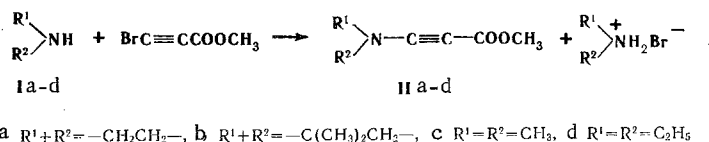


# SYNTHESIS OF 1-METHOXYCARBONYLETHYNYLAZIRIDINES AND METHOXY-CARBONYLYNAMINES

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We have established that the previously unknown 1-ethynyl-substituted aziridines IIa, b are formed in the reaction of aziridines Ia, b with methyl bromopropiolate in a molar ratio of 2:1 in absolute ether at  $-10^{\circ}\text{C}$ :



The products are mobile liquids that can be stored well in aprotic solvents but darken rapidly and resinify in the free form. Compound IIa, with bp  $25\text{--}27^{\circ}\text{C}$  (0.01 mm), was obtained in 75% yield. IR spectrum:  $1710$  ( $\text{C}=\text{O}$ ) and  $2230\text{ cm}^{-1}$  ( $\text{C}\equiv\text{C}$ ). PMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ : 3.65 (3H, s,  $\text{CH}_3$ ) and 2.29 ppm [4H, s,  $\text{N}(\text{CH}_2)_2$ ]. Compound IIb, with bp  $34\text{--}36^{\circ}\text{C}$  (0.01 mm), was obtained in 52% yield. IR spectrum:  $1710$  ( $\text{C}=\text{O}$ ) and  $2225\text{ cm}^{-1}$  ( $\text{C}\equiv\text{C}$ ). PMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ : 3.70 (3H, s,  $\text{CH}_3$ ), 2.20 (2H, s,  $\text{CH}_2$ ), and 1.45 ppm (6H, s  $\text{CH}_3$ ).

1-Ethynylaziridines IIa, b are analogs of the widely known class of ynamines [1, 2]. The synthesis of functionally substituted ynamines [3, 4] is a multistep and rather laborious process. Data on the one-step synthesis of cyano ynamines by the reaction of secondary amines with chlorocynoacetylene are available [5]. In order to confirm the ynylaziridine structure of IIa, b we studied the reaction of methylbromopropiolate with dimethyl- and diethylamines. We found that methoxycarbonylamines IIc, d are formed in 80-90% yields under conditions similar to those in the synthesis of ynylaziridines IIa, b. The structures of the ynamines obtained were proved rigorously by the complete agreement of the physicochemical characteristics of IIc, d with the literature data [3, 4].

Thus the reaction of methyl bromopropiolate with aziridines and secondary amines is a convenient method for the synthesis of functionally substituted 1-ethynylaziridines and ynamines.

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