TRANSFORMATION OF 3-MORPHOLINOANTHRA[1,9-cd]-6-ISOXAZOLONE

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The intermolecular insertion of nitrenes into the C-H bond at a tetrahedral carbon center leads to various heterocyclic compounds [1].

We have found that the transformation of 3-morpholinoanthra[1,9-cd]-6-isoxazolone (I) to imidazoline IV and then to imidazole V may proceed via an unusual [2] pathway, which includes a step involving intramolecular dehydrogenation by nitrene II of the adjacent carbon atoms of the morpholine ring. The resulting 1-amino-2-dehydromorpholinoanthraquinone (III) was isolated in 78% yield by refluxing I in pyridine for 2.5 h.



The conversion of I to III was observed chromatographically when isoxazolone I was refluxed in dioxane, DMF, toluene, and other solvents. Isoxazolone I was converted to imidazoline IV in 67% yield in refluxing dioxane. Compound IV was capable of undergoing dehydrogenation to imidazole V in, for example, refluxing o-dichlorobenzene (V was obtained in 80% yield). The compositions and structures of III-V were confirmed by the results of elementary analysis and IR and PMR spectroscopic data. Compound III had mp 156-157°C (from (CHCl₃). UV spectrum (ethanol), λ_{max} (log ε): 513 nm (3.99). IR spectrum (mineral oil): 3450, 3300 (NH₂); 1675⁻¹ (C=O). PMR spectrum (d_6-DMSO): 7.08-8.33 (m, 8H, aromatic and NH₂ protons); 5.58, 6.33 ppm (two d, 2H, olefinic protons). Compound IV had mp 195-200°C (it was converted to V, which melted at 267-268°C in this case). UV spectrum (ethanol), λ_{max} (log ε): 1620 cm⁻¹ (C=O). Compound V had mp 269-270°C (from CH₃OH). UV spectrum (ethanol), λ_{max} (log ε): 370 nm (3.92).

LITERATURE CITED

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