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Reactions of 2-Nitro- and 2-Bromo-2-nitroethenylphosphonates with Anthracene

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Abstract—Bis(2-chloroethyl) 2-nitro- and 2-bromo-2-nitroethenylphosphonates react with anthracene along two competing pathways: [4+2] cycloaddition and electrophilic substitution; in the case of the bromo derivative, the resulting products undergo dehydrobromination under the reaction conditions to form anthracene- and dihydroanthracene-containing nitroethenylphosphonates.

Phosphorylated nitro- and *gem*-halonitroethenes are highly reactive. These compounds were used to prepare phosphorus-containing arylamino- and aminoarylnitroethanes; nitro enamines and aminonitrostyrenes; and indolylnitroethanes and nitrovinylindoles [1–9]. Previously we studied the reactions of nitro- and *gem*-bromonitroethenylphosphonates with 1,3-dienes (2,3-dimethyl-1,3-butadiene, cyclopentadiene, furan, 1,3-cyclohexadiene) [10–12].

In this study we examined the behavior of nitro- and *gem*-bromonitroethenylphosphonates **I** and **II** in the Diels–Alder reaction with anthracene as diene component.

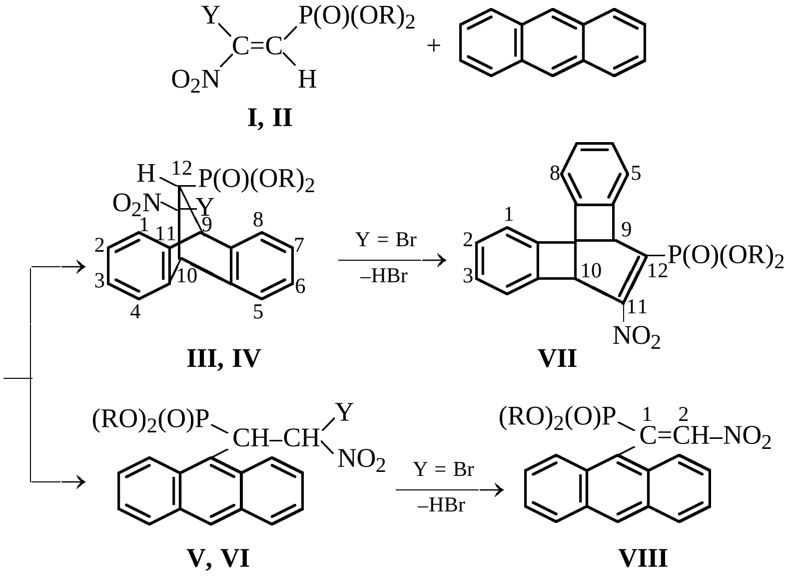
It is known that anthracene reacts with nitroethylene and its alkyl and aryl derivatives under severe conditions (in an ampule at 110–150°C) to form the corresponding nitroethanoanthracenes in 1–36% yields [13–16]. The low yield of the substituted ethanoanthracenes is accounted for in these papers by the aromaticity of anthracene, distinguishing it from other dienes [16], and by the possible retro-diene process largely characteristic of anthracene derivatives. At the same time, β-phenylsulfonylnitroethene containing one more electron-withdrawing substituent (SO_2Ph) in the vicinal position relative to the nitro group reacts with anthracene under relatively mild conditions (refluxing in toluene for 3 h), with 90% yield of the adduct [17, 18].

We found that, in contrast to the above examples, bis(2-chloroethyl) 2-nitroethenylphosphonate **I** and 2-bromo-2-nitroethenylphosphonate **II** react with anthracene peculiarly. First, the reactions occur under more severe conditions compared to the reaction with the sulfonyl-containing nitroalkene: The Diels–Alder adducts **III** and **IV** are formed in low yields (20 and 18%, respectively) upon refluxing of **I** or its brominated analog **II** with anthracene in benzene for 17 h. Second, the reaction mixtures contained, along with **III** and **IV**, also products **V** and **VI**, apparently formed by electrophilic substitution involving an attack of electron-deficient nitroethenylphosphonate molecules at the electron-excessive *meso*-position of anthracene [19].

