

An Unprecedented Reaction of Diethyl Azodicarboxylate with Imidazolium Ylides

R. Alan Jones,<sup>a</sup> José Sepúlveda Arques,<sup>b\*</sup> Elena Zaballos Garcia,<sup>b</sup> Paul A. Bates,<sup>c</sup> and Michael B. Hursthouse<sup>c</sup>

<sup>a</sup> School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

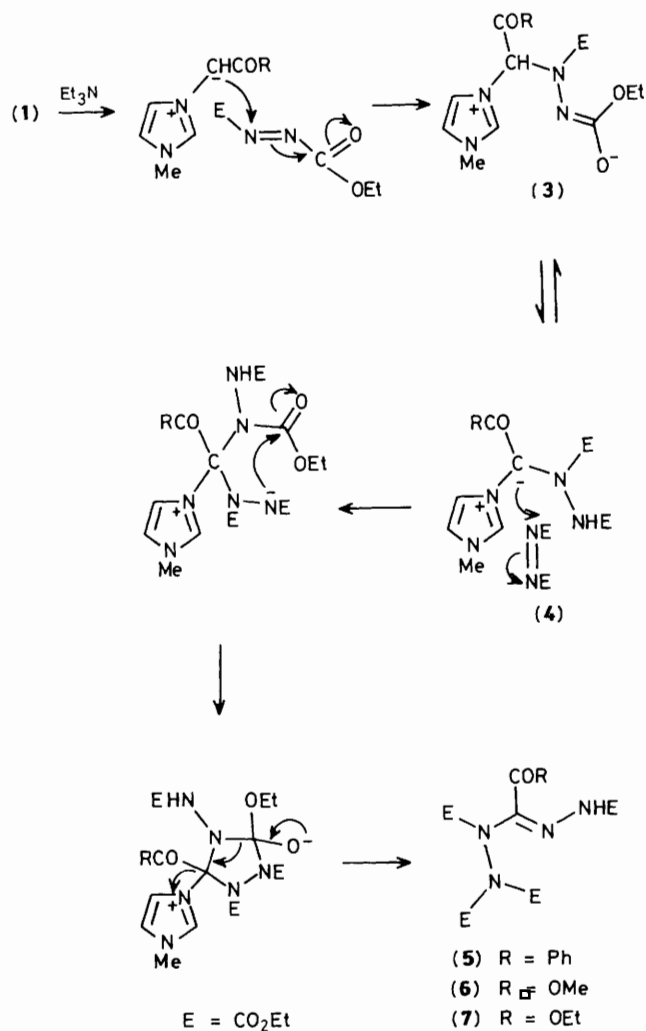
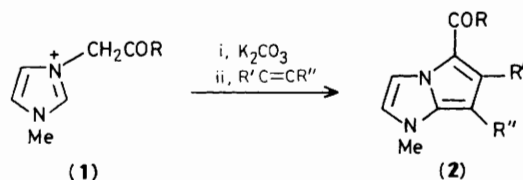
<sup>b</sup> Facultad de Farmacia, Universidad de Valencia, Valencia 46010, Spain

<sup>c</sup> Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, U.K.

3-Phenacyl- and 3-alkoxycarbonylmethyl-1-methylimidazolium bromides react with two molecules of diethyl azodicarboxylate in the presence of triethylamine with the extrusion of the imidazole ring and the concomitant migration of an ethoxycarbonyl group to yield 3-substituted tetraethyl 1,2,4,5-tetra-azapent-3-ene-1,1,2,5-tetracarboxylates (5), the structure of which has been confirmed by X-ray crystallography, (6), and (7).

Diethyl azodicarboxylate (DEAD) has been reported to form cycloadducts with a range of 1,3-dipolar compounds<sup>1</sup> and, in view of the difference in reactivity of DEAD and of dimethyl acetylenedicarboxylate (DMAD) with vinylazoles,<sup>2</sup> it was of interest to compare the known reaction of acetylenic esters with imidazolium ylides,<sup>3</sup> (1) → (2), with the corresponding reaction of the ylides with DEAD.

