Rapid Efficient Route to 3-Hydroxy-o-phenylenediamine Derivatives and Derived Benzoxazolines

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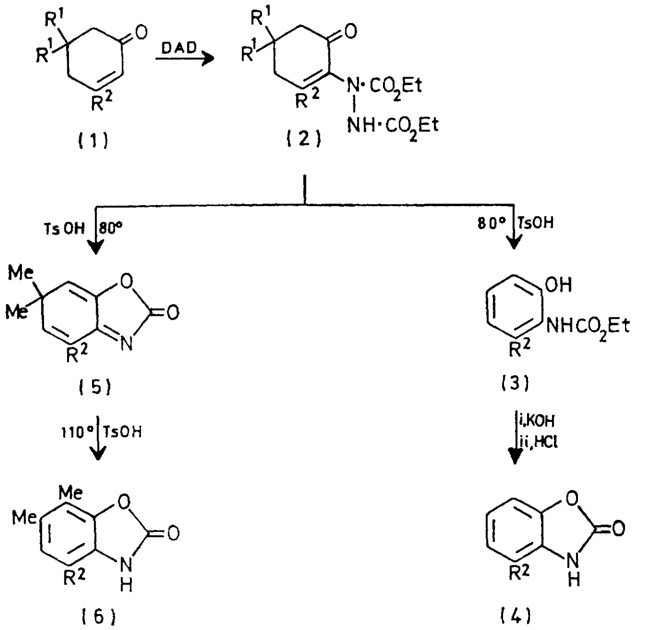
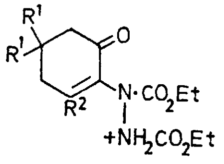
Summary Polyfunctionalized aromatic urethanes and heterocyclic compounds are obtained from hydrazino-substituted enaminoketones.

Enaminoketones have been shown[1,2] to react with electrophiles at C or at O, depending upon factors such as the basicity of the substrates, reagents, and conditions. The enaminoketones (**1a** and **b**) react with diethyl azodicarboxylate regiospecifically at C-2 to give the adducts (**2a**), m.p. 144—145° and (**2b**), m.p. 116—117° respectively, in quantitative yield.† Upon treatment with toluene-*p*-sulphonic acid in refluxing benzene, under nitrogen, (**2a**) and (**2b**) give the substituted benzenes (**3a**), m.p. 108—109° and (**3b**), m.p. 72—74°. The 2(3*H*)-benzoxazolone derivatives (**4a**), m.p. 232—234°, and (**4b**), m.p. 205—207°, are formed from (**3a**) and (**3b**), respectively, by dissolution in aqueous-alcoholic KOH, followed by neutralization with HCl.



TsOH = p-$MeC_6H_4SO_3H$; DAD = $EtO_2C{\cdot}N{=}N{\cdot}CO_2Et$.
a: R^1 = H; R^2 = morpholino
b: R^1 = H; R^2 = pyrrolidin-4-yl
c: R^1 = Me; R^2 = morpholino
d: R^1 = Me; R^2 = pyrrolidin-4-yl



(2′)

Although the bases in the parent enaminoketones are different both in geometry and in basicity, the reactions of (**1a**) and (**1b**) proceed at almost the same rate, in contrast to the enamines.[3]

A similar sequence of reactions takes place with the enaminoketones (**1c**) and (**1d**). However, in this case the urethanes cannot be formed from (**2c**), m.p. 119°, and (**2d**), m.p. 68—70°, since the heterocyclic products (**5c**), m.p. 143—145°, and (**5d**), m.p. 136—138°, are obtained. A similar compound with a quinonoid structure leading to an aromatic product has been proposed recently.[4] The intensely coloured quinonoid compounds (**5c**) and (**5d**) are easily converted into (**6c**), m.p. 218—220°, and (**6d**), m.p. 212—215°, respectively, by a '1,2-shift' of either methyl group. This sigmatropic rearrangement was carried out in refluxing deaerated toluene with an acid catalyst.

The driving force for the reaction of (**2**) may be cleavage of the N–N bond in the protonated species (**2′**).

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† All new compounds had analytical and spectroscopic properties in accord with the assigned structures.

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[4] O. E. Edwards, G. Bernath, J. Dixon, J. M. Paton, and D. Vocelle, *Canad. J. Chem.*, 1974, **52**, 2123.