

Synthesis and Spectral Characteristics of Unsymmetrical Porphirazines with Triphenylmethyl Groups

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Abstract—Nitration of 4-alkoxy (Alk = Me, Et)-2-(1-nitro-2,3,3-trichloro-2-propenylidene)benzazetines with anhydrous HNO₃ in glacial acetic acid afforded the corresponding 4-alkoxy-3-nitro-2-(1-nitro-2,3,3-trichloro-2-propenylidene)benzazetines. Reaction of compounds obtained with amines involved an isomerization of the benzazetine system into a benzazete one accompanied with conversion of the nitro compound into an aci-form. As a result formed 2,3,3-trichloro-1-(4-alkoxy-3-nitrobenzazet-2-yl)-2-propene-1-nitronic acids salts. The reaction of 4-methoxy-3-nitro-2-(1-nitro-2,3,3-trichloro-2-propenylidene)benzazetine with benzoyl chloride furnished as final product a mixed anhydride of 2,3,3-trichloro-1-(4-alkoxy-3-nitrobenzazet-2-yl)-2-propene-1-nitronic acid.

Benzazetine derivatives are poorly studied nowadays due to their relative inaccessibility and instability of a number of known representatives that is especially characteristic of substances with unsubstituted NH group benzazetinea [1–3]. We recently developed a convenient preparation procedure for stable benzazetines with a nitrotrihalopropenylidene substituent attached to position 2 of the ring by as new heterocyclization process of available 1-azoly-1-arylamino-2-nitrotrihalobutadienes [4]. The arising benzazetines are stabilized by electron density redistribution due to efficient intramolecular interaction between nitro and amino groups.

The goal of this study is investigation of nitration of the previously synthesized 4-alkoxy-2-(1-nitro-2,3,3-trichloro-2-propenylidene)benzazetines **I** and **II** [4] and of some chemical properties of the formed compounds. The reaction of benzazetines **I** and **II** with nitric acid and a nitrating agents may presumably occur either at benzene ring or at amino group. We established that at the use as nitrating agent of a mixture of anhydrous nitric acid and glacial acetic acid the process cleanly proceeded at 10–15°C and afforded in 95–97% yield the substitution products at the position 3 of benzene ring, the corresponding 4-alkoxy-3-nitro-2-(1-nitro-2,3,3-trichloro-2-propenylidene)benzazetines **III** and **IV**.

The composition and structure of obtained compounds **III** and **IV** are proved by elemental analysis, IR, ¹H and ¹³C NMR, and mass spectra. In the IR spectrum of benzazetines **III** and **IV** to symmetric and antisymmetric

