m.r. solvents were $CDCl_3$ or d_6-DMSO and uv/visible spectra determined for ethanol solutions. I.r. spectra were recorded for KBr discs.

General Procedure for Preparation of Ylides (3), (6), and (7) - A solution of the appropriate salt (2) (0.004 moles) in anhydrous acetonitrile (30 ml) was vigorously stirred at ambient temperature with anhydrous potassium carbonate (0.6 g). During three hours a yellow paste formed, then the propiolate ester (0.004 moles) was added, and stirring continued (8 h). The mixture was filtered, the filtrate evaporated under reduced pressure to give an orange gum, purified by chromatography. Analytical data and yields of ylides are given in Table 1, ^1H n.m.r. spectral data in Table 2, ^{13}C n.m.r. data in Table 3. In three cases varying amounts of the ylide (8) were also isolated (see below).

By using dimethyl acetylenedicarboxylate instead of propiolate esters, ylides (6) and (7) were obtained, in generally higher yield because of the absence of any 1:2 adducts. In most cases a small amount of 3-methyltriazolopyridine was also isolated.

General Procedure for Conversion of Ylides (3) to Ylides (8). - A solution of the ylide (3) and an equimolar amount of the appropriate propiolate in anhydrous acetonitrile was stirred at ambient temperature (24 h), then evaporated to give almost pure ylide (8) in virtually quantitative yield. Yields obtained by this route are given in Table (1) thus (90).

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