Application of ^{1}H-^{13}C HMBC NMR spectroscopy for identification of regioisomeric polycyclic dihydrofurans

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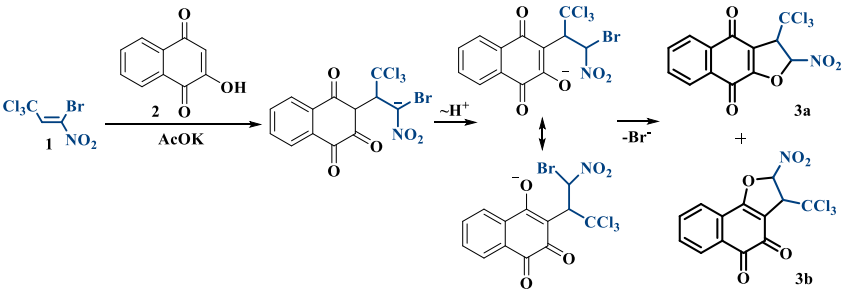
The study of the interaction of 1-bromo-1-nitro-3,3,3-trichloropropene 1 with 2-hydroxy-1,4-naphthoquinone (lawsone) 2 showed that the reaction leads to the formation of a mixture of isomers – condensed 2-nitro-3-trichloromethyl-2,3-dihydrofurans of linear 3a and angular 3b structures, the ratio is ~1:1. The regioisomers were separated using preparative thin-layer chromatography.



The ^{1}H NMR spectra of the isolated compounds 3a, b contain doublets of protons of the dihydrofuran fragment $C^{3}H$ 5.08 ppm and $C^{2}H$ 6.46 ppm (^{3}J = 1.9 Hz) for 3a; $C^{3}H$ 5.02 ppm and $C^{2}H$ 6.51 ppm (^{3}J = 1.6 Hz) for 3b. J-coupling constants ^{3}J ($C^{2}H/C^{3}H$) of the methine protons of the dihydrofuran ring for both isomers indicate their *trans* configuration. The signals of the protons of the naphthoquinone ring $C^{\beta}H$ appear in multiplets at 7.76-7.92 ppm, the protons of $C^{\alpha}H$ form pairs of doublets at 8.17 and 8.23 ppm (3a), 7.93 and 8.25 ppm (3b). The close value of the chemical shifts of $C^{\alpha}H$ protons in 3a allows us to attribute to it the structure of linear dihydrofuran, a significant difference in the chemical shifts of isomer 3b allows us to consider its structure as angular.

The hypothesis is confirmed by the results of the ^{1}H-^{13}C HMBC NMR spectroscopy experiment. Thus, in the HMBC spectrum of compound 3a (Figure 1), cross peaks of doublets of $C^{5}H$ and $C^{8}H$ and two carbonyl carbons C^{4} and C^{9} (8.17/178.92 ppm and 8.22/175.70 ppm) are observed, which clearly proves its linear structure.

Our accepted assignment of regioisomers is additionally confirmed by X–ray diffraction analysis performed for their representative, compound 3a (Figure 2). Its molecule is a linear tricyclic condensed dihydrofuran with a *trans* configuration of $C^{2}H$ and $C^{3}H$ protons.

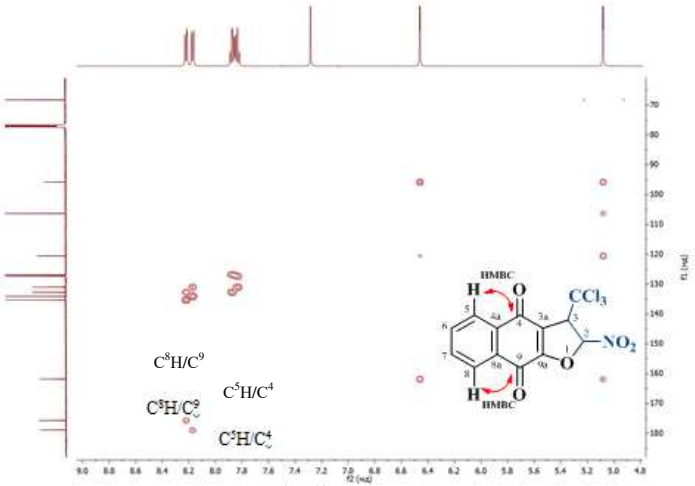


Figure 1. The fragment of ^{1}H-^{13}C HMBC spectrum of compound 3a

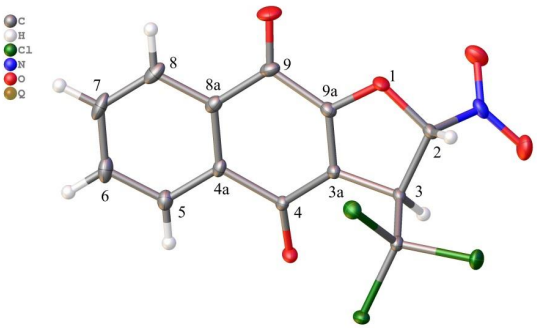


Figure 2. X-ray diffraction analysis of compound 3a

Thus, 1D ^{1}H NMR spectroscopy in combination with 2D methods (^{1}H-^{13}C HMBC) makes it possible to unambiguously determine the structure of polyheterocyclic structures.

Acknowledgements

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