INTRAMOLECULAR INSERTION OF AMINOALKOXYCARBONYLCARBENES

INTO THE N-H BOND

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Examples are known for intramolecular transformations of carbenes generated by denitration of alkyldiazoacetates involving insertion of the carbene carbon atom into the C-H bond of the alkoxy group [1]. In addition, intermolecular insertion of alkoxycarbonylcarbenes into the N-H bond has been described [2, 3].

We have discovered the formation of products of intramolecular insertion of the carbon atom of an aminoalkoxycarbonylcarbene obtained by the thermocatalytic decomposition of 2methylaminoethyl ester of diazoacetic acid (I) into the N-H bond

$$N_{2}CHCOOCH_{2}CH_{2}NHCH_{3} \xrightarrow{Rh(OAc)_{2}} \left[\begin{array}{c} O \\ \parallel \\ O \\ -N_{2} \end{array} \right] \xrightarrow{O} CH: \\ \downarrow \\ NH \\ CH_{3} \end{array} \xrightarrow{O} \left[\begin{array}{c} 0 \\ \parallel \\ O \\ \downarrow \\ CH_{3} \end{array} \right] \xrightarrow{O} \left[\begin{array}{c} 0 \\ \parallel \\ O \\ \downarrow \\ N-CH_{3} \end{array} \right] \xrightarrow{O} (II)$$

The slow addition of a solution of 5 mmoles (I) in 5 ml dichloroethane to a suspension of 50 µmoles Rh(OAc)₂ in 10 ml dichloroethane heated to 60°C gives nitrogen liberation and the formation of N-methyl-2-morpholinone (II) which was isolated by vacuum distillation in 20% yield, bp 60°C (2.5 mm), 92% purity, n_D^{20} 1.4753. IR spectrum (v, cm⁻¹): 1680 (C=0). PMR spectrum (δ, ppm, in CCl₄): 3.94 s (CH₂CO), 3.80 t (CH₂O), 3.20 t (CH₂N), 2.86 (CH₃), molecular weight 115 (mass spectrometry).

Performing this reaction at 20-25°C leads to a reduction in the yield of (II) down to 10%.

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