Chemistry of Heterocyclic Compounds, Vol. 45, No. 6, 2009

THE QUESTION OF THE REGIODIRECTION OF THE [2+3] CYCLOADDITION REACTION OF TRIPHENYLNITRONE TO NITROETHENE

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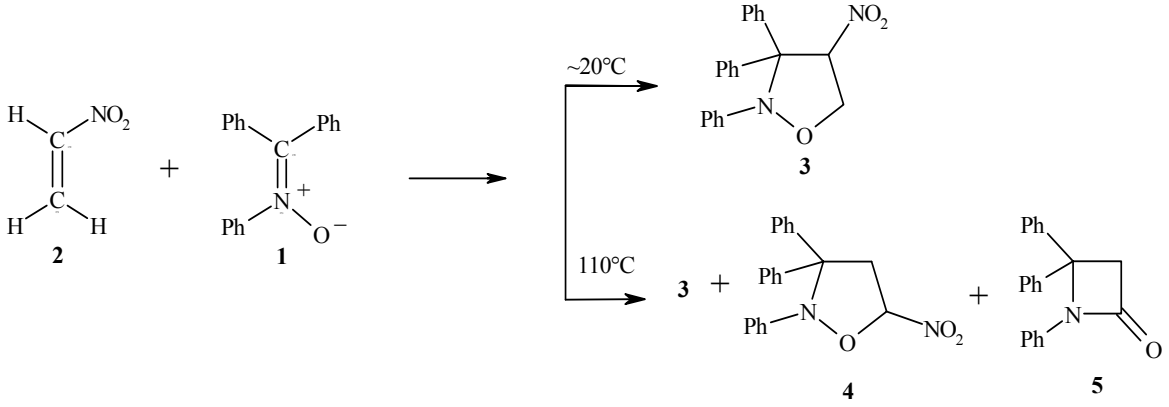
Keywords: nitroalkenes, nitrones, [2+3] cycloaddition, regioselectivity.

It was reported in paper [1] that at room temperature the [2+3] cycloaddition of triphenylnitrone (**1**) to nitroethene (**2**) led to the formation of 4-nitro-2,3,3-triphenylisoxazolidine (**3**) while at 110°C a mixture of compounds was formed, consisting of the nitroisoxazolidine **3**, 5-nitro-2,3,3-triphenylisoxazolidine (**4**), and 2,3,3-triphenylazetidinone (**5**) in a ratio of ~1:1:0.5. However, it should be noted that only the isoxazolidine **3** was isolated in a pure state. The compounds, named by the authors the isoxazolidine **4** and the azetinone **5** were isolated from the product mixture by column chromatography in the form of mixture so that their structures were completely unverified.



Since we had shown previously that in reactions of the nitrone **1** with other conjugated nitroalkenes (1-nitropropene-1 [2, 3], 3,3,3-trichloro-1-nitropropene-1 [3, 4], 2-methoxycarbonyl-1-nitroethene [3]) no 5-nitroisoxazolidines were formed at all, whereas the 4-nitroisoxazolidines were practically the only heterocyclic reaction products, the temperature dependence of the regioselectivity represented in [1] seemed to us debatable. Therefore we have repeated the experiment as described in paper [1]. In the first place we have studied the course of the reaction using HPLC at room temperature. As would be expected, in the reaction mixture,

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No.6, 932-934, June, 2009. Original article submitted September 16, 2008. Revised version submitted April 6, 2009.

independently of the course of the reaction, we observed only one product, the structure of which was established as the nitroisoxazolidine **3** (R_f = 11.7 min) on the basis of elemental analysis and spectral data. Monitoring the reaction at a temperature of 110°C showed that on increasing the temperature cycloaddition of nitrone **1** to the nitroalkene **2** also led to a single cycloadduct which was shown to be the same nitroisoxazolidine **3**. Benzophenone was also formed in small amounts (R_f = 8.4 min). Under the reaction conditions it gradually decomposes forming preferebly the initial materials. We showed in separate experiments that the nitroisoxazolidine is a thermally unstable compound. We also confirmed that nitroethene polymerized at high temperatures [3, 5]. Simultaneously nitrone **1** was slowly converted into benzophenone [6, 7]. Its presence in the reaction mixture was confirmed by HPLC.

