1,3-Polar Addition of 1,3-Oxazolium-4-olates with Protic Reagents

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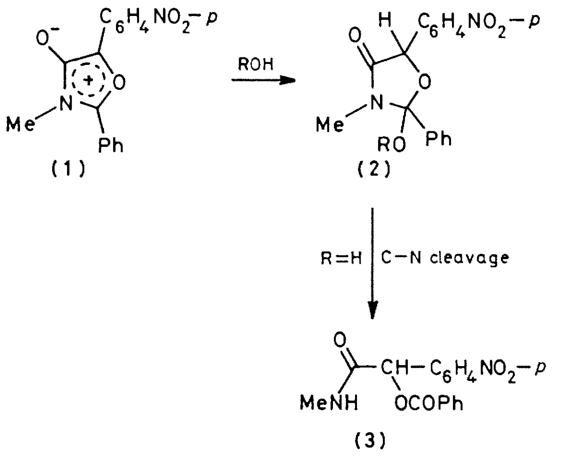
Summary 1,3-Oxazolium-4-olates react with water and alcohols to give 1,3-polar adducts, 1,3-oxazolidin-4-one derivatives, which, with water, undergo ring opening in two ways depending on the structure of the adduct.

SINCE our synthesis of 1,3-oxazolium-4-olates (isomünchnones) by the intramolecular carbene–carbonyl reaction of imide carbenes,[1] we have investigated the reactivity of members of this novel class of mesoionic compounds which have a carbonyl ylide resonance structure.[2]

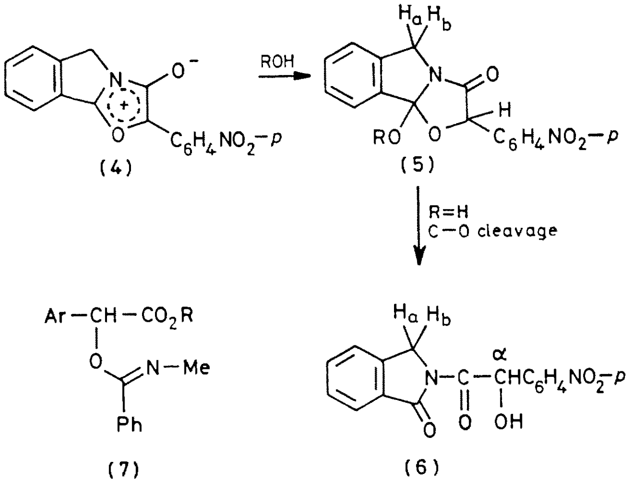
When red isomünchnone (**1**) was treated with water–dioxane it decolourised within 1 min at room temperature. Work-up afforded the single product, *N*-methyl-α-benzoyloxy-α-*p*-nitrophenylacetamide (**3**), quantitatively, the structure of which was confirmed by spectral data [m.p. 184–187 °C; i.r. 3250 (NH), 1720 (ester), and 1665 cm^{-1} (amide); ^{1}H n.m.r., τ 1·65–2·60 (m, 9H), 3·33 (br s, NH), 3·57 (s, 1H), and 7·13 (d, Me, *J* 5·0 Hz)]. The formation of (**3**) can be explained by 1,3-polar addition of water to the isomünchnone followed by ring opening of the intermediate (**2a**) with cleavage of the C–N bond (Scheme 1).



SCHEME 1 **a**; R = H
b; R = Me
c; R = Et
d; R = Pr^i

1,3-Polar adducts were also obtained when alcohols were used instead of water. Reaction of (**1**) with methanol at 55 °C gave two isomers of the 1:1 adduct (**2b**) which have similar i.r. and n.m.r. patterns indicating that the adducts differ in configuration at the C-2 methoxy group [major isomer, 68%, m.p. 120—123 °C; i.r., 1720 cm^{-1} (cyclic amide); ^{1}H n.m.r., τ 1·70—2·70 (m, 9H), 4·37 (s, 1H), 6·53 (s, OMe), and 7·27 (s, NMe); minor isomer, 20%, m.p. 173—175 °C; i.r., 1725 cm^{-1} (cyclic amide); ^{1}H n.m.r., τ 1·57—2·20 (m, $NO_2C_6H_4$), 2·40— 2·57 (m, Ph), 4·37 (s, 1H), 6·72 (s, OMe), and 7·23 (s, NMe)]. Reaction of (**1**) with ethanol and propan-2-ol gave the adducts (**2c**) and (**2d**) respectively as one isomer [(**2c**) 63%, m.p. 97—99 °C, i.r., 1725 cm^{-1} (C=O); ^{1}H n.m.r., τ 1·57—2·60 (m, 9H), 4·33 (s, 1H), 5·90—6·70 (m, 2H, OCH_2), 7·28 (s, 3H, NMe), 8·60 (t, 3H, Me, *J* 7·0 Hz); (**2d**) 70%, m.p. 183—184 °C; i.r., 1720 cm^{-1} (C=O); ^{1}H n.m.r., τ 1·67—2·68 (m, 9H), 4·33 (s, 1H), 5·95 (septet, 1H, *J* 6·5 Hz, OCH), 7·27 (s, NMe), and 8·63 (t, 6H, *J* 6·5 Hz, 2 × Me)]. No reaction with t-butyl alcohol was observed, however. In the n.m.r. spectra of (**2c**) and (**2d**), the two $MeCH_2O$ protons and the two Me_2CHO groups were nonequivalent owing to the asymmetric centre at C-2. Structure (**7**) which would be expected if isomünchnone reacted analogously to münchnones[3] is excluded because of the absence of the i.r. imidate absorption and the nonequivalence of the two methylene protons of (**2c**) and the two geminal methyl groups of (**2d**).

The reaction of the bicyclic isomünchnone (**4**) with water gave *N*-(α-hydroxy-*p*-nitrophenylacetyl)phthalimidine (**6**), by ring opening of the intermediate (**5a**) with C–O bond cleavage (Scheme 2) [(**6**) 80%, m.p. 145—146 °C; i.r., 3450 (OH), 1735 (cyclic imide), and 1690 cm^{-1} (imide); ^{1}H n.m.r., τ 1·70—2·60 (m, 8H), 3·63 (d, 1H, *J* 7·8 Hz), 5·02 (d, 1H, *J* 17·6 Hz), 5·22 (d, 1H, *J* 17·6 Hz), and 5·38 (d, 1H, *J* 7·8 Hz, OH)]. The bicyclic adduct (**5b**) was obtained from reaction of (**4**) with methanol [(**5b**) 70%, m.p. 168—169 °C, i.r., 1720 cm^{-1} (C=O); ^{1}H n.m.r., τ 1·70—2·70 (m, 8H), 4·02 (s, 1H), 5·17 (d, 1H, *J* 14·2 Hz), 5·55 (d, 1H, *J* 14·2 Hz), and 6·42 (s, OMe)]. That the methylene protons H_a and H_b of (**6**) did not appear as a singlet but



SCHEME 2 **a**; R = H
b; R = Me

rather as an AB quartet may be explained by the non-equivalency of those protons owing to the remote asymmetric carbon atom Cα. The 1,3-polar addition of water and alcohols to isomünchnones indicates that the structure of mesoionic 1,3-oxazolium-4-olates has a large degree of carbonyl ylide character.

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