A New Route to 1*H*-1,5-Benzodiazepinones

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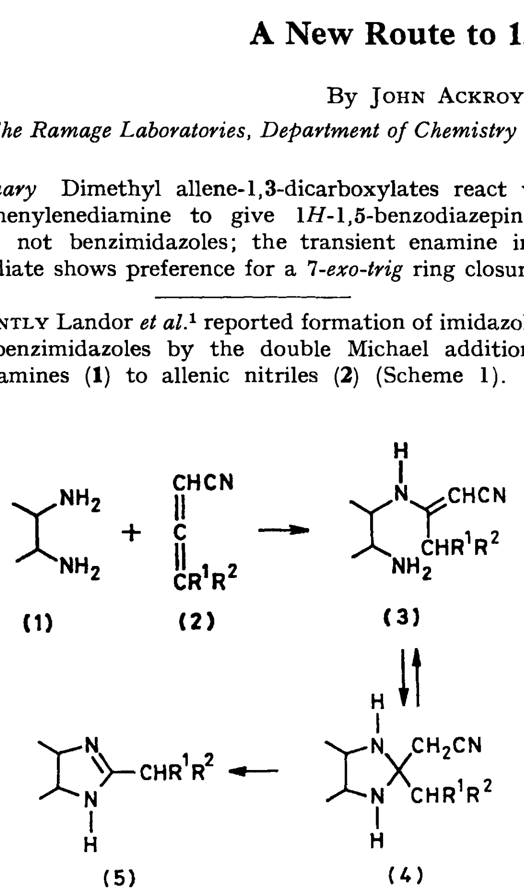
Summary Dimethyl allene-1,3-dicarboxylates react with *o*-phenylenediamine to give 1*H*-1,5-benzodiazepinones and not benzimidazoles; the transient enamine intermediate shows preference for a 7-*exo-trig* ring closure.

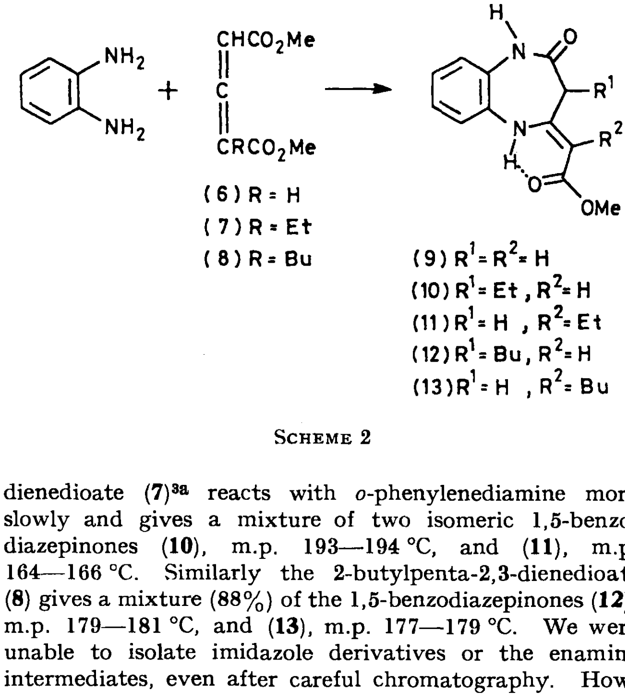
RECENTLY Landor *et al.*[1] reported formation of imidazolines and benzimidazoles by the double Michael addition of 1,2-diamines (**1**) to allenic nitriles (**2**) (Scheme 1). The ring closure of the isolated enaminic nitrile (**3**) may be formulated as a 5-*exo-trig* process,[2] (**3**)→(**4**). We now report that reactions of the dimethyl allene-1,3-dicarboxylates[3] (**6**), (**7**), and (**8**) with *o*-phenylenediamine show a preference for seven-membered ring formation and the 1*H*-1,5-benzodiazepinones (**9**), (**10**), (**11**), (**12**), and (**13**) are formed to the exclusion of benzimidazoles (Scheme 2).



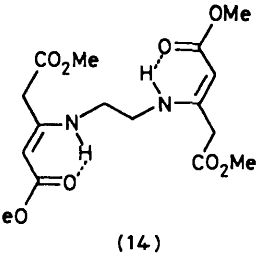
R¹ = Me, Et, or Pr; R² = Me, Et, or H.

SCHEME 1

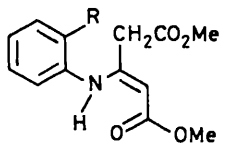
o-Phenylenediamine reacts at *ca.* 20 °C in methanol with dimethyl penta-2,3-dienedioate[3b] (**6**) to give the 1*H*-1,5-benzodiazepinone (**9**) (63%).[4] Dimethyl 2-ethylpenta-2,3-dienedioate (**7**)[3a] reacts with *o*-phenylenediamine more slowly and gives a mixture of two isomeric 1,5-benzodiazepinones (**10**), m.p. 193—194 °C, and (**11**), m.p. 164—166 °C. Similarly the 2-butylpenta-2,3-dienedioate (**8**) gives a mixture (88%) of the 1,5-benzodiazepinones (**12**), m.p. 179—181 °C, and (**13**), m.p. 177—179 °C. We were unable to isolate imidazole derivatives or the enamine intermediates, even after careful chromatography. However it is unlikely that ring closure to the diazepinone occurs after prior amidation because reaction of 2-amino-



SCHEME 2



(14)



(15) R = H
(16) R = OH
(17) R = NH₂

ethylamine with dimethyl penta-2,3-dienedioate in methanol rapidly precipitates the bisenamine adduct (**14**), m.p. 161—163 °C, M^+, 372·1530, ν_{max} 1727 (ester), 1658 (H-bonded conjugated ester), and 1610 cm^{-1} (conjugated olefin).† Furthermore the enamines (**15**) and (**16**) have been isolated when aniline and *o*-hydroxyaniline add to dimethyl penta-2,3-dienedioate.[5]

Thus it appears that 1*H*-1,5-benzodiazepinone formation occurs by a 7-*exo-trig* ring closure of the enamine intermediate (**17**) to the exclusion of the alternative 5-*exo-trig* process. The full mechanistic implications of these results will be discussed in the full paper.

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† All new compounds gave correct analytical and spectral data.

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