4-DIAZOMETHYLCOUMARINS AS STABLE DIAZOALKANES. THEIR FACILE ISOMERIZATION INTO BENZOPYRANO[3,4-c]PYRAZOL-4(3H)-ONES

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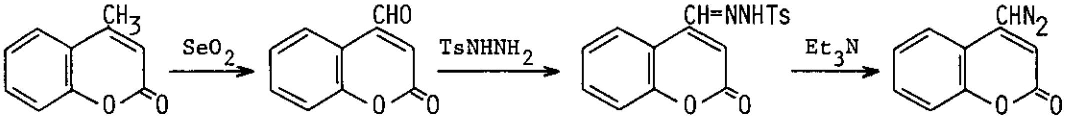
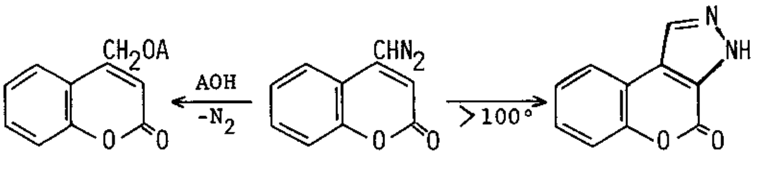
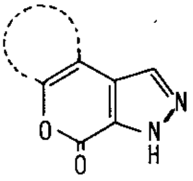
During studies on diazoalkanes as potential fluorogenic reagent for acidic substances, we have synthesized 4-diazomethylcoumarin (IIa) and several of its 7-substituted or benzo-condensed homologs (II) as a new type of solid diazoalkanes. II could be readily obtained in good yields from the corresponding 4-methyl derivatives (I) by their SeO_2 oxidation into 4-carboxaldehydes followed by Et_3N-mediated mild Bamford-Stevens reaction of their tosylhydrazones.



Ia IIa

Yellow crystals of II are all remarkably stable, with excellent storage life (over a year) at room temperature. In $CHCl_3$ or THF solution most of II are also stable on reflux, reacting normally with acids or alcohols with liberation of nitrogen. However, at higher temperatures (in refluxing toluene, etc.) II were shown to suffer electrocyclic isomerization into benzopyrano[3,4-c]-pyrazol-4(3H)-ones (III). The thermal cyclization was facile for all of II, terminating in a short period ($<$60 min.) with very high yields ($>$85 %). Isomerization of 5,6-benzo-condensed homolog of II was observed even at room temperature. The structures of III were confirmed mainly from their NMR spectra.





A: RCO, RSO_2, R IIa IIIa IV

The present set of transformations starting from I through stable diazoalkane intermediate II appears to provide a convenient route to various 4,5-condensed (benzo, naphtho, etc.) homologs of pyrano[3,4-c]pyrazol-7(1H)-one (IV).