Tetrahedron Letters No. 6, pp 413 - 416, 1975. Pergamon Press. Printed in Great Britain.

1,3-DIPOLAR CYCLOADDITION OF BENZIMIDAZOLIUM YLIDES WITH DIMETHYL ACETYLENE-DICARBOXYLATE - A RE-INVESTIGATION

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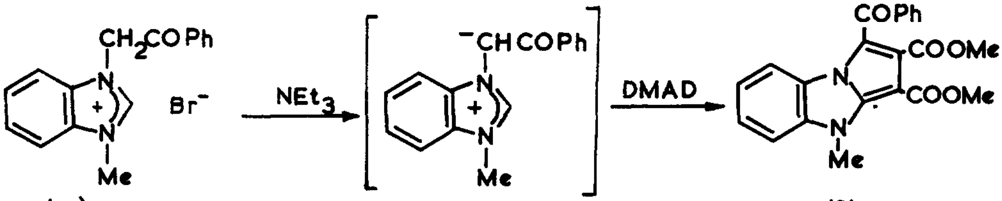
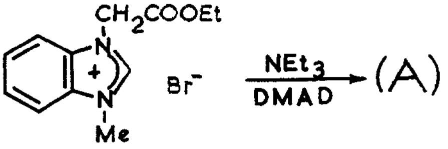
(**Received in UK 16 December 1974; accepted for publication 6 January 1975**)

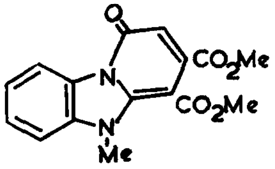
1-Methyl-3-phenacylbenzimidazolium bromide (1) yields the corresponding ylide (2) with a base (in situ) which reacts normally with dimethyl acetylenedicarboxylate (DMAD) to give the pyrrolobenzimidazole (3). However the corresponding 1-methyl-3-(ethoxycarbonylmethyl) benzimidazolium bromide (4) under the same conditions gives rise to a stable cycloaddition product (A) m.p. 255-7° involving loss of a molecule of ethanol. Controversy over the structure of this product exists in that Japanese workers[1] favoured the pyridobenzimidazole structure (5) (on the grounds of appropriate u.v., m.s., n.m.r., i.r.[2] and analytical data) while a Roumanian group[3] preferred the remarkable structure (6) (in particular since the 2-deuterio derivative of (4) gave the cycloaddition product still bearing deuterium - this



(1) (2) (3)



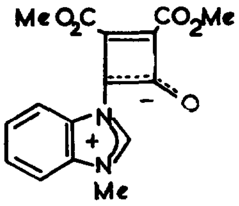
(4)



(5)

according to

Ogura and Kikuchi[1]



(6)

according to

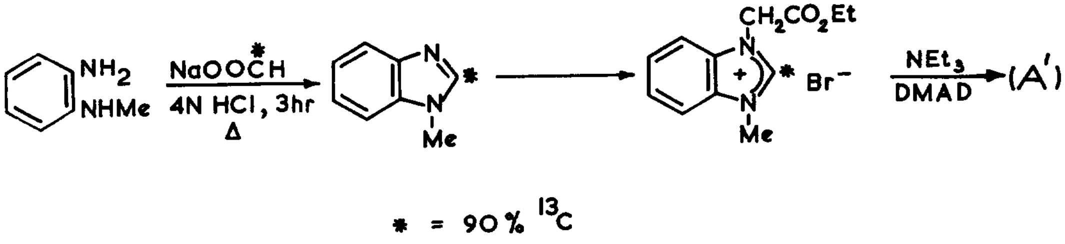
Zugravescu et al[3]

evidence does not eliminate a concerted rearrangement of D however).

Since both structures are equivocal the product was further examined. The ^{13}C n.m.r. spectrum (Table 1) immediately ruled out a benzimidazole-type structure in that no low-field absorption characteristic of the C-2 of a benzimidazole (e.g. benzimidazole-141.5 ppm; 1-methylbenzimidazole-143.5 ppm; (4)-143.3 ppm) is observed. Furthermore when the 2-position of (4) was labelled with ^{13}C, prepared as shown in Scheme 1, the cycloaddition product (A$'$) contained a CH group labelled (123.79 ppm)† with long range coupling to the two ester CO resonances (2.6 and 4.8 Hz) and to one other quaternary carbon (120.48 ppm, 5.8 Hz). A new perspective was clearly necessary.

