Formation and Reactions of Mesoionic Anhydro-4-hydroxy-1,3-dioxolium Hydroxides

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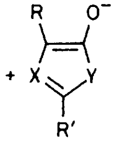
A novel mesoionic system, anhydro-4-hydroxy-1,3-dioxolium hydroxide, was formed by intramolecular carbene–carbonyl reaction on catalytic decomposition of α-diazoacetic benzoic anhydrides and trapped with acetylenic compounds to give furan derivatives as final products.

Although many types of mesoionic compounds (**1b**—**d**) containing a 5-membered 1,3-heterocyclic system have been synthesized,[1] mesoionic anhydro-4-hydroxy-1,3-dioxolium hydroxide (**1a**) is unknown because of its instability; it is the least stable example of compounds (**1**). We found that an intramolecular carbene–carbonyl reaction *via* the decomposition of a diazo-imide in an inert solvent is a useful method for the synthesis of the unstable mesoionic system because of the formation of an inert leaving molecule, nitrogen.[2]



(**1**)

a; X = Y = O

b; X = O, Y = NR″

c; X = NR″, Y = O

d; X = Y = NR″

We report the first successful generation of mesoionic 1,3-dioxolium-4-oxide (**1a**) by catalytic decomposition of diazoacetic benzoic anhydrides (**4**), which were produced from benzoyl chloride (**3**) and diazoacetic acid derivatives (**2**) synthesized by a novel method.†

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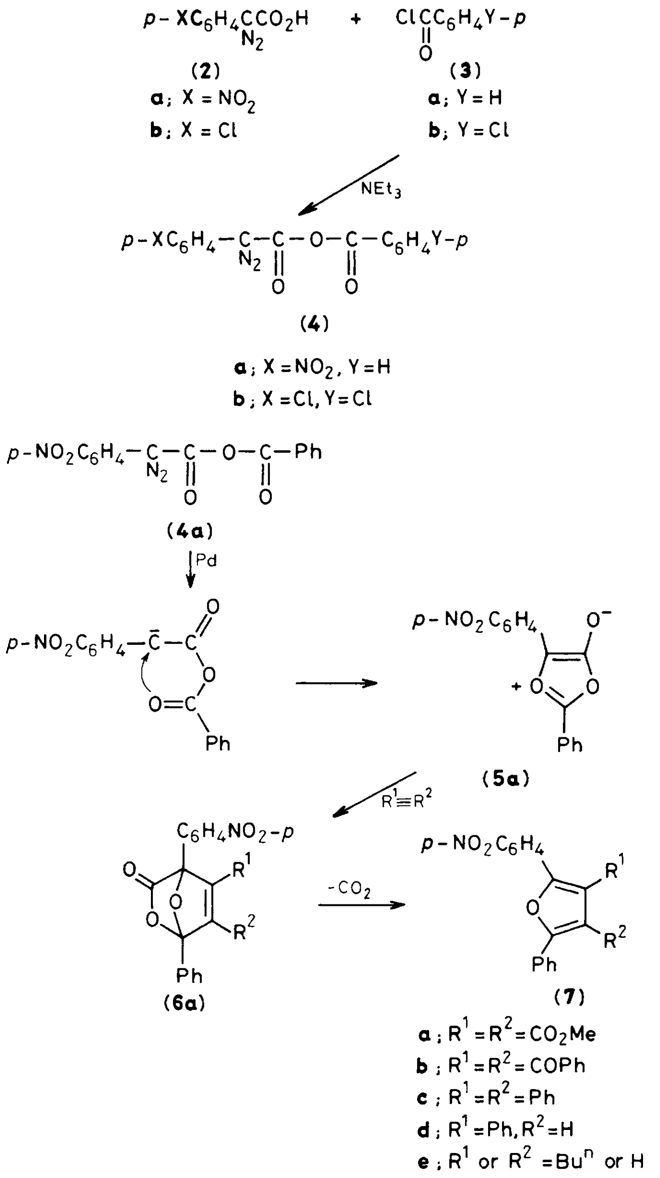
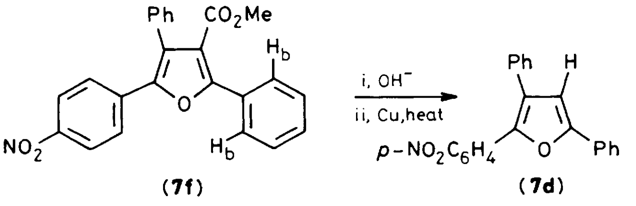
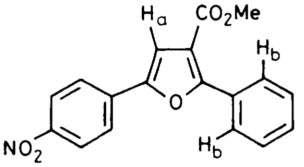
† α-Diazoacetic acid derivatives (**2a**, **b**) were synthesized by the alkaline fission at pH 10 of α-diazoacetoxyethyldimethylsulphonium iodide.



