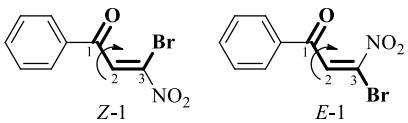
Homo- and heteronuclear NMR spectroscopy experiments in studying structure of 3-bromo-3-nitro-1-phenylprop-2-en-1-one

Adyukov I.S., Pelipko V.V., Baichurin R.I., Makarenko S.V.
Herzen State Pedagogical University of Russia, Department of Organic Chemistry, Laboratory of Nitrocompounds, Center of collective use at the Faculty of Chemistry "Instrumental methods for the study of nitro compounds, coordination, biologically active substances and nanostructured substances" 48 Moyka River Embankment, Saint Petersburg 191186, Russia
E-mail: kohrgpu@yandex.ru
http://kohrgpu.ru, http://ckpo.herzen.spb.ru/?page=organic-chemistry

3-Bromo-3-nitro-1-phenylprop-2-en-1-one **1** is a representative of highly reactive β-functionalized nitroalkenes, that we synthesized according to a literature method [1].

This compound **1** could possibly exist in form of *E*- or *Z*-isomers (C=C) and *s-cis* or *s-trans* conformational isomers (C=O, C=C) which make it an attractive structure for studying by 1D and 2D NMR spectroscopy methods.

The goal of this study was to determine the fine structure of 3-bromo-3-nitro-1-phenylprop-2-en-1-one **1** based on NMR spectroscopy data.



One set of signals in ^{1}H NMR spectrum indicated that compound **1** is stereochemically homogeneous in $CDCl_3$ solution. The C^2H proton signal appears as a singlet at 8.49 ppm in the ^{1}H NMR spectrum of bromonitropropenone **1**, and the aromatic ring protons signals appear as multiplets in the ranges of 7.53-7.57 ppm (H^m), 7.67-7.70 ppm (H^p), and 7.94-7.96 ppm (H^o) respectively (Fig. 1). The ^{13}C-{^{1}H} NMR spectrum also contains one set of signals for all structural fragments (Fig. 2).

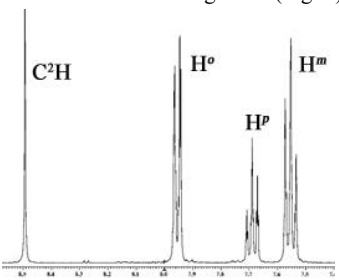


*Figure 1. ^{1}H NMR spectrum of **1** ($CDCl_3$)*

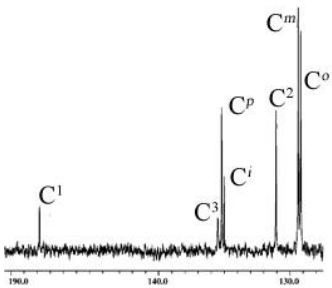


*Figure 2. ^{13}C NMR spectrum of **1** ($CDCl_3$)*

Signals assignment in ^{13}C-{^{1}H} NMR spectra of bromonitropropenone 1 was made by using both ^{1}H-^{13}C HMQC and ^{1}H-^{13}C HMBC experiments. The ^{1}H-^{13}C HMQC spectrum (Fig. 3) revealed cross-peaks between C^2H proton signal (8.49 ppm) and carbon atom signal at 131.06 ppm, as well as between signals of aromatic protons H^o (7.94-7.96 ppm), H^p (7.67-7.70 ppm), and H^m (7.53-7.57 ppm) and carbon atoms at 129.18, 135.19, and 129.36 ppm, respectively. The assignment of quaternary carbon atoms signals was based on ^{1}H-^{13}C HMBC experiment results. Specifically, in the ^{1}H-^{13}C HMBC spectrum of compound **1** (Fig. 4), the C^2H proton signal (8.49 ppm) formed a single cross-peak with the carbon atom at

135.49 ppm (C^3), while the signal of aromatic ring ortho-protons (7.94-7.96 ppm) showed cross-peaks with the carbon atoms at 178.81 ppm (C^1=O) and 135.00 ppm (C^i).

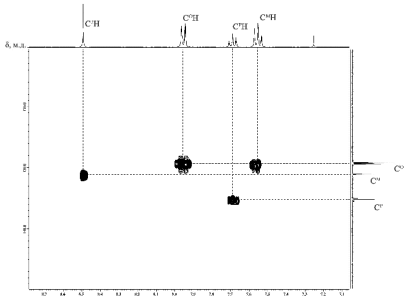


*Figure 3. ^1H-^{13}C HMQC spectrum of **1** ($CDCl_3$)*

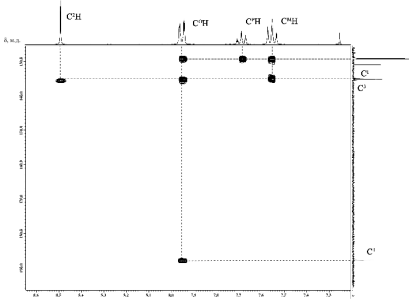


*Figure 4. ^1H-^{13}C HMBC spectrum of **1** ($CDCl_3$)*

Studying compound 1 by ^1H-^{15}N HMBC method revealed that the nitrogen atom of nitro group corresponds to a signal at -16.3 ppm that forms a cross-peak with a C^2H proton signal (8.49 ppm) which correlates with a literature data [2].

Furthermore ^1H-^1H NOESY experiment (Fig. 5) showed that C^2H and Ho proton signals exhibit a NOE effect, indicating their proximity in space and hence s-cis configuration of the C=C and C=O bonds in the molecule.

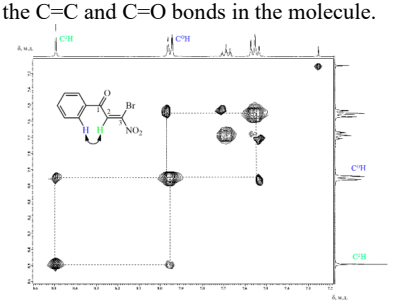


*Figure 5. ^1H-^1H NOESY spectrum of **1** ($CDCl_3$)*

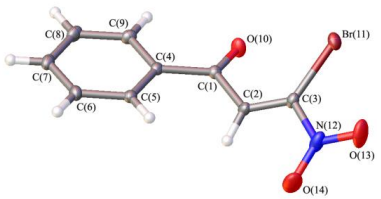


*Figure 6. X-ray analysis of **1***

Assumption about a structure of studying molecule that we had made above is strongly supported by the results of X-ray structural analysis, which prove that compound **1** has a Z-*s-cis* configuration (Fig. 6).

Therefore, by utilizing homo- and heterocorrelation experiments of NMR spectroscopy in studying 3-bromo-3-nitro-1-phenylprop-2-en-1-one **1** allowed a reliable assignment of atoms signals in ^1H, ^{13}C, and ^{15}N NMR spectra, and establish *s-cis* configuration of the molecule.

Acknowlegments

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References

1. Choudhury A. R., Manna M. S., Mukherjee S. *Chem. Sci.*, 2017, *8*, 6686-6690.
2. Kuritsyna M.A., Pelipko V.V., Kataeva O.N., Baichurin R.I. et al. *Rus. Chem. Bull.,* 2021, *70*, 1605-1612.