The imidazolium ylides were generated *in situ* in acetonitrile by the addition of triethylamine to the appropriate imidazolium bromides (1; R = Ph, OMe, and OEt). Subsequent reaction of the ylides with DEAD at 20 °C yielded a crystalline product (5)† m.p. 89–90 °C (decomp.) from (1; R = Ph) and (6)† and (7),† as oils, from (1; R = OMe and OEt, respectively), the spectral properties of which indicated the



† Satisfactory elemental analyses (C, H, N) were obtained for (5), (6), and (7). Spectroscopic data: (5)  $M^+$  466;  $\nu_{\max}$  (CHCl<sub>3</sub>) 3370, 1770sh, and 1740 cm<sup>-1</sup>;  $\delta_H$  (CDCl<sub>3</sub>) 1.37 (t, 9H), 1.23 (t, 3H), 4.17 (q, 2H), 4.38 (q, 6H), 7.40–7.45 (m, 3H), 8.22 (br d, 2H), and 8.70 (br s, 1H);  $\delta_C$  (CDCl<sub>3</sub>) 14.2 (q, 3 × C), 14.4 (q), 61.9 (t), 64.2 (t), 64.4 (t, 2 × C), 128.8 (d), 128.9 (d), 134.2 (d), 135.6 (s), 138.6 (br s), 151.1 (s), 153.2 (s), and 185.1 (s). (6),  $M^+$  420;  $\nu_{\max}$  (CHCl<sub>3</sub>) 3310, 1760sh, 1740, and 1720sh cm<sup>-1</sup>;  $\delta_H$  (CDCl<sub>3</sub>) 1.27 (t, 3H), 1.29 (t, 3H), 1.32 (t, 6H), 3.89 (s, 3H), 4.24 (q, 2H), 4.27 (q, 2H), 4.33 (q, 4H), and 10.6 (br s, 1H);  $\delta_C$  (CDCl<sub>3</sub>) 14.1 (q, 2 × C), 14.3 (q), 14.4 (q), 53.0 (q), 62.4 (t), 63.3 (t), 64.2 (t, 2 × C), 129.3 (br s), 151.2 (s), 152.5 (s), and 159.4 (s). (7),  $\nu_{\max}$  (Nujol) 3300, 1750br, and 1720sh cm<sup>-1</sup>;  $\delta_H$  (CDCl<sub>3</sub>) 1.20–1.40 (overlapping t, 15H), 4.10–4.50 (overlapping q, 10H), and 10.67 (br s, 1H);  $\delta_C$  (CDCl<sub>3</sub>) 13.9 (q), 14.1 (q, 2 × C), 14.3 (q), 14.4 (q), 62.4 (t), 62.5 (t), 63.6 (t), 64.1 (t, 2 × C), 120.4 (br s), 151.2 (s), 152.5 (s), and 158.9 (s).

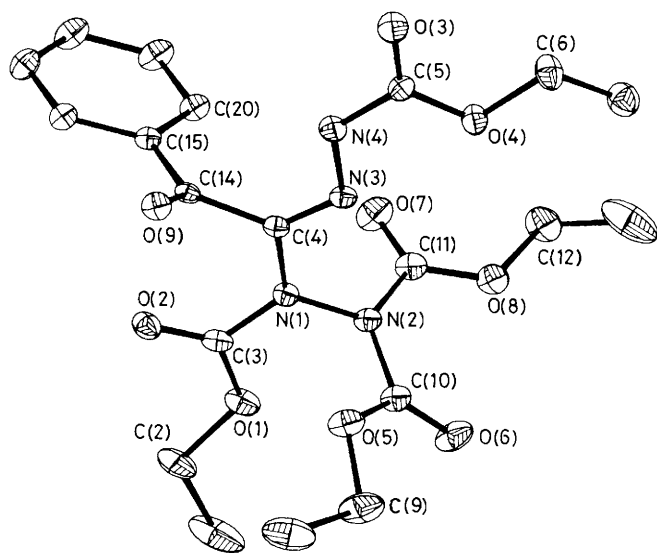
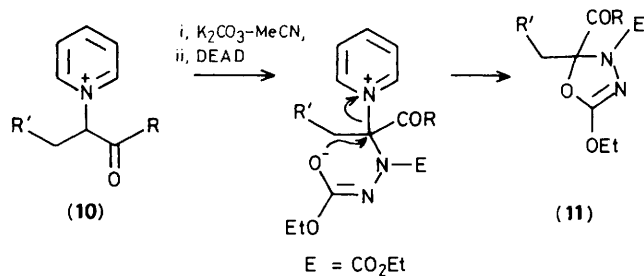
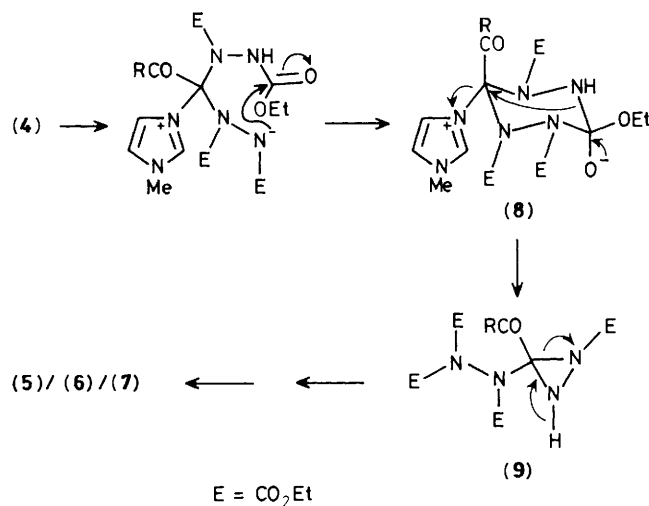


