1,3-Dipolar Cycloaddition of Mesoionic Anhydro-4-hydroxy-1,3-dioxolium Hydroxides with Olefinic Dipolarophiles

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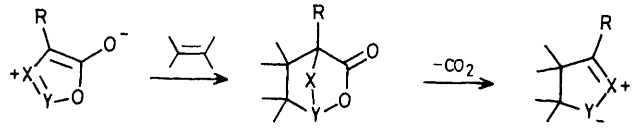
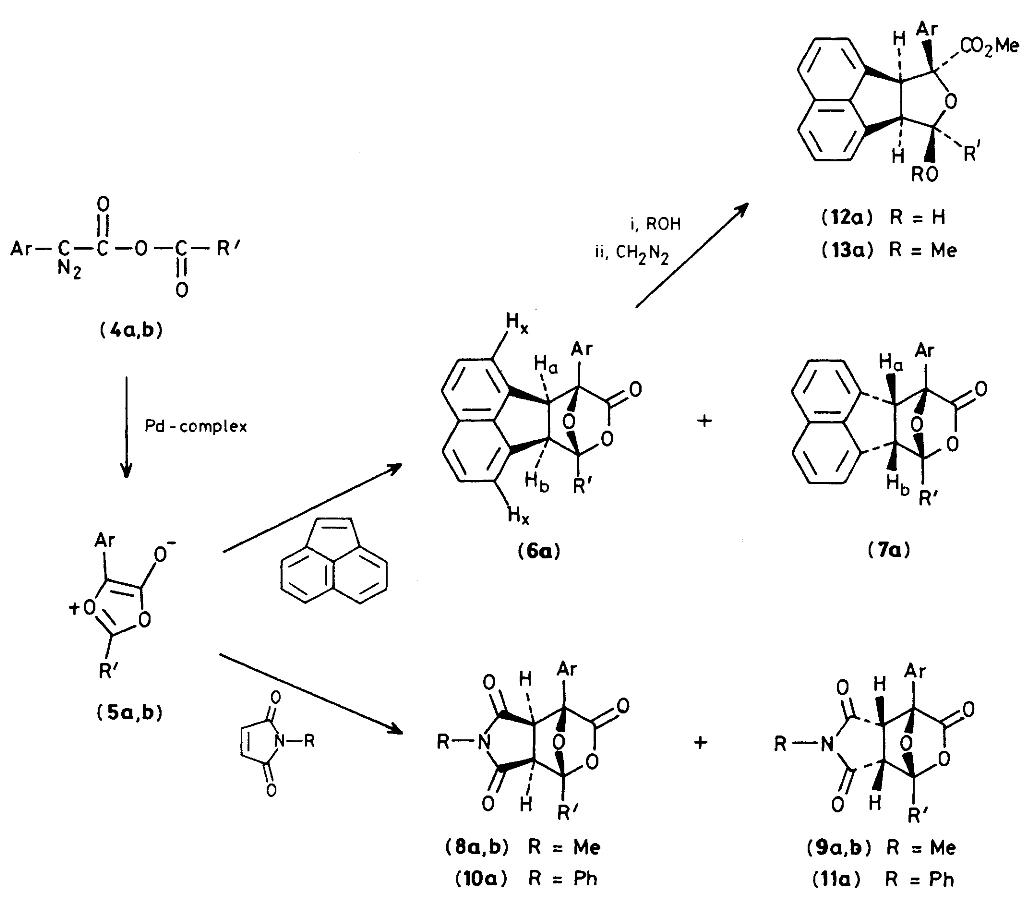
Stable cycloadducts between mesoionic compounds containing a lactone moiety and olefinic dipolarophiles were isolated for the first time from mesoionic 1,3-dioxolium-4-oxides, generated *in situ* by the intramolecular carbene–carbonyl reaction of α-diazo-acetic benzoic and -bis(acetic) anhydrides.

Although mesoionic compounds containing a lactone moiety, such as sydnones (**1a**) and munchnones (**1b**), undergo 1,3-dipolar cycloaddition with olefinic dipolarophiles, they do not give stable cycloadducts which can be isolated or detected directly. The cycloadducts (**2a,b**) undergo spontaneous decarboxylation to give (**3a,b**) followed by further reaction.[1] We report the first examples of stable cycloadducts between mesoionic compounds containing a lactone moiety and olefinic dipolarophiles. These cycloadducts were isolated



(**1**) (**2**) (**3**)

a; X = NR′, Y = N
b; X = NR′, Y = CR″
(**c**; X = O, Y = CR′)



