STUDIES ON FURAN DERIVATIVES. I. A NEW PREPARATION OF ACETYLENES FROM α-ARYL- OR α-2-FURYL-β-2-(5-NITROFURYL)VINYLAMINES

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β-2-(5-Nitrofuryl)acetylenes (II) were synthesized by the deamination of α-aryl- or α-2-furyl-β-2-(5-nitrofuryl)vinylamines (I).

Recently, it has been found that α-aryl- or α-2-furyl-β-2-(5-nitrofuryl)vinylamines (I) were easily obtained from α-aryl- or α-2-furyl-β-2-(5-nitrofuryl)acryloyl azides.[1] New nitrofuran type compounds were expected to be formed various reactions with I. The present paper deals with new general one-step synthesis for β-2-(5-nitrofuryl)acetylenes (II) from I.

In the literature regarding the preparation of acetylenes from 1,2-disubstituted vinylamines by elimination, Hofmann elimination of quaternized enamines has only been reported.[2]

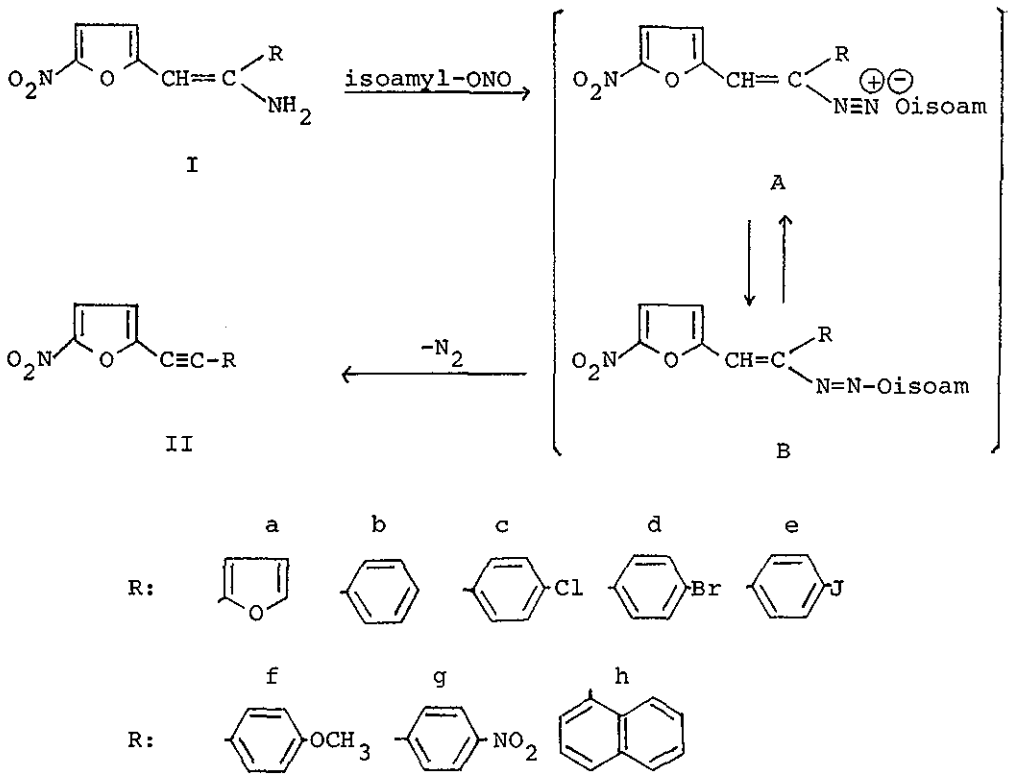
When an excess of isoamyl nitrite was added to a solution of I in anhydrous dioxane at 80°, acetylenes (II) were formed in good yield; the end of reaction could be recognized by a cease of evolution of nitrogen gas (2~3 hr). The structure of IIa is confirmed by the results of various spectral data and the elemental analysis. The ultraviolet spectrum of IIa showed the absorption maximum at 360 nm which shifted to the short wavelength region in comparison with the corresponding β-2-(5-nitrofuryl)vinyls.[3] The infrared spectrum showed the absorption band at 2200 cm^{-1} attributed to a triple bond. In addition, the nuclear magnetic resonance spectrum (δ ppm in acetone-d_6) showed the following signals; two protons on the nitrofuran ring (7.13, 1H, d, J= 4 Hz, C_4-H and 6.71, 1H, d, J= 4 Hz, C_3-H) and three protons on the furan ring (7.30, 1H, d, J= 2 Hz, C_5,-H, 6.18, 1H, d-d, J= 2;3 Hz, C_4,-H and 6.62, 1H, d, J= 3 Hz, C_3,-H).

The elemental analysis supported a molecular formula $C_{10}H_5O_4N$.

The compounds IIb-h also showed the reasonable results in their various spectra.

This method seems to be especially useful for the nitrofuran derivatives whose general synthesis of β-2-(5-nitrofuryl)acetylenes has been hitherto difficult.

Moreover, there would be possibilities for the application of this method to the other stable primary vinylamines.



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