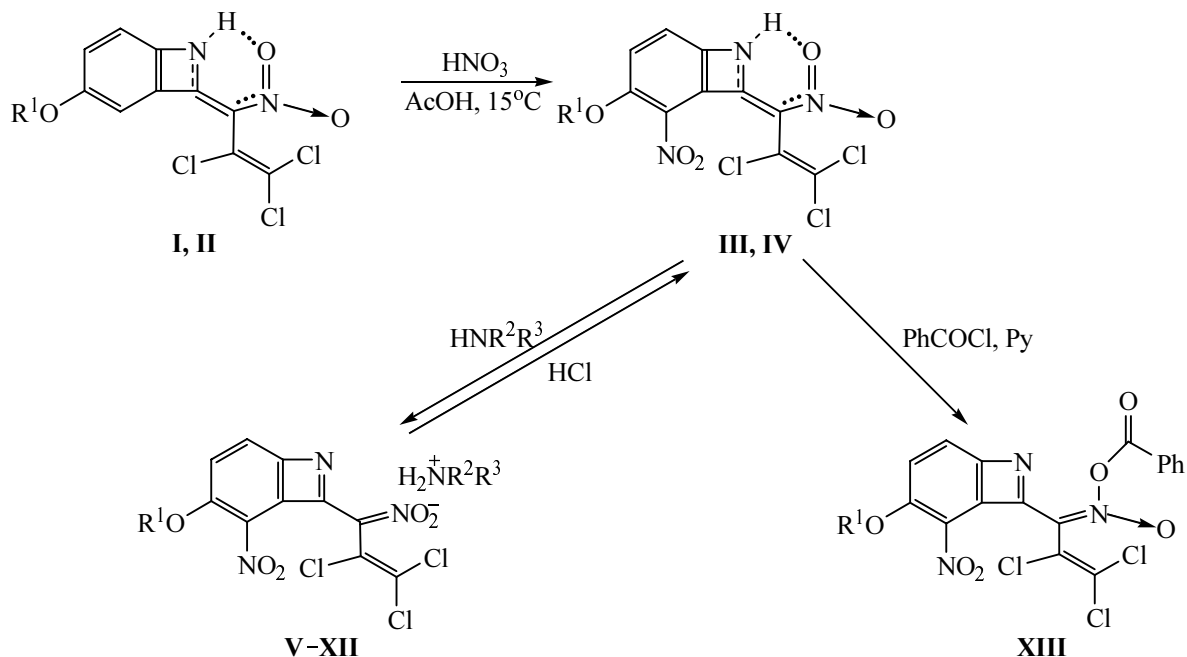
vibrations of nitro groups belong absorption bands at 1348–1386 and 1530–1553 cm⁻¹, vibrations of the C=C bonds give rise to bands in the region 1491–1496 and 1556–1640 cm⁻¹, a very strong absorption band at 1676 (**III**) and 1658 cm⁻¹ (**IV**) corresponds to C=N bonds arising from redistribution of the electron density between nitro and amino groups in the molecules of benzazetines **III** and **IV** with formation of a six-membered ring that stabilizes the molecule and that is characteristic of nitroenamines [5]. The broadened bands in the 3310–3350 cm⁻¹ range originate from vibrations of the bonded NH groups and they additionally confirm the intramolecular interaction between NH and nitro groups. The nitro group position at the C³ atom of the benzene ring is unambiguously confirmed by the character and multiplicity of signals in the ¹H NMR spectra of compounds **III** and **IV**. Alongside the signals of the hydrogen-containing alkoxy groups two doublets are observed in the spectra with chemical shifts 7.48 and 7.66 ppm for compound **III** and 7.73 and 7.86 ppm for compound **IV** belonging to the hydrogen atoms at the aromatic ring. The coupling constant of the aromatic protons ³J amounts to 9 Hz unambiguously indicating their *ortho*-position in agreement with the literature data on substituted benzene derivatives [6].

In the mass spectra of compounds **III** and **IV** groups of molecular ion peaks are present where the ratio of isotope peaks is 100:98:32:3.5 indicating the presence in the molecule of three chlorine atoms [7, 8]. Fragment peaks are also observed in the spectra originating from

the loss of chlorine, nitro and alkyl groups under the electron impact.

We investigated the reactions of obtained nitro-substituted benzazetines **III** and **IV** with some amines and benzoyl chloride. We applied as amines morpholine, piperidine, diethylamine, and *tert*-butylamine. It was established that in ether or benzene the reaction of amines with benzazetines **III** and **IV** is accompanied by conversion

of the benzazetine system into a benzazete one, and there-with in the side nitrochloroaliphatic chain arises an acinitro form, and the resulting products are the corresponding salts of nitronic acids **V–XII** obtained in 79–97% yield. Salts **V–XII** are stable compounds, well soluble in water, alcohol, acetone, sparingly soluble in hydrocarbons. Treating the salts with hydrochloric acid provided the initial compounds **III** and **IV** in a quantitative yield.



$\text{R}^1 = \text{CH}_3$ (**I, III, V, VII, IX, XI, XIII**), C_2H_5 (**II, IV, VI, VIII, X, XII**); $\text{R}^2 = \text{H}$, $\text{R}^3 = t\text{-Bu}$ (**V, VI**); $\text{R}^2 = \text{R}^3 = \text{Et}$ (**VII, VIII**); $\text{R}^2, \text{R}^3 = (\text{CH}_2)_5$ (**IX, X**); $\text{R}^2, \text{R}^3 = (\text{CH}_2)_2\text{O}(\text{CH}_2)_2$ (**XI, XII**).