Under more severe conditions (refluxing in toluene for 21 h), the yield of **IV** in the reaction of **II** with anthracene increased to 42%. However, in so doing, the reaction was complicated by intramolecular dehydrohalogenation of **IV** to bis(2-chloroethyl) 9,10-dihydro-9,10-(11-nitroetheno)-antracen-12-ylphosphonate **VII** and of **VI** to bis(2-chloroethyl) 1-(anthracen-9-yl)-2-nitroethenylphosphonate **VIII**. Compounds **VII** and **VIII** were isolated pure by column chromatography in 7 and 6% yields, respectively. Compound **VII** was also prepared directly by dehydrohalogenation of 9,10-dihydro-9,10-(11-bromo-11-nitroethano)anthracene **IV** in the presence of pyridine in 25% yield.

The structures of phosphorylated 9,10-dihydro-9,10-(11-nitroethano)anthracenes **III** and **IV** were determined by comparing their ^1H NMR and IR spectra with those of the structurally related compounds described in the literature, e.g., 9,10-dihydro-9,10-(12-phenylsulfonyl-11-nitroethano)anthracene [18].

The ^1H NMR spectra of **III** and **IV** contain well separated signals from aromatic ring (H^1–H^4, H^5–H^8), bridgehead (H^9, H^{10}), and bridge (H^{11}, H^{12}) protons (Fig. 1, Table 1). The protons of two aromatic rings give multiplets at 7.20–7.43 ppm; the bridgehead protons H^{10} and H^9 in the spectrum of **IV** give two separate signals (a singlet and a doublet of doublets, respectively). The signals from the bridge protons H^{11} and H^{12} lie in the range 4.41–5.13 ppm, and each of these protons gives a separate signal split owing to



R = CH_2CH_2Cl, Y = H (**I, III, V**), Br (**II, IV, VI**); R = CH_2CH_2Cl (**VII, VIII**).

coupling with the adjacent proton. The phosphorus signal is a singlet at 25.5 ppm. No doubling of the signals of ring protons and phosphorus nuclei is observed in the ^1H and ^{31}P NMR spectra of **III** and **IV**, which suggests that these compounds are stereochemically uniform. However, the magnetically anisotropic aromatic rings in **III** and **IV** make the protons of the chloroethoxy groups nonequivalent, probably because of their different steric orientation relative to the benzene rings [20].