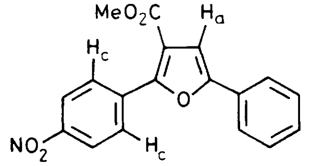
When small pieces of a π-allyl palladium complex were added to the benzene solution of diazo-acid anhydride (**4a**) and dimethyl acetylenedicarboxylate at 80 °C, furandicarboxylate (**7a**), m.p. 162—163 °C was crystallized from the reaction mixture (86% yield); n.m.r., δ 3.87 (s, 3H), 3.90 (s, 3H), 7.35—7.53 (m, 3H), 7.70—7.90 (m, 2H), 8.00, 8.25 (ABq, *J* 9.0 Hz, $C_6H_4NO_2$-*p*). The reaction with dibenzoylacetylene gave the corresponding furan (**7b**), and the reaction with diphenylacetylene gave small amounts of the furan (**7c**). The formation of the furan (**7a, b,** or **c**) indicates the generation of mesoionic 1,3-dioxolium-4-oxide (**5a**) by intramolecular carbene–carbonyl reaction, which undergoes 1,3-dipolar cycloaddition with triple bonds to give adducts (**6a**) followed by elimination of carbon dioxide to afford the furans. The reactions with phenylacetylene and hex-1-yne gave single furans (**7d** and **e**), respectively. When methyl phenylpropiolate was used in the reaction with (**5a**) the furan (**7f**) was obtained.‡ The structure of (**7d**) was supported by the decarboxylation of (**7f**) leading to (**7d**). However, in the reaction of methyl propiolate with (**5a**), a lack of regiocontrol was observed as compared to the formation of the single isomer (**7g**) in the reaction between methyl propiolate and isomunchnon (**1b**)[3] which has a similar carbonyl ylide resonance structure but an amide moiety in place of the ester moiety of (**5**). Two isomers of the furans (**7g** and **h**) were obtained in the ratio 7:3 and 70% yield. Assignment of (**7g**) and (**7h**) was performed on the basis of the n.m.r. spectra: (**7g**), δ 3.87 (s, 3H), 7.25 (s, 1H), 7.35—7.65 (m, 3H), 7.95—8.10 (m, 2H), 7.78, 8.23 (ABq, C_6H_4-NO_2-*p*); (**7h**), 3.88 (s, 3H), 7.07 (s, 1H), 7.25—7.55 (m, 3H), 7.55—7.85 (m, 2H), 8.27 (s, 4H). The furan ring proton H_a resonated at lower field in (**7g**) than in (**7h**) owing to $C_6H_4NO_2$-*p*, and the H_b protons of (**7g**) and H_c protons of (**7h**) shifted to lower field because of the ester group.



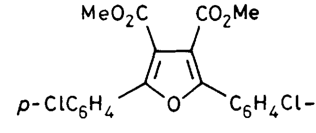
(**7f**) (**7d**)



(**7g**)



(**7h**)



(**7i**)

Although $Cu(acac)_2$ (Hacac = $MeCOCH_2COMe$) was not an effective catalyst for the decomposition of the diazo-acid anhydride (**4a**), (**4b**) did decompose in its presence giving the furan (**7i**) (74%) in the presence of dimethyl acetylenedicarboxylate.

As described above, formation of mesoionic 1,3-dioxolium-4-oxide (**5**) and reaction of its carbonyl ylide moiety with triple bonds were confirmed by isolation of the furans, however, attempts to isolate (**5**) were unsuccessful. When a palladium catalyst was added to the solution of (**4a**), the colour of the solution around the catalyst changed to red for an instant, and when the crystalline diazo-anhydride was exposed to light, it turned red: these colourations also suggest the transient formation of (**5a**). Further evidence for the generation of (**5**) was obtained by isolation of adducts of (**5**) with olefinic dipolarophiles without decarboxylation which will be reported elsewhere. The lower stability of this new type of mesoionic system (**5**) compared to the other mesoionic systems should be interpreted in terms of poor ability of oxygen to partake in resonance.

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References

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‡ H_b protons of (**7f**) appeared at lower field (δ 7.80—7.95) because of the 3-ester group.