Thus our investigations showed that the cycloaddition of nitrone **1** to nitroalkene **2** occurs regioselectively independently of the temperature. The fractions isolated from the product mixture by the authors of paper [1] contained most likely the nitroisoxazolidine **3** and benzophenone, contaminated by oligomers of nitroethene, but none of the expected nitroisoxazolidine **4** and the azetidinone **5**. The presence of benzophenone , caused the apperance of the C=O stretching band (ν 1750 cm^{-1}) in the IR spectrum, which the authors of paper [1] attributed as a sign of the presence of azetidinone **5**.

It should be underlined that the observed regioselectivity of the reaction correlates well with the diagram of the HMO interactions of the substrates [8].

Monitoring of the reactions and control of the purity of compounds was carried out using a Knauer liquid chromatograph (detector UV Smartline 2500, Lichrospher 100-10 RP18 4×240 mm column, eluent 50% (by volume) THF, rate of flow of eluent 1.3 cm^3/min, λ 254 nm). Melting points were measured with a Boetius PHMK-05 apparatus. IR spectra of KBr tablets were measured on a Bio-Rad FTS 175 C apparatus, ^{1}H NMR spectra of $CDCl_3$ solutions with TMS as internal standard with a Tesla BS-567C (80 MHz) spectrometer. Electron impact mass spectra were measured with a Varian MAT-112 instrument (ionization energy 70 eV). UV spectra were recorded with a Specord 75 instrument. Elemental analyses were carried out with a Perkin Elmer PE-2400 CHN analyzer.

Triphenylnitrone 1 and nitroethene 2 were prepared by known methods [9, 10].

4-Nitro-2,3,3-triphenylisoxazolidine (3). Mp 132-135°C (dec). IR spectrum, ν, cm^{-1}: 1562 and 1374 (NO_2), 932 and 918 (isoxazolidine ring). UV spectrum (MeOH), λ_{max}, nm (log ϵ): 211 (4.29), 243 (3.80). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.08 (1H, dd, *J* = 5.6, *J* = 7.6, H-4); 5.11 (1H, dd, *J* = 5.6, *J* = 10.0, H-5); (1H, dd, *J* = 7.6, *J* = 10.0, H-5'). Mass spectrum, *m/z* ($I_{rel,}$ %): 346 $[M]^+$ (50), 273 [M-H_2C=$CHNO_2$] (29), 257 [M-O–H_2C=$CHNO_2$] (5), 180 [M-O–H_2C=$CHNO_2$-C_6H_5] (32), 91 [C_6H_5N] (100). Found, %: C 72.82; H 5.24; N 8.09. $C_{21}H_{18}N_2O_3$. Calculated, %: C 72.71; H 5.12; N 8.10.

REFERENCES

1. M. Burdisso, R. Gandolfi, and P. Grünanger, *Tetrahedron*, **45**, 5579 (1989).
2. R. Jasiński, M. Kwiatkowska, and A. Baranski, *Khim. Geterotsikl. Soedin.,* 1545 (2006). [*Chem. Heterocycl. Comp.,* **42**, 1334 (2006)].
3. R. Jasiński, *Ph .D. Thesis,* Cracow Univ. of Technol. Kraków, 2004.
4. R. Jasiński, E. Brandel, and A. Barański, *Polish J. Chem.,* **78**, 83 (2004).
5. V. V. Perekalin, A. A. Sopova and E. S. Lepina, *Unsaturated Nitrocompounds* [in Russian], Moscow (1966).
6. K. Tae-Rin and L. Kwang-Il, *Bull. Korean Chem. Soc.,* **12**, 273 (1991).
7. J. Villareal, T. S. Dobashi, and E. J. Grubbs, *J. Org. Chem.,* **43**, 1890 (1978).
8. R. Jasiński, A. Tsenzhkovska, A. Lyubimtsev, and A. Barański, *Khim. Geterotsikl. Soedin.,* 243 (2004). [*Chem. Heterocycl. Comp.,* **40**, 206 (2004)].
9. M. Stadinger and M. Miescher, *Helv. Chim. Acta,* **2**, 568 (1919).
10. G. D. Buckley and C. W. Scaife, *J. Chem. Soc.,*1417 (1947).