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CYCLOADDITION OF 1-AZIRINES WITH NITRILE OXIDES. FORMATION OF CARBODIIMIDES.

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In the course of our work on the symmetry-allowed thermal $[\pi^4 + \pi^2]$ cycloadditions of the rigid C=N bond of 1-azirines,[1,2] we examined a 1,3-dipolar cycloaddition to the three-orbital 4π electron system of nitrile oxides.[3,4] We discovered that aromatic nitrile oxides react exothermically with 1-azirines to furnish carbodiimides in $>80\%$ isolated yields.

Thus when 3-methyl-2-phenyl-1-azirine (I)[1] was treated with 2,4,6-trimethylbenzonitrile oxide[5] in anhydrous ether at 0^0 for 15 min, and the product carefully purified by preparative layer chromatography (controlled atmosphere development), the carbodiimide (II) was obtained as white plates, mp 39-41 (decomp.). Its infrared spectrum (Nujol) showed N=C=N absorption at 2120 cm^{-1} and C=O absorption at 1675 cm^{-1}. Its nmr spectrum (in dry $CDCl_3$)[8] showed absorptions at (δ values) 1.54 (d, J = 7.0 Hz, 3H), 2.20 (s, 6H), 2.29 (s, 3H), 4.93 (q, J = 7.0 Hz, 1H), 6.78 (s, br, 2H), and 7.22 to 8.05 (m, 5H).

The carbodiimide was highly hygroscopic, and hydrolysis to the urea (III) mp 196^0, proceeded rapidly and quantitatively.

A possible mechanism for the formation of the carbodiimide (Fig. 1) assumes the initial formation of a cycloadduct which undergoes ring cleavage and a 1,2-shift of the R group. The initially formed cycloadduct is capable of valence tautomerism.

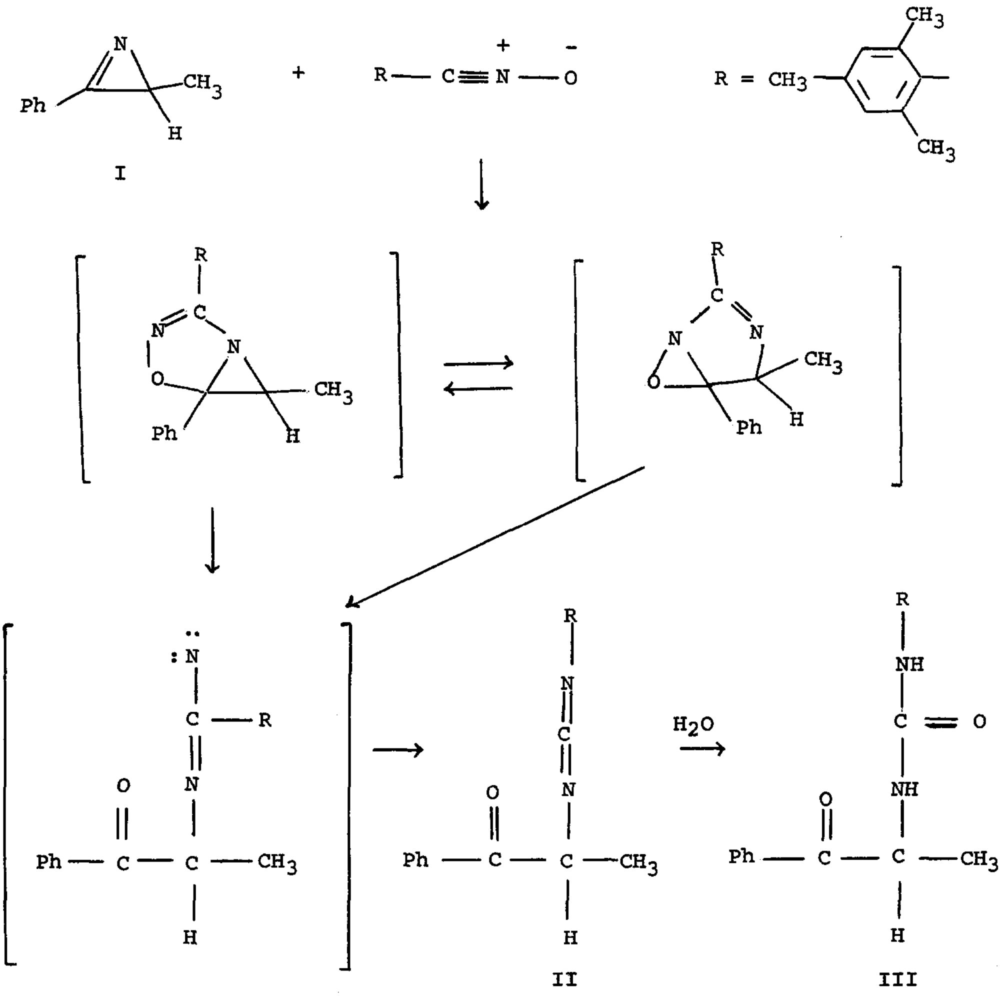

Figure 1

The generality of this transformation was established by preparation of carbodiimides from 2,3-diphenyl-1-azirine and 2-phenyl-1-azirine.[10] Further investigation on the direct spectral observation of the initial cycloadducts is in progress.

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(8) The abbreviations, s = singlet, d = doublet, q = quartet, and br = broad.

(9) Elemental analyses for urea derivatives were satisfactory and the infrared and nmr spectra were consistent with the assigned structures. Satisfactory elemental analyses could not be obtained for the carbodiimides because of their hygroscopic tendency and instability.

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