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LETTERS TO THE EDITOR

Nitro- and Trichloromethyl-Functionalized Norbornenes

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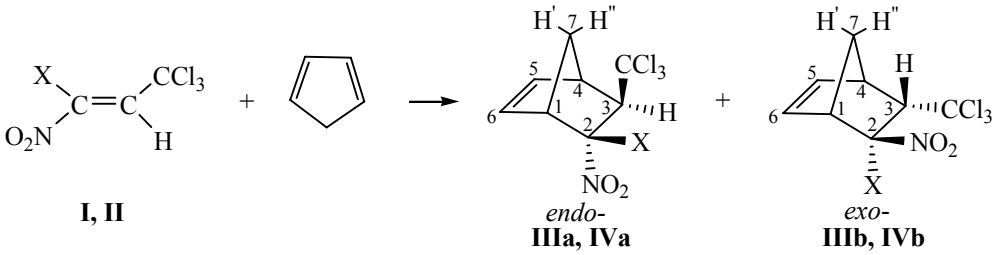
Electron-deficient conjugated nitroalkenes are active dienophiles in the Diels–Alder reactions [1–3]. The introduction of the second electron-withdrawing substituent [CO_2R, $P(O)(OR)_2$, SO_3R, NO_2] into the nitroalkene molecule not only enhances the reactivity of the double bond C=C, but also extends the synthetic potential of the adducts due to the possibility of transforming the substituents into the pharmacophore groups [COOH, SO_3H, $P(O)(OH)_2$, NH_2] [4, 5]. Therefore functionalized adducts of diene synthesis are successfully used as intermediates in the synthesis of natural compounds (epibatidine, efanofin, estrogenic hormones) [1, 6, 7] and drugs (e.g., antiviral preparation, morphine) [8, 9].

It is known that some compounds having a trichloromethyl group in the molecule show fumigant [10] and antimicrobial [11] activity. A convenient method for preparing such substances may be cycloaddition reaction using trichloromethyl-containing nitroalkenes as dienophiles. However, data on the use of these compounds in the diene synthesis is limited to a few examples [12, 13], wherein the spectral characteristics of the formed adducts were not discussed. 1-Bromo-1-nitro-3,3,3-trichloropropene was not used in the Diels–Alder reactions.

We showed that interaction of trichloromethylnitroalkenes **I**, **II** with cyclopentadiene proceeds efficiently under mild conditions (in the solvent-free conditions at room temperature) using equimolar amounts of reactants to form nitronorbornene derivatives **III**, **IV**.

Mitigating the reaction conditions by keeping the reaction mixture at 18–20°C instead of 17-hour boiling (as was done by Yuriev and Zefirov [13]) allowed us increasing the yields of the adducts up to 96%. Nitronorbornenes were obtained as mixtures of *endo* (NO_2)-**IIIa**, **IVa** and *exo*(NO_2)-**IIIb**, **IVb** stereoisomers with a predominant content of **IIIb** and **IVa** isomers in the respective mixtures. The purification and separation of the crude reaction products by column chromatography on silica gel afforded compounds **IIIb** and **IVa** as diastereomerically pure crystalline substances. Minor products **IIIa** and **IVb** were not individually identified.



I, II — *endo*- **IIIa, IVa** — *exo*- **IIIb, IVb**

X = H (**I, IIIa, IIb**), Br (**II, IVa, IVb**).

The composition of the obtained compounds **III** and **IV** was confirmed by elemental analysis data, and their structure, by the IR, ^1H, and ^{13}C NMR spectroscopy. The correct signals assignment was proved by comparison of the data obtained with the corresponding characteristics of the known analogs [14, 15]. Analytical criteria described in [14–16, 17] were used in determining the assignment to the *endo*-(NO_2) or *exo*-(NO_2)-isomer.

Synthesis of the starting nitroalkenes **I**, **II** was carried out according to the known methods [18, 19].