The reaction of 4-methoxy-3-nitro-2-(1-nitro-2,3,3-trichloro-2-propenylidene)benzazetine **III** with benzoyl chloride did not occur at boiling the reagents in benzene, but the process in the presence of pyridine with equimolar amounts of reagents afforded mixed anhydride of benzoic and nitronic acid, benzoic-2,3,3-trichloro-1-(4-methoxy-3-nitrobenzazet-2-yl)-2-propene-1-nitronic anhydride (**XIII**) in 72% yield. The presence of pyridine in the reaction mixture presumably facilitates the isomerization of the benzazetine into benzazete system and proton transition from amino to nitro group giving an *aci*-form that reacts further with benzoyl chloride. The liberating hydrogen chloride is bound by pyridine.

Salts **V–XII** and anhydride **XIII** were identified with the use of elemental analysis, IR, ^1H and ^{13}C NMR, and mass spectra. In the IR spectra of compounds vibrations of $\text{C}=\text{N}$ bonds appear as absorption bands in the region

$1627\text{--}1669\text{ cm}^{-1}$, to the symmetric and antisymmetric vibrations of $\text{N}=\text{O}$ bonds belong absorption bands in the region $1345\text{--}1386$ and $1510\text{--}1550\text{ cm}^{-1}$ respectively. The NH_3^+ and NH_2^+ groups of salts **V, VI**, and **VII–XII** are characterized by broad bands with several maxima in the region $2980\text{--}2600\text{ cm}^{-1}$. The vibrations of $\text{C}=\text{O}$ group of anhydride **XIII** give rise to a strong absorption band at 1784 cm^{-1} .

In the ^1H NMR spectra of salts **V–XII** alongside the proton signals of alkoxy groups, amine groups, and those of benzene ring in the region δ 7.20–7.35 ppm appear broadened singlets corresponding to groups NH_3^+ (**V, VI**) and NH_2^+ (**VII–XII**). In the ^1H NMR spectrum of anhydride **XIII** the singlet is present of methoxy group at 3.97 ppm and a multiplet in the region 7.40–8.25 ppm belonging to the protons from the benzazete moiety and the benzoic fragment. The intergral intensities are consistent with the assumed structure.

In the mass spectra of salts **V–XII** the molecular ion peaks are lacking, and groups of ions are observed originating from elimination of amine molecule, chlorine atoms, and nitro groups. In the mass spectrum of the mixed anhydride **XIII** a group of molecular ion peaks is observed with the ratio of isotope peaks intensities (100:98:32:3.5) confirming the presence of three chlorine atoms in the molecule [7, 8]. In the spectrum appeared also peaks of fragment ions arising at elimination of benzoyl fragment, methoxy group, nitro group, and chlorine atom.

EXPERIMENTAL

IR spectra of compounds were recorded on Fourier spectrophotometer Protege-460 from samples pelletized with KBr. ^1H and ^{13}C NMR spectra were registered on spectrometer Tesla-567A (100 MHz) from solutions in CD_3COCD_3 , chemical shifts were measured from TMS. Mass spectra were taken on a mass spectrometer MKh-1320 at ionizing electrons energy 50 eV.

4-Methoxy-3-nitro-2-(1-nitro-2,3,3-trichloro-2-propenylidene)benzazetine (III). To a dispersion of 2 g (6 mmol) of benzazetine **I** in 20 ml of glacial acetic acid at 15°C was added 8 ml of anhydrous nitric acid (d 1.5); therewith the mixture got homogeneous, and it was stirred for 6 h. Afterwards it was poured on ice, the precipitate formed was filtered off, washed with water, ether, and recrystallized from ether–hexane mixture, 6:1. We obtained 2.13 g (97%) of compound **III**, mp $164\text{--}166^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1351, 1385 ($\nu_s \text{NO}_2$), 1531, 1553 ($\nu_{as} \text{NO}_2$), 1491, 1588, 1640 (C=C), 1676 (C=N), 3350 (NH). ^1H NMR spectrum, δ , ppm: 3.97 s (3H, CH_3O), 7.49 d (1H arom, 3J 9.3 Hz), 7.66 d (1H arom, 3J 9.3 Hz), 11.20 br.s (1H, NH). ^{13}C , δ , ppm: 58.75 (CH_3O), 120.25, 121.31 (CH arom), 119.69, 123.13, 127.93, 128.73, 133.05, 136.67, 148.97, 153.91 (C arom, C diene). Found, %: C 36.38; H 1.73; Cl 28.79; N 11.64. $[M]^+$ 365. $\text{C}_{11}\text{H}_6\text{Cl}_3\text{N}_3\text{O}_5$. Calculated, %: C 36.04; H 1.65; Cl 29.02; N 11.46. M 366.55.