Figure 1. The molecular structure of compound (5) showing atomic numbering.



presence of four ethyl ester groups and the absence of the imidazole ring in both products.<sup>†</sup> The spectral data also confirmed the retention of the benzoyl group in (5) and of the methoxycarbonyl group in (6). 1,2-Bis(ethoxycarbonyl)hydrazine<sup>4</sup> was a by-product of all of the reactions.

X-Ray crystallographic analysis established unequivocally the structure of (5) (Figure 1),<sup>3‡</sup> confirming the loss of the imidazole ring. Analogous structures proposed for (6) and (7) are based upon the close similarities in the spectral data for (5), (6), and (7).

The formation of (5), (6), and (7) can be rationalised in terms of an initial nucleophilic attack by the imidazolium ylide on DEAD, (1) → (3). Under the basic conditions a prototropic shift regenerates a ylide (4), which reacts with a second molecule of DEAD. Intramolecular nucleophilic attack by the amidic anion upon the ester group leads to the transfer of the ethoxycarbonyl group from one hydrazino group to the other with concomitant extrusion of the imidazole ring, (4) → (5)/(6)/(7). An alternative intramolecular rearrangement *via* a six-membered ring intermediate would require the subsequent formation of a three-membered ring for the extrusion of the imidazole system, (4) → (8) → (9) → (5)/(6)/(7), and is improbable. The closest analogy to the observed reaction sequence is the formation of 5-acyl-1,3,4-oxadiazolines<sup>5</sup> from the 1:1 reaction of pyridinium ylides with DEAD, (10) → (11).

We gratefully acknowledge a grant (to J. S. A.) from C.A.I.C.Y.T. and the S.E.R.C. for provision of the X-ray systems and for financial support.

Received, 1st August 1986; Com. 1101

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‡ Crystal data for (5): C<sub>20</sub>H<sub>26</sub>N<sub>4</sub>O<sub>9</sub>, *M* = 466.44, triclinic, space group *P* $\bar{1}$ , *a* = 8.369(3), *b* = 10.151(4), *c* = 14.485(5) Å,  $\alpha$  = 98.61(3),  $\beta$  = 87.15(3),  $\gamma$  = 74.76(3)°, *U* = 1169 Å<sup>3</sup>, *Z* = 2, *F*(000) = 492, Cu-K $\alpha$  radiation,  $\lambda$  = 1.5418 Å,  $\mu$  = 0.67 cm<sup>-1</sup>; *D*<sub>c</sub> = 1.323 g cm<sup>-3</sup>, 4115 independent reflections, 2332 with *I* > 1.5  $\sigma$ (*I*) used, direct methods, SHELXS-84, *R* = 0.066, *R*<sub>w</sub> = 0.065. Non-hydrogen atoms refined anisotropically, all hydrogen atoms placed in calculated positions (C–H = 0.96 Å, *V* = 0.10 Å<sup>3</sup>). Phenyl ring refined as a rigid group (C–C = 1.395 Å). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.