2-Nitro-3-trichloromethylbicyclo[2.2.1]hept-5-ene (IIIa, IIIb). Yield 96%, **IIIa**:**IIIb** = 1:5. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1363, 1553 (NO_2). ***endo*(NO$_2$)-(IIIa).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.74 d (1H, C^7H', $^2J_{HH}$ 9.81 Hz), 2.40 d (1H, C^7H'', $^2J_{HH}$ 9.81 Hz), 3.29 d.d (1H, C^4H, $^3J_{HH}$ 1.83, $^3J_{HH}$ 3.36 Hz), 3.51 d.d (1H, C^1H, $^3J_{HH}$ 3.78, $^3J_{HH}$ 2.75 Hz), 3.60 d.d (1H, C^3H, $^3J_{HH}$ 4.92, $^3J_{HH}$ 1.83 Hz), 5.12 d.d (1H, C^2H, $^3J_{HH}$ 4.92, $^3J_{HH}$ 3.78 Hz), 6.11 d.d (1H, C^6H, $^3J_{HH}$ 2.75, $^3J_{HH}$ 5.55 Hz), 6.69 d.d (1H, C^5H, $^3J_{HH}$ 5.55, $^3J_{HH}$ 3.36 Hz). $^{13}C–\{^1H\}$ NMR spectrum, δ_C, ppm: 46.20, 46.80 (C^7), 47.46 (C^4), 49.33 (C^1), 65.28 (C^3), 87.40 (C^2), 99.57 (CCl_3), 134.04 (C^6), 140.96 (C^5). ***exo*(NO$_2$)-(IIIb).** Mp 28–30° C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.78 d (1H, C^7H', $^2J_{HH}$ 9.40 Hz), 2.19 d (1H, C^7H'', $^2J_{HH}$ 9.40 Hz), 3.37 d.d (1H, C^4H, $^3J_{HH}$ 2.95, $^3J_{HH}$ 2.83 Hz), 4.27 d.d (1H, C^3H, $^3J_{HH}$ 4.86, $^3J_{HH}$ 2.95 Hz), 3.39 d.d (1H, C^1H, $^3J_{HH}$ 1.61, $^3J_{HH}$ 3.36 Hz), 4.49 d.d (1H, C^2H, $^3J_{HH}$ 4.86, $^3J_{HH}$ 1.61 Hz), 6.26 d.d (1H, C^6H, $^3J_{HH}$ 3.36, $^3J_{HH}$ 5.55 Hz), 6.42 d.d (1H, C^5H, $^3J_{HH}$ 5.55, $^3J_{HH}$ 2.83 Hz). $^{13}C–\{^1H\}$ NMR spectrum, δ_C, ppm: 46.83 (C^4), 48.13 (C^7), 52.30 (C^1), 65.93 (C^3), 88.11 (C^2), 99.48 (CCl_3), 132.87 (C^6), 138.38 (C^5). Found, %: C 37.38, 37.41; H 3.00, 3.05; N 5.45, 5.48. $C_8H_8Cl_3NO_2$. Calculated, %: C 37.43; H 3.11; N 5.45.

2-Bromo-2-nitro-3-Trichloromethylbicyclo[2.2.1]-hept-5-ene (IVa, IVb). Yield 93%, **IVa**:**IVb** = 5:1. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1343, 1559 (NO_2). ***endo* (NO$_2$)-(IVa).** Mp 57–59°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.01 d (1H, C^7H', $^2J_{HH}$ 10.22 Hz), 2.77 d (1H, C^7H'', $^2J_{HH}$ 10.22 Hz), 3.40 d.d (1H, C^4H, $^3J_{HH}$ 2.06, $^3J_{HH}$ 2.80 Hz), 3.85 d (1H, C^3H, $^3J_{HH}$ 2.06 Hz), 3.82 d (1H, C^1H, $^3J_{HH}$ 3.24 Hz), 6.10 d.d (1H, C^5H, $^3J_{HH}$ 2.80, $^3J_{HH}$ 5.55 Hz), 6.66 d.d (1H, C^6H, $^3J_{HH}$ 5.55, $^3J_{HH}$ 3.24 Hz). $^{13}C–\{^1H\}$ NMR spectrum, δ_C, ppm: 46.76 (C^7), 48.99 (C^4), 59.50 (C^1), 66.05 (C^3), 94.53 (C^2), 99.01 (CCl_3), 135.10 (C^5), 142.77 (C^6). ***exo* (NO$_2$)-(IVb).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.68 d (1H, C^7H', $^2J_{HH}$ 10.10 Hz), 1.89 d (1H, C^7H'', $^2J_{HH}$ 10.10 Hz), 3.57 d (1H, C^4H, $^3J_{HH}$ 2.70, $^3J_{HH}$ 3.36 Hz), 4.56 d (1H, C^3H, $^3J_{HH}$ 2.70 Hz), 4.00 d (1H, C^1H, $^3J_{HH}$ 2.90 Hz), 6.22 d.d (1H, C^5H, $^3J_{HH}$ 3.36, $^3J_{HH}$ 5.52 Hz), 6.61 d.d (1H, C^6H, $^3J_{HH}$ 2.90, $^3J_{HH}$ 5.52 Hz). Found, %: C 28.83, 28.87; H 2.05, 2.09; N 4.20, 4.25. $C_8H_7Br·Cl_3NO_2$. Calculated, %: C 28.61; H 2.09; N 4.17.

The ^{1}H and ^{13}C NMR spectra ($CDCl_3$) were taken on a Jeol ECX400A spectrometer [400 MHz (^{1}H), 100 MHz (^{13}C)] using residual proton signals of deuterated solvent as internal reference. The IR spectra ($CHCl_3$) were registered on a Shimadzu IR Prestige-21 Fourier-spectrometer in chloroform.

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