Table 1. The ^{13}C n.m.r. spectrum of compound A in $MeSO_3H$

Me's (ppm)	Aromatics (ppm) (multiplicity in off-resonance spectrum)	CO's (ppm)
32.98, 54.48, 56.48	115.07(s) 116.98(d) 119.13(d) 120.48(s) 123.18(s) 123.81(s+d) 126.28(s) 129.42(d) 130.39(d)	156.72, 165.22 169.76



Scheme 1

The published and above evidence, particularly the high-field absorption of most of the sp^2 carbons suggested that compound (A) was a pyrrole derivative, and a reasonable structure (8) that accommodates all the evidence is shown in Scheme 2 together with a rationale for its

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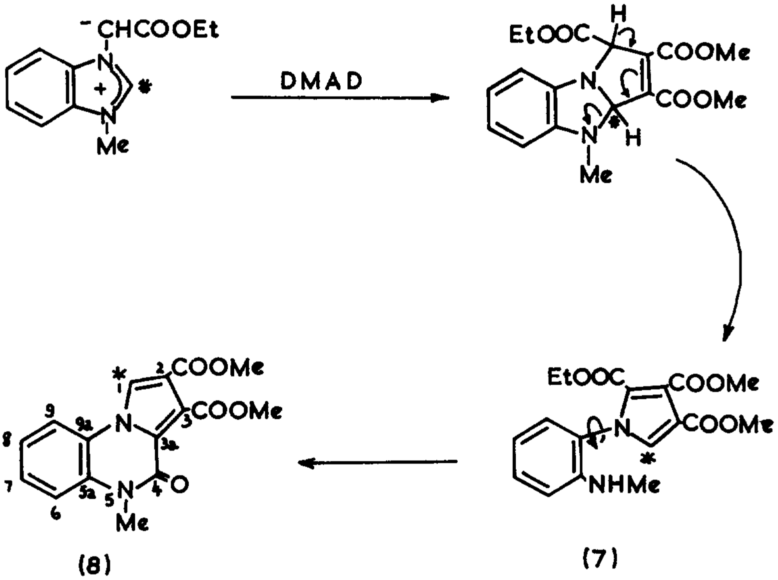
† one-bond C-C coupling was not discernable since the carbon to which coupling could occur was superimposed by the labelled carbon absorption.

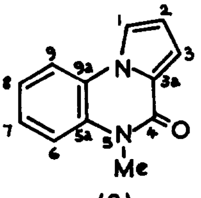
formation. Thus a 1,3-dipolar cycloaddition is followed by a tautomeric shift of an acidic



Scheme 2

proton resulting in the pyrrole (7) which can cyclise to the pyrroloquinoxaline (8).

Further evidence in support of this structure derives from a comparison with the known pyrrolo[1,2-a]quinoxaline (9)[4]. The close similarity of the respective u.v. spectra (Table 2)



(9)

and the ^{13}C n.m.r. spectra (Table 3) together with the i.r. spectral resemblance gives weight the pyrroloquinoxaline structure (8). Attempts to decarboxylate the acid derived from (8) unfortunately caused tar formation, giving no (9).

Table 2. U.V. spectra of the pyrrole[1,2-a]quinoxalines (8) and (9) in chloroform

Cpd.	λ_{max} nm (ε)						
(8)	250(30060)	263inf(14931)	-	-	304sh(8250)	315(12180	329(10020)
(9)	251(10570)	261sh(8210)	280(2740)	293sh(3680)	303inf(5190)	315(8400)	329(7080)

Table 3. Assignment of ^{13}C n.m.r. absorptions to (8) and (9)

Carbon	(8)	(9)
	ppm	ppm
1	123.81	115.81
2	123.18*	115.81
3	120.48	115.81
3a	115.07	115.81
5a,9a	126.28,123.81*	126.25, 124.68
6,9	116.98, 119.13	116.96, 118.75
7,8	130.39, 129.42	128.44, 127.88
N-Me	32.98	32.33
CO-N	156.72	154.98
2-COOMe	169.76	-
3-COOMe	165.22	-
COOMe's	54.48, 56.48	-

References

1. H. Ogura and K. Kikuchi, J. Org. Chem. 1972, 37, 2679.
2. I.r. (KBr) 1740, 1710 (COOMe), 1655cm^{-1}(CO); u.v. λ_{max}(EtOH) 243(log ε 4.23), 314(3.71), 328 nm (3.62); n.m.r.δ($CDCl_3$) 3.64 (s, NMe) 3.91, 4.04 (s, COOMe's), 7.42(s) 7.50(m,Ar H's) 8.21(s) (this last resonance was described as a doublet by Ogura and Kikuchi); m.s. 314 (M^+).
3. I. Zugravescu, J. Herdan and I. Druta, Rev. Roumaine de Chim., 1974, 19, 649.
4. G. W. H. Cheeseman and B. Tuck, J. Chem. Soc. (C), 1966, 852.