New Reagent System containing CrO_3 and Syntheses of Neo-lignans

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Oxidations of 1-arylprop-1-enes by the new reagent systems, CrO_3–HBF_4–MeCN or CrO_3–$HClO_4$–MeCN gave the 4-aryltetralones (**1a**) and (**1c**), and the tetrahydrofuran (**3**) which are precursor molecules for aryltetrahydronaphthalene and tetrahydrofuran neo-lignans.

Chromic anhydride (among other metal oxides) has been widely used as a reagent in oxidations of organic compounds and several kinds of reagent systems[1] and reagents, namely, Collin's reagent, pyridinium chlorochromate (PCC), pyridinium dichromate (PDC),[2] and 2,2′-bipyridinium chlorochromate,[3] have been developed recently. Although several solvents such as water, acetone, acetic acid, acetic anhydride, pyridine, and dimethylformamide are involved in different reagent systems using CrO_3, little attention has been paid to solvent effects. Interest has centred, recently, on the solvent effects for reactions of metals and metal ions with a view to activating organic substrates[4] and formation of complexes with donor solvents leading to changes in redox potentials.[5]

We have studied the behaviour of CrO_3 in donor solvents particularly in acidic media as an alternative to Jones' reagent. CrO_3 in MeCN in the presence of aqueous HBF_4 or $HClO_4$ gives improved oxidations of 1-arylprop-1-enes relative to reagents other than Jones' reagent.

Oxidation of (*E*)-1-(3,4-dimethoxyphenyl)prop-1-ene by the system CrO_3 (100 mg)–MeCN (8 ml) in 42% aqueous HBF_4 (2 ml) gave after a few minutes the tetralone (**1a**), m.p. 124—126 °C, in 16% yield as the only identifiable product.† Reduc-

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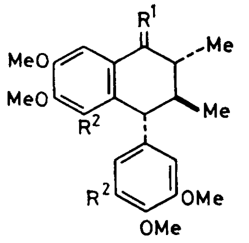
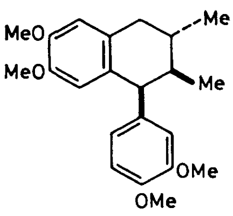
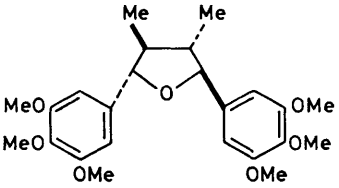
† Reactions at a lower temperature (−30 °C) or under high dilution gave complex products including veratraldehyde and (**1a**), the latter in lower yield than at room temperature.



(1) a; R^1 = O, R^2 = H
b; R^1 = H_2, R^2 = H
c; R^1 = O, R^2 = OMe
d; R^1 = H_2, R^2 = OMe



(2)



(3)

tion of (**1a**) by $NaBH_4$ in CF_3CO_2H[6] gave (**1b**), m.p. 115—117 °C, which is identical to (±)-galbulin.[7] The structure of (**1a**) was assigned by considering the latter result, and from its n.m.r. data which showed a coupling constant of 10 Hz between C(3)–H and C(2)–H. Catalytic reduction on 10% Pd–C of (**1a**), though, afforded a novel tetralin (**2**), m.p. 102—103 °C; n.m.r. ($CDCl_3$) δ 0.74 [3H, d, J 5.9 Hz, C(3)–Me], 1.15 [3H, d, J 6.8 Hz, C(2)–Me], 1.91—2.18 [2H, m, C(2)–H, C(3)–H], 2.45—2.82 [2H, m, C(1)–H], 2.91 [1H, d, J 7.2 Hz, C(4)–H], 3.96 (3H, s, OMe), 3.87 [6H, s, $(OMe)_2$], 3.88 (3H, s, OMe), 6.60—6.74 (4H, m, Ar–H) and 6.78 [1H, s, C(5)–H]. The structure of (**2**) can be postulated from the following n.m.r. data: (i) the C(3)–Me resonance occurs at δ 0.74 owing to the shielding effect of the phenyl group, and (ii) there is a coupling constant of 7.2 Hz between C(3)–H and C(4)–H.

Oxidations of (*E*)- and (*Z*)-1-(3,4,5-trimethoxyphenyl)prop-1-enes by the same reagent system gave the tetralone (**1c**), m.p. 135—137 °C, and the tetrahydrofuran (**3**), m.p. 126—128 °C, which is identical to (±)-grandisin,[8] in 14.3 and 17.7% yield, respectively. Compound (**1c**) was reduced to the tetralin (**1d**),[6] m.p. 130—132 °C, with $NaBH_4$ in CF_3CO_2H.

Oxidations of 1-arylprop-1-enes by CrO_3–MeCN with aqueous $HClO_4$ instead of aqueous HBF_4 led to similar results. However, Jones' reagent and the oxidising system CrO_3–MeCN–H_2SO_4(aq.) gave only the corresponding aldehydes.

To unravel the contrasting nature of these oxidation reactions we measured electrode potentials of CrO_3 in some donor solvents. The highest reduction potential, 1632 mV *vs.* the saturated calomel reference electrode (S.C.E.), occurred in MeCN whilst in Ac_2O and Me_2CO the potentials were, respectively, 1381 and 1094 mV *vs.* S.C.E. For the acid media the electrode potentials of CrO_3–HBF_4–MeCN, CrO_3–H_2SO_4–MeCN, and CrO_3–HBF_4–Me_2CO were 1174, 1098, and 1078 mV *vs.* S.C.E., respectively.

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