# Unusual Incorporation of the Cyano Group of t-Butylcyanoketen into a Cycloadduct. *X*-Ray Structure of the Pyrimido[1,6-*e*][1,3,5]dioxazine Formed

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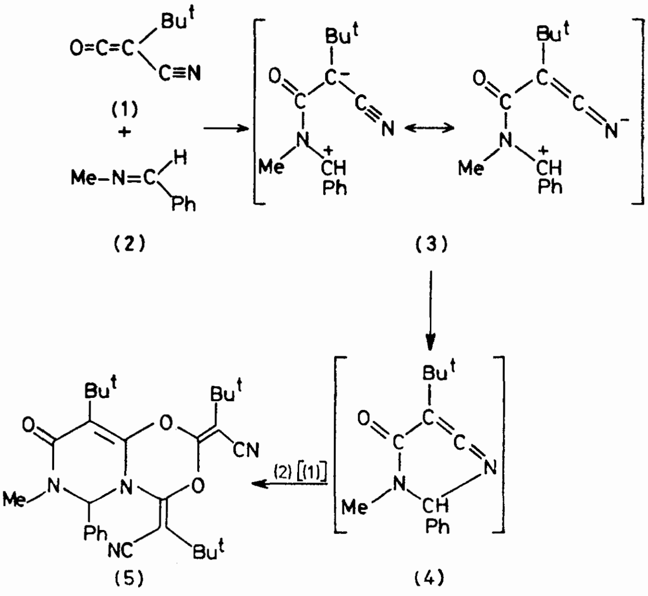
*Summary* The cycloaddition of t-butylcyanoketen (**1**) and *N*-methylbenzylideneamine affords the binuclear heterocycle (**5**), which seems to result from the interception of the intermediate highly strained ketenimine (**4**) by an excess of (**1**); the crystal and molecular structure of (**5**) has been determined.

IN the cycloaddition chemistry of ketens, t-butylcyanoketen (**1**) is increasingly studied because of its ready accessibility and high reactivity.[1] While there is some controversy on the question of concerted *vs.* zwitterionic mechanisms in the reaction of (**1**) with olefins,[2] the isolation of 2:1 adducts in the cycloadditions of (**1**) with azomethines clearly demonstrates the intermediacy of a dipole (**3**).[3] A 3:1 adduct (m.p. 131—132 °C) is also formed in very low yield (3%) in the reaction with (**2**) indicating an irregularity in the reaction course. Interestingly, the yield of the 3:1 adduct is increased to 45% if the azomethine (**2**) is added to an excess of (**1**) in the presence of a catalytic amount of triphenylphosphine. As spectroscopic data failed to give conclusive evidence as to the structure of the 3:1 adduct, an *X*-ray structural investigation was carried out.



Crystals are monoclinic, space group $P2_1/c$, with $a = 14{\cdot}945(3)$, $b = 9{\cdot}465(1)$, $c = 21{\cdot}655(2)$ Å, $\beta = 112{\cdot}70(2)°$, $D_c = 1{\cdot}16$ g cm$^{-3}$, and $Z = 4$. On a Syntex P2$_1$ diffractometer, 4311 independent reflections were recorded using graphite-monochromated Cu-$K_\alpha$ radiation. Structure solution by MULTAN followed by least squares refinement, with anisotropic thermal parameters for non-hydrogen atoms and with fixed tetrahedral geometry of the methyl groups, gave a final $R$ of 0·057.‡

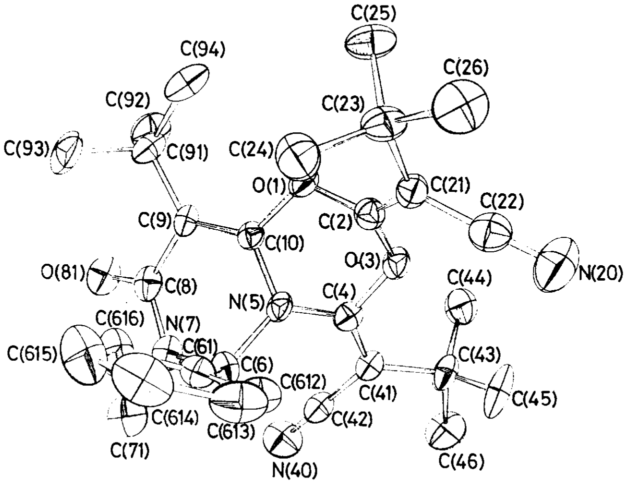


FIGURE. ORTEP drawing of (5) showing 35% probability ellipsoids. Important bond distances, in Å, are: O(1)–C(2), 1·365; C(2)–C(21), 1·329; C(4))–C(41), 1·333; C(4)–N(5), 1·393; C(8)–O(81), 1·225; C(9)–C(10), 1·335 (e.s.d.'s 0·004 Å).

The calculated molecular structure (Figure) discloses the 3:1 adduct to be the pyrimido[1,6-*e*][1,3,5]dioxazine derivative (**5**). Unusual features of the structure are the lack of mesomeric interaction between the amide carbonyl group C(8),0(81) and the double bond between C(9) and C(10) as indicated by the relatively long C(8)–C(9) distance (1·516 Å) as well as by a torsional angle 0(81)–C(8)–C(9)-C(10) of 159°, and the non-planarity of the keten *ON*-acetal unit around C(4), the angle between the planes O(3), C(4), N(5) and C(41), C(42),C(43) being 8·2°.

This formulation (**5**) for the 3:1 adduct demonstrates that one of the three cyano groups involved is incorporated into the framework of the heterocyclic rings. Probably this happens at the stage of the intermediate dipole (**3**), where alkylation of the nitrogen of the cyano group carrying a partial negative charge by the cation part of the dipole to give the ketenimine (**4**) is conceivable, though the assistance of triphenylphosphine in this step cannot be rationalized at present. The cyclization of (**3**) presents a new facet in the reactivity of 1,4-dipoles, whereas for intermolecular reactions *N*-alkylation of nitrile anions has been reported before to occur where there is steric hindrance.[4] The heterocumulene (**4**) is of special interest because of the extraordinary ring strain to be expected for this compound.[5] This ring strain is relieved by immediate cycloaddition with two additional keten molecules (**1**) to give (**5**). In contrast to the usual course of reaction between C=N systems and ketens, here *both* keten molecules react across the C=O bond. However, it has been established before that cycloaddition across the carbon–heteroatom $\pi$-bond of heterocumulenes may be preferred in examples of strained reaction partners.[6]

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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.

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