Chemistry of Heterocyclic Compounds, Vol. 38, No. 6, 2002

REACTION OF 4-AZIDOQUINOLINE N-OXIDE WITH DIMETHYL ACETYLENEDICARBOXYLATE

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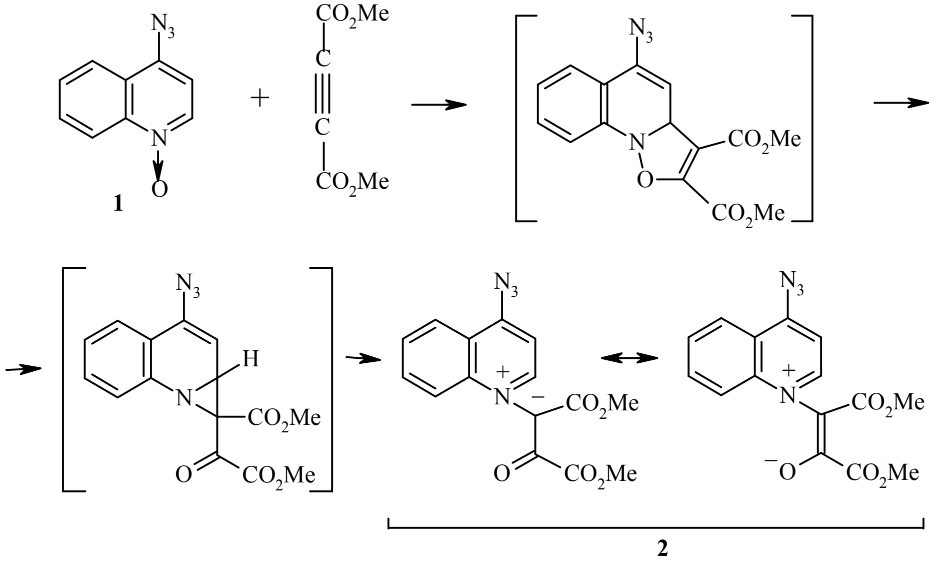
The reaction of 4-azidoquinoline N-oxide with dimethyl acetylenedicarboxylate occurs via a 1,3-dipolar cycloaddition mechanism at the N-oxide and not at the azide group.

Keywords: heteroaromatic N-oxides, N-ylides, 1,3-dipolar cycloaddition.

Aromatic N-oxides are analogs of such 1,3-dipoles as nitrones and can take part in a cycloaddition reaction with unsaturated compounds [1, 2]. However since the dipole of the N-oxides is partially included in the aromatic system, which is disturbed by the formation of new bonds, the initial [3+2] cycloadducts spontaneously rearrange to the more stable aromatic compounds. In addition, it is usually reckoned that heteroaromatic N-oxides are less active in the processes described than are nitrones and other acyclic 1,3-dipoles (azides, aliphatic diazo compounds, nitriloxides etc.). Reports of the 1,3-dipolar cycloaddition reactions of heteroaromatic N-oxides containing 1,3-dipoles other than an N-oxide group are absent in the literature.

In this work we have carried out the reaction of 4-azidoquinoline N-oxide (**1**) with a typical dipolarophile (the dimethyl ester of acetylenedicarboxylic acid) and obtained unexpected results. The addition of the diester occurs at the N-oxide group of the azide **1**, despite the presence in the latter of the active acyclic dipolar azide group.



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The structure of the α-[N-(4-azidoquinolinium)]-α,β-biscarbomethoxy-β-oxoethylylide (**2**) was confirmed by IR and ^{1}H NMR spectroscopic data. A very strong band is present at 2105 cm^{-1} in the IR spectrum of betaine **2** due to the asymmetric stretching vibration of the azide group as well as a weaker band for the symmetric stretching vibration for this group at 1310 cm^{-1}. The strong absorption band for the N→O group seen in the starting N-oxide at 1292 cm^{-1} is absent. In addition, the IR spectrum of betaine **2** shows absorption bands for the C=C double bond at 1620 and the C=O bond at 1723 and 1685 cm^{-1}. The ^{1}H NMR spectrum shows signals for all six aromatic protons and for the 6 protons of the methyl groups.

The starting N-oxide **1** was prepared in about 80% yield by a simple method newly developed by us from the 4-nitroquinoline *via* treatment with sodium azide in the dark for 2-3 days at room temperature.

Compound **1** has been obtained before in 45% yield from 4-chloroquinoline N-oxide and sodium azide at 115-125°C in a sealed ampul [3]. In its turn, the starting 4-chloroquinoline N-oxide was prepared from 4-nitroquinoline N-oxide and acetyl chloride.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AM-500 spectrometer (500 MHz) using TMS as internal standard and DMSO-d$_6$ as solvent. IR Spectra were recorded for 1-2% solutions of the compounds in chloroform on a UR-20 spectrometer and UV spectra in 96% ethanol solutions on a Specord UV-vis spectrometer. Monitoring of the course of the reactions was carried out using TLC in the system chloroform–ethanol (10:1).

4-Azidoquinoline N-Oxide (1). Sodium azide (0.14 g, 2.2 mmol) and water (1 ml) with several drops of ethanol were added to a solution of 4-nitroquinoline N-oxide (0.38 g, 2 mmol) in dioxane (3 ml). The reaction mixture was held at room temperature in the dark for 2-3 days (monitoring by TLC). Solvent was evaporated *in vacuo*, the residue was treated with water (2 ml), and the product **1** was extracted with chloroform (2 × 5 ml). The extract was dried over anhydrous sodium sulfate, chloroform was evaporated off in vacuo, and the residue was recrystallized from acetone to give the light sensitive product **1** (0.30 g, 80.6%); mp 140-142°C (with decomp.) (mp 141-142 °C with decomp. [3]). IR spectrum, ν, cm^{-1}: 2093 (asym. N$_3$ stretch), 1292 (N→O), 1318 (sym. N$_3$ stretch). Electronic spectrum: λ_{max}, nm (log ε): 233 (4.31), 258 (3.96), 355 (3.88).

α-[N-(4-Azidoquinolinium)]-α,β-biscarbomethoxy-β-oxoethylylide (2). Dimethyl acetylenedicarboxylate (0.071 g, 0.5 mmol) was added to a solution of the N-oxide (0.093 g, 0.5 mmol) in chloroform (2 ml). The mixture was stirred at room temperature in the dark for 3-5 h until all of the starting N-oxide **1** had disappeared (by TLC). Solvent was removed in vacuo and the residue was recrystallized from toluene to give the product **2** (0.13 g, 79.3%) as a light yellow, powdery material with mp 171-172°C (with decomp.). ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm, *J* (Hz): 9.05 (1H, d, $J = 7.8$, 2-H); 8.55 (1H, d, $J = 7.8$, 8-H); 8.43 (1H, d, $J = 7.8$, 5-H); 8.12 (1H, m, 7-H); 7.92 (1H, m, 6-H); 7.15 (1H, d, $J = 7.8$, 3-H); 3.96 (3H, s, OCH$_3$); 3.78 (3H, s, OCH$_3$). IR spectrum, ν, cm^{-1}: 2105 (asym. N$_3$ stretch), 1723, 1685 (C=O), 1620 (C=C), 1310 (sym N$_3$ stretch). Electronic spectrum, λ_{max}, nm (log ε): 213 (4.20), 241 (4.32), 260 (4.14), 293 (3.93), 330 (3.85), 400 (3.65). Found, %: C 54.50; N 17.15. $C_{15}H_{12}N_4O_5$. Calculated, %: C 54.88; N 17.07.

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