An Unusual Furan Cycloadduct from *N*-Phenylbetaine and Dimethyl Acetylenedicarboxylate. The Crystal and Molecular Structure of Dimethyl 5-(3-*N*-Phenyliminoprop-1-enyl)furan-2,3-dicarboxylate

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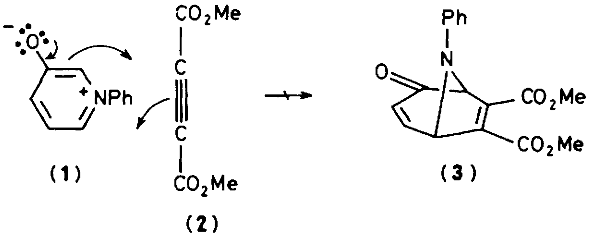
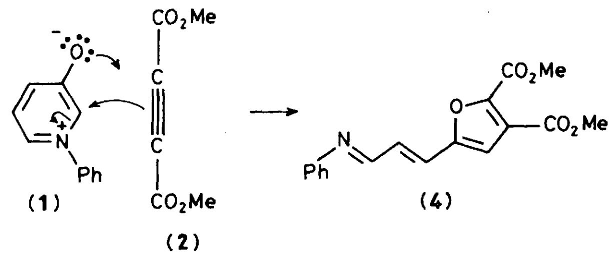
Cycloaddition of dimethyl acetylenedicarboxylate with betaines such as 1-phenyl-3-oxidopyridinium does not yield the expected bicyclic product; instead, addition occurs at the exocyclic oxygen atom and ring carbon 2 of the betaine, with concomitant opening of the pyridine ring.

The cycloaddition of substituted acetylenes with betaines such as 1-phenyl-3-oxidopyridinium (**1**) normally yields bicyclic products[1] formed by the addition of the acetylene at the 2- and 6-positions in the pyridine ring. We have investigated[2] several of these reactions with a variety of mono- and di-substituted acetylenes using various polar solvents. Cycloaddition to form the expected bicyclic products[1] was found to occur with all the acetylenes studied with the exception of reactions involving dimethyl acetylenedicarboxylate (**2**) (DMAD). Thus, the reaction of betaine (**1**) with (**2**) in dry acetonitrile at 30 °C gave a yellow crystalline material as the major product. Chromatography on neutral aluminium oxide followed by recrystallization from diethyl ether gave yellow crystals [m.p. 112—113 °C; i.r.(Nujol) 1 720, 1 605, 1 580, and 1 500 cm^{-1}; u.v. (ethanol) λ_{max} (log ϵ) 208 (4.15), 227 (4.16), 325 (4.31), and 353 nm (4.22); *m/z*, 313 (12%); n.m.r. (CDCl$_3$) δ 3.83 (s, 3H), 3.90 (s, 3H), 6.83 (d, 1H), 6.91 (s, 1H), 6.96 (m, 1H), 7.25 (m, 5H), and 8.2 (d, 1H)]. Elemental analyses were consistent with the formula $C_{17}H_{15}NO_5$.





The above n.m.r. data are not consistent with a bicyclic system[3] as shown by (**3**). Our *X*-ray analysis of the yellow crystalline reaction product unequivocally establishes the structure as shown in (**4**) and in Figure 1 (all protons were clearly located) revealing that in the special case of reaction of betaines such as (**1**) with DMAD (**2**), cycloaddition does not take place at the 2- and 6-positions of the betaine. Instead, addition occurs at the exocyclic oxygen atom and ring carbon 2, with concomitant opening of the pyridine ring. The observed n.m.r. spectrum is of course fully compatible with this structure.

Previous theoretical studies have shown that the preferred orientation of addition of 2π-addends would be across the oxygen and the 2-position of betaines such as (**1**) if some

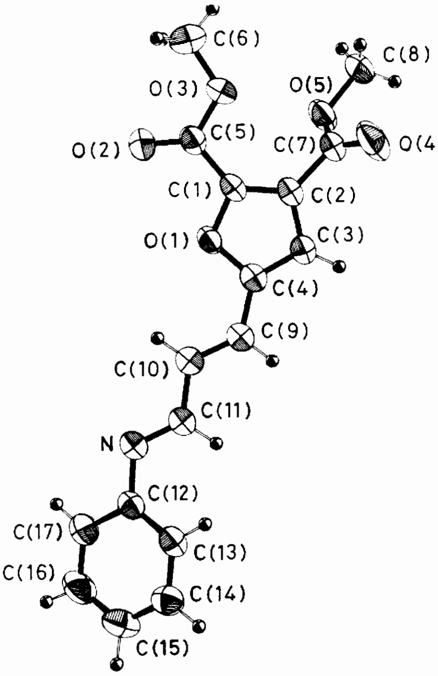


Figure 1. A view of the reaction product (**4**), showing the crystallographic numbering scheme.

stable adduct could result.[4] The reaction described here is obviously an example of this.

Crystal data for (**4**): $C_{17}H_{15}NO_5$, $M_r = 313.3$, monoclinic, $a = 8.578(4)$, $b = 20.007(3)$, $c = 9.448(2)$ Å, $\beta = 102.97(2)°$, $U = 1580.0$ Å^3, $D_c = 1.32$ g cm^{-3}, $Z = 4$, $F(000) = 656$, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) $= 0.91$ cm^{-1}. Space group $P2_1/a$ (alternative setting of C_{2h}^5, No. 14) from systematic absences $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$, 2 788 observed reflections, $R = 0.038$.

Intensity data were collected to a maximum θ of 25° on an Enraf Nonius CAD-4 diffractometer. The structure was solved using Multan-80[5] and refined[6] by least-squares calculations.†

In the solid state (**4**) adopts a conformation with the olefinic side chain maximally extended. The bond lengths are in accord with an essentially localized double bond system with double bond lengths C(1)–C(2) 1.358(2), C(3)–C(4) 1.359(2), C(9)–C(10) 1.328(2), and C(11)–N 1.276(2) Å, and single bond lengths C(2)–C(3) 1.412(2), C(4)–C(9) 1.437(2), and C(10)–C(11) 1.445(2) Å. The remaining details of bond lengths are unexceptional; some (mean) values are C–C(phenyl) 1.376(2), C=O 1.195(2), C(sp^2)–O 1.347(2), C(sp^3)–O 1.446(2), and C(sp^2)–N 1.276(2) Å.

The molecule shows considerable intramolecular overcrowding which is relieved by angle bending and out-of-plane deformations. The plane of one carboxymethyl group [C(2), C(7), O(4), O(5)] is rotated 54.9° out of the furan-ring plane and the other [C(1), C(5), O(2), O(3)] by 9.6°. These rotations are accompanied by marked angle distortions [C(5)–C(1)–C(2) 134.0(1) and C(1)–C(2)–C(7) 129.0(1)°] and out-of-plane displacements [C(5) is 0.143 Å from the furan-ring plane]. The plane through exocyclic atoms C(4), C(9), C(10), C(11), C(12), and N is only rotated 1.5° out of the furan-ring plane, but there are significant angle enlargements to accommodate 1,3 H • • • H interactions between the C(11)-H and C(13)-H atoms and N–C(12)–C(13) [123.6(1)°] is 5.8° larger than N–C(12)–C(17) [117.8(1)°].

We have also found that addition products with a ratio of 1 : 2 and 1 : 4 betaine to dimethylacetylene dicarboxylate can be prepared.[2]

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.