Formation and Reaction of Carbonyl Ylides. Structure of 2 : 1-Cycloadducts of 1-Methoxy-2-benzopyrylium-4-olate with Isocyanates

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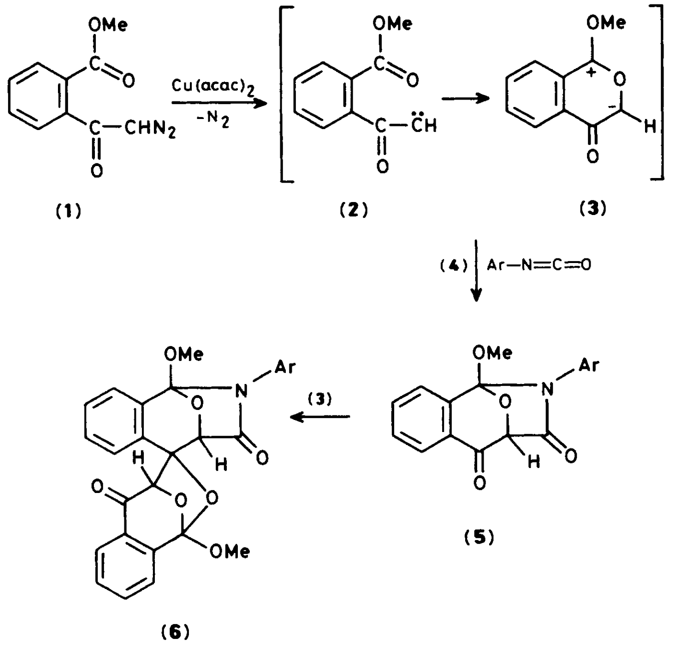
The Cu(acac)$_2$-catalysed (Hacac = pentane-2,4-dione) decomposition of *o*-methoxycarbonyl-α-diazoacetophenone in the presence of aryl isocyanates gave 2 : 1-adducts of the intermediate 1-methoxy-2-benzopyrylium-4-olate with isocyanates; the crystal structure of one such adduct has been determined.

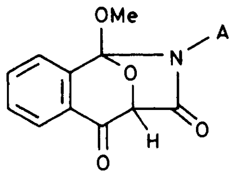
The chemistry of carbonyl ylides has been studied extensively in view of its mechanistic and synthetic interest.[1] We have already reported the successful formation of carbonyl ylides *via* the carbene–carbonyl reaction.[2] As a continuation of our work on the 1,3-dipolar cycloaddition of carbonyl ylides with various dipolarophiles such as ethylenic, acetylenic, and carbonyl compounds,[3] we now report the first example of the 1,3-dipolar cycloaddition of 1-methoxy-2-benzopyrylium-4-olate (**3**) with isocyanates to give 2:1 adducts. Isocyanates have a cumulated oxazadiene system composed of C=N and C=O double bonds, both of which could be the reaction site for 1,3-dipolar cycloadditions of carbonyl ylides on the basis of previous work.[4]

The diazo compound (**1**) was decomposed in benzene solution at 80 °C in the presence of *p*-nitrophenyl isocyanate (2 mol. equiv.) and a catalytic amount of Cu(acac)$_2$. Silica gel

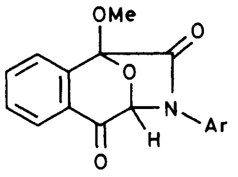


a; Ar = p-$O_2NC_6H_4$
b; Ar = Ph

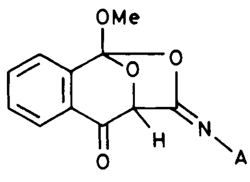
Scheme 1. Hacac = pentane-2,4-dione.



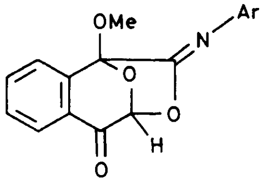
(5A)



(5B)



(5C)



(5D)

column chromatography of the reaction mixture gave a crystalline product in 44% yield, m.p. 243—245 °C. Elemental analyses and spectroscopic data indicate that the product is the 2:1 adduct (**6a**) of the intermediate 1-methoxy-2-benzopyrylium-4-olate (**3**) with p-nitrophenyl isocyanate (**4a**). The i.r. spectrum of (**6a**) has bands at 1707 and 1742 cm^{-1} due to cyclic carbonyl groups, and its ^1H n.m.r. spectrum has two MeO (δ 3.67 and 4.02) and two methine signals (δ 5.09 and 5.18). Although the corresponding 1:1 adduct (**5a**) could be detected (*ca.* 4% yield) in the n.m.r. spectrum of the reaction mixture [δ 3.06 (s, OMe) and 5.14 (s, CH)], it could not be isolated. Phenyl isocyanate (**4b**) gave a similar 2:1 adduct (**6b**) in 32% yield. In this case no 1:1 adduct (**5**) was observed despite detailed analysis of the products by medium-pressure column chromatography. This indicates that the second attack of (**3**) on (**5**) is much faster than the first, consuming the (**5**) produced in the initial addition.

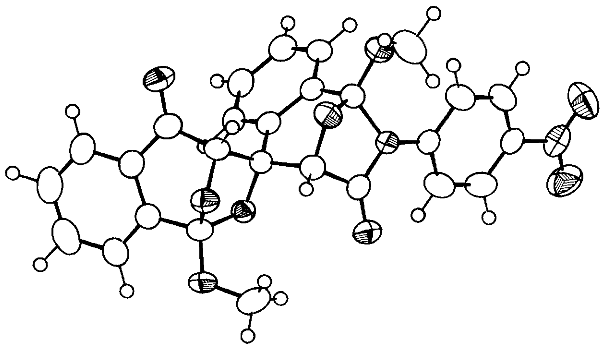


Figure 1. ORTEP drawing of the X-ray crystal structure of (**6a**).

For the first cycloaddition of (**3**) on the isocyanate, four structures (**5A**)—(**5D**) are possible for the 1:1 adduct. MNDO calculations suggest that (**5C**) is the most probable, according to Sustmann's equation.[5] That is, the reaction is controlled by the HOMO of (**3**) and the TLUMO† of (**4**), bonding between the atoms with the largest atomic coefficients affording the adduct (**5C**). However, it was difficult to determine the mode of the first cycloaddition from spectroscopic analysis of the 2:1 adduct.

The structure of (**6a**) was determined by X-ray structural analysis‡ (Figure 1), and indicates that the first attack of (**3**) on isocyanate proceeded site- and regio-selectively; that is the attack took place on the N=C double bond in a manner different from that predicted by the MNDO calculations. The second attack of (**3**) on the 1:1 adduct (**5a**) was confirmed to be directed to the carbonyl group originating from (**3**), in a similar way to that observed in the reaction between (**3**) and acenaphthylene.[6] Efforts to isolate the 1:1 adduct are in progress.

Received, 1st May 1986; Com. 581

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† TLUMO indicates the third LUMO which is the actual LUMO of the isocyanate group π-system.

‡ *Crystal data:* $C_{27}H_{20}O_9N_2$, M_r = 516.46, orthorhombic, space group $P2_12_12_1$, a = 11.5802(6), b = 23.009(1), c = 8.6162(12) Å, U = 2295.78(36) Å^3, Z = 4, λ(Mo-K_α) = 0.7709 Å, θ—2θ scan, 2518 reflections with $F > 2\sigma(F)$, $2\theta_{max.}$ = 55°, R = 0.0378. 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. Full details will be published elsewhere.