Ar = p-$NO_2C_6H_4$

a; R′ = Ph
b; R′ = Me

without decarboxylation from mesoionic 1,3-dioxolium-4-oxide (**1c**), successfully generated by us earlier.[2]

When the diazo-anhydride (**4a**) was catalytically decomposed in the presence of acenaphthylene in benzene at 60—70 °C, slightly yellowish crystals were formed (71% yield, m.p. 206—207 °C), which were shown to be the 1 : 1 adduct of the mesoionic 1,3-dioxolium-4-oxide (**5a**) with acenaphthylene by elemental and spectroscopic analysis. The i.r. spectrum of this 1 : 1 adduct showed a lactone absorption at 1794 cm^{-1}, and the ^1H n.m.r. spectrum exhibited absorption at δ 4.57(d, 1H, J 6.0 Hz), 4.82(d, 1H, J 6.0 Hz), 6.24(d, 1H, J 7.2 Hz), 6.32(d, 1H, J 7.2 Hz), and 7.00—8.27(m, 13H), thus the product was assigned as the *exo*-cycloadduct (**6a**). The small J_{ab} value (6.0 Hz) and the observation of aromatic protons H_x at high field (δ 6.24 and 6.32) supported this assignment. The n.m.r. spectrum of the filtrate showed the formation of the *endo*-adduct (**7a**) which exhibited an AB quartet at δ 4.61 and 4.93 (J_{ab} 8.1 Hz).

Catalytic decomposition of (**4a**) in the presence of *N*-methylmaleimide gave a mixture of the *exo*-cycloadduct (**8a**) and the *endo*-cycloadduct (**9a**) in a ratio of 2 : 1. The *exo*-adduct (**8a**) (m.p. 202—204 °C, yield 61%), crystallized from the reaction mixture, showed lactone and imide absorptions at 1817, 1781, and 1708 cm^{-1}. The ^1H n.m.r. spectrum of (**8a**) showed signals at δ 2.83(s, 3H), 3.80(d, 1H, J 6.3 Hz), 4.07(d, 1H, J 6.3 Hz), and 7.45—8.45(m, 9H), while the ^1H n.m.r. spectrum of (**9a**) exhibited absorption at δ 3.03(s, 3H), 3.90(d, 1H, J 8.7 Hz), 4.18(d, 1H, J 8.7 Hz), and 7.45—8.40(m, 9H). The *exo*-adduct (**10a**) and *endo*-adduct (**11a**) were also formed in a ratio of 3 : 2 from the reaction of (**5a**) with *N*-phenylmaleimide. Furthermore 1,3-dioxolium-4-oxide (**5b**) also reacted with *N*-methylmaleimide to give a mixture of the *exo*-adduct (**8b**) and *endo*-adduct (**9b**) in a ratio of 5 : 1.

While (**1a**) and (**1b**) are stable and isolable, (**1c**) is too unstable to be isolated. When palladium catalyst was added to the solution of (**4a**) in the absence of a dipolarophile, the colour of the solution around the catalyst changed to red instantly, but disappeared in a few seconds, indicating that (**5a**) is a short-lived species. Nevertheless, the isolation of cycloadducts in considerable yields indicates that the rates of cycloaddition are very fast.

The cycloadducts (**6**)—(**11**) are stable in the solid state; however, they gradually undergo hydrolysis by moisture in solution. Hydrolysis or methanolysis of (**6a**) followed by treatment with diazomethane afforded the esters (**12a**) or (**13a**), respectively.[†] The other cycloadducts obtained were also found to undergo methanolysis or hydrolysis to give the corresponding esters or the further isomerized esters.

As described above, 1,3-dipolar cycloadducts (**2c**) of mesoionic compounds containing a lactone moiety with olefinic dipolarophiles were isolated, without decarboxyla-

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[†] The structures of (**12a**) and (**13a**) were determined on the basis of their n.m.r. spectra, which show a very similar pattern; the ^1H n.m.r. spectrum of (**13a**) showed δ 3.19(s, 3H), 3.92(s, 3H), 4.63(d, 1H, J 7.2 Hz), 5.60(d, 1H, J 7.2 Hz), 5.98(d, 1H, J 7.2 Hz), 6.30(d, 1H, J 7.2 Hz), and 6.80—7.96 (m, 13H).

tion, for the first time, using the system (**1c**), in contrast to (**1a**) and (**1b**). This is probably owing to the greater instability of the decarboxylation product (**3c**) constructed from a carbonyl ylide structure, compared with (**3a**) and (**3b**) which are constructed from an azomethine imine and an azomethine ylide, respectively.

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