3-Nitro-4-ethoxy-2-(1-nitro-2,3,3-trichloro-2-propenylidene)benzazetine (IV) was prepared in a similar way by nitration of 2-(1-nitro-2,3,3-trichloro-2-propenylidene)-4-ethoxybenzazetine (**II**). Yield 95%, mp $172\text{--}173^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1348, 1386 ($\nu_s \text{NO}_2$), 1530, 1545 ($\nu_{as} \text{NO}_2$), 1496, 1556, 1596, 1620 (C=C), 1658 (C=N), 3310 (NH). ^1H NMR spectrum, δ , ppm: 1.35 t (3H, CH_3), 4.33 q (2H, CH_2O), 7.73 d (1H arom, 3J 9.3 Hz), 7.86 d (1H arom, 3J 9.3 Hz), 11.30 br.s (1H, NH). ^{13}C , δ , ppm: 15.20 (CH_3), 68.02 (CH_2O), 120.20, 122.55

(CH arom), 119.70, 123.18, 127.93, 128.77, 133.50, 136.64, 148.26, 153.98 (C arom, C diene). Found, %: C 37.58; H 2.47; Cl 27.73; N 11.17. $[M]^+$ 379. $\text{C}_{12}\text{H}_8\text{Cl}_3\text{N}_3\text{O}_5$. Calculated, %: C 37.87; H 2.12; Cl 27.85; N 11.04. M 380.57.

2,3,3-Trichloro-1-(4-methoxy-3-nitrobenzazet-2-yl)-2-propene-1-nitronic acid tert-butylammonium salt (V). To a dispersion of 0.74 g (2 mmol) of benzazetine **III** in 30 ml of anhydrous benzene was poured a solution of 0.16 g (2.2 mmol) of *tert*-butylamine in 10 ml of benzene, and the reaction mixture was stirred at 20°C for 4 h. The precipitate was filtered off, washed with benzene and hexane, and dried in a vacuum to obtain 0.73 g (83%) of compound **V**, mp $151\text{--}153^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1345, 1382 (NO_2), 1513, 1545 (NO_2), 1461, 1610, 1636 (C=C, C=N). ^1H NMR spectrum, δ , ppm: 1.35 s (9H, CH_3C), 3.95 s (3H, CH_3O), 7.25 br.s (3H, NH_3^+), 7.61 br.s (2H arom). Found, %: C 40.85; H 4.12; Cl 24.37; N 12.96. $[M - \text{Me}_3\text{CNH}_2]^+$ 365. $\text{C}_{15}\text{H}_{17}\text{Cl}_3\text{N}_4\text{O}_5$. Calculated, %: C 40.97; H 3.90; Cl 24.19; N 12.74. M 439.71.

Compounds **VI–XII** were prepared similarly from benzazetines **III** and **IV** and appropriate amines.

2,3,3-Trichloro-1-(4-ethoxy-3-nitrobenzazet-2-yl)-2-propene-1-nitronic acid tert-butylammonium salt (VI). Yield 97%, mp $163\text{--}165^\circ\text{C}$ (decomp.). IR spectrum, ν , cm^{-1} : 1348, 1382 ($\nu_s \text{NO}_2$), 1514, 1547 ($\nu_{as} \text{NO}_2$), 1454, 1607, 1642 (C=C, C=N). ^1H NMR spectrum, δ , ppm: 1.30 t (3H, $\text{CH}_3\text{CH}_2\text{O}$), 1.46 s (9H, CH_3C), 4.25 q (2H, CH_2O), 7.35 br.s (3H, NH_3^+), 7.57 br.s (2H arom). Found, %: C 42.08; H 4.03; Cl 23.19; N 12.51. $[M - \text{Me}_3\text{CNH}_2]^+$ 379. $\text{C}_{16}\text{H}_{19}\text{Cl}_3\text{N}_4\text{O}_5$. Calculated, %: C 42.36; H 4.22; Cl 23.44; N 12.35. M 453.72.

2,3,3-Trichloro-1-(4-methoxy-3-nitrobenzazet-2-yl)-2-propene-1-nitronic acid diethylammonium salt (VII), 80%, mp $134\text{--}136^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1347, 1385 ($\nu_s \text{NO}_2$), 1512, 1550 ($\nu_{as} \text{NO}_2$), 1439, 1607, 1669 (C=C, C=N). ^1H NMR spectrum, δ , ppm: 3.95 s (3H, CH_3O), 3.02–3.30 m (4H, CH_2NCH_2), 3.61–3.86 m (4H, CH_2OCH_2), 7.25 br.s (2H, NH_3^+), 7.75 br.s (2H arom). Found, %: C 40.02; H 3.19; Cl 23.49; N 12.31. $[M - \text{C}_4\text{H}_9\text{NO}]^+$ 365. $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{N}_4\text{O}_6$. Calculated, %: C 39.71; H 3.34; Cl 23.44; N 12.35. M 453.69.

2,3,3-Trichloro-1-(4-ethoxy-3-nitrobenzazet-2-yl)-2-propene-1-nitronic acid morpholine salt (XII). Yield 96%, mp $168\text{--}170^\circ\text{C}$ (decomp.). IR spectrum, ν , cm^{-1} : 1347, 1383 ($\nu_s \text{NO}_2$), 1510, 1549 ($\nu_{as} \text{NO}_2$), 1451, 1602, 1627 (C=C, C=N). ^1H NMR spectrum, δ , ppm: 1.34 t (3H, CH_3), 3.06–3.33 m (4H, CH_2NCH_2), 3.69–

3.95 m (4H, CH₂OCH₂), 4.29 q (2H, CH₂O), 7.35 br.s (2H, NH₂⁺), 7.72 br.s (2H arom). Found, %: C 41.25; H 3.99; Cl 22.82; N 12.11. [*M*-C₄H₉NO]⁺ 379. C₁₆H₁₇Cl₃N₄O₆. Calculated, %: C 41.09; H 3.67; Cl 22.74; N 11.98. *M* 467.70.

Benzoic-2,3,3-trichloro-1-(4-methoxy-3-nitrobenzazet-2-yl)-2-propene-1-nitronic anhydride (XIII). A mixture of 0.74 g (2 mmol) of 1,2-dihydrobenzazete **III**, 0.34 g (2.4 mmol) of benzoyl chloride, and 0.19 g (2.4 mmol) of pyridine in 80 ml of benzene was stirred at 20°C for 10 h. Then the solution was filtered, evaporated to dryness, the residue was washed with hexane and extracted with ether. The ether solution was diluted with hexane, the separated precipitate was filtered off, washed with hexane, and dried in a vacuum to give 0.68 g (72%) of anhydride **XIII**, mp 96–98°C. IR spectrum, ν, cm⁻¹: 1351, 1382 (NO₂), 1527, 1546 (NO₂), 1489, 1599, 1640, 1658 (C=C, C=N), 1784 (C=O). ЯМР ¹H NMR spectrum, δ, ppm: 3.97 s (3H, OCH₃), 7.40–8.25 m (7H, C₆H₅ and C₆H₂). Found, %: C 46.17; H 1.99; Cl 22.78; N 8.61. [*M*]⁺ 469. C₁₈H₁₀Cl₃N₃O₆. Calculated, %: C 45.93; H 2.15; Cl 22.60; N 8.39. *M* 470.66.

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