The geometric structure of **III** and **IV**, as in the case

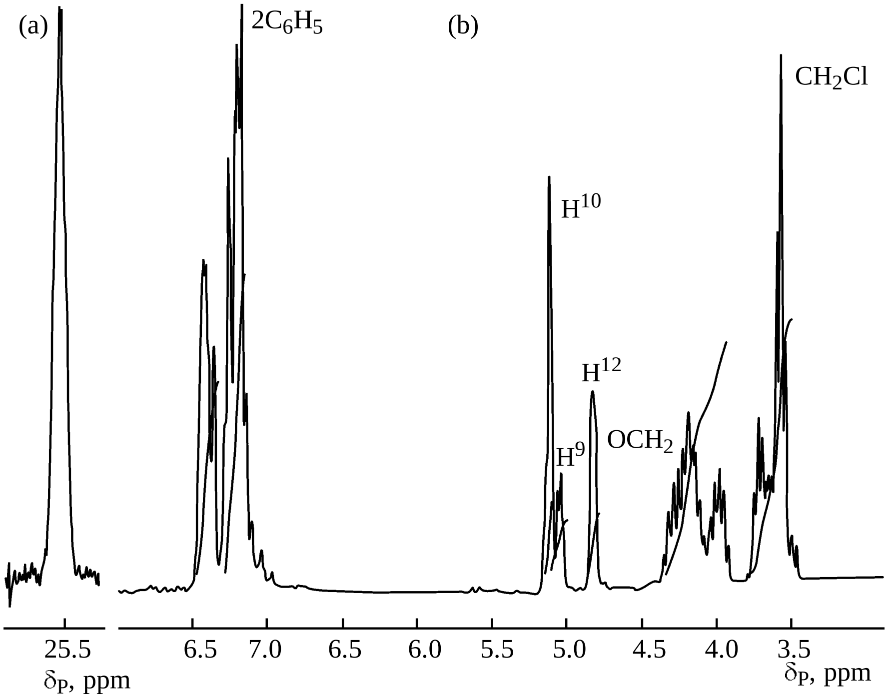


Fig. 1. (a) ^{31}P–{^1H} and (b) ^1H NMR spectra of bis(2-chloroethyl) 9,10-dihydro-9,10-(11-bromo-11-nitroethano)anthracen-12-ylphosphonate **IV** in $CDCl_3$.

Table 1. ^1H and ^{31}P NMR spectra of phosphorylated 9,10-dihydro-9,10-(11-nitroethano)anthracenes **III** and **IV** in $CDCl_3$

Comp. no.	^1H NMR spectrum, δ, ppm (*J*, Hz)							^{31}P NMR spectrum, δ_P, ppm
	H^9	H^{10}	H^{11}	H^{12}	OCH_2	CH_2Cl	Ar	
III	4.81 (J_{H^9P} 4.5, $J_{9,12}$ 1.5)	5.40 ($J_{10,11}$ 4.0)	5.13 ($J_{10,11}$ 4.0, $J_{11,12}$ 2.5, $J_{H^{11}P}$ 4.0)	4.41 ($J_{9,12}$ 1.5, $J_{11,12}$ 2.5, $J_{H^{12}P}$ 10.2)	4.02 m, 4.19 m	3.50 m, 3.65 m	7.23 m, 7.43 m	25.5
IV	5.08 (J_{H^9P} 17.0, $J_{9,12}$ 3.2)	5.15 s	–	4.88 ($J_{H^{12}P}$ 3.0, $J_{9,12}$ 3.2)	4.00 m, 4.20 m	3.50 m, 3.67 m	7.20 m, 7.42 m	25.5

Table 2. ^1H and ^{31}P NMR spectra of nitro phosphoryl anthracene derivatives **V**, **VI**, and **VIII** in $CDCl_3$

Comp. no.	^1H NMR spectrum, δ, ppm (*J*, Hz)					^{31}P NMR spectrum, δ_P, ppm
	H^1	H^2	OCH_2	CH_2Cl	Ar	
V	4.82 ($J_{H^1H^2}$ 5.0, $^2J_{HP}$ 3.8)	5.20 ($J_{H^1H^2}$ 5.0, J_{H^2P} 7.6)	4.00 m	3.56 m	7.20 m, 7.40 m	17.5
VI	5.00 ($^3J_{HH}$ 2.9, $^2J_{HP}$ 0)	6.37 ($^3J_{HH}$ 2.9, J_{H^2P} 3.0)	4.20 m	3.70 m	7.20 m, 7.42 m	17.0
VIII	–	7.2 (Ar)	4.20 m	3.70 m	7.0–7.2 m, 7.3–7.5 m	8.4

of the model compound, stereochemically uniform *trans*-disubstituted 9,10-dihydro-9,10-(12-phenylsulfonyl-11-nitroethano)anthracene [18], corresponds to the *trans* arrangement of the phosphoryl and nitro groups. Specifically this orientation is characteristic of these substituents in the starting nitro- and halonitroethenylphosphonates, and it is known that the Diels–Alder reaction is characterized by preservation of the configuration of the dienophile [21, 22]. In the case of **III**, such a geometry is confirmed by the coupling constant $^3J_{H^{11}P}$ 4 Hz, corresponding to the dihedral angle $HC^{11}C^{12}P$ within 0°–90° [23].

The suggested structure of **VII** is supported by its ^{31}P NMR spectrum containing a signal at 8.5 ppm, which corresponds to the phosphorus atom at an sp^2-hybridized carbon atom, and ^1H NMR spectrum (δ, ppm): 5.3 s (H^9), 6.5 s (H^{10}), 7.0–7.3 m, 7.7–7.9 m ($2C_6H_4$), 4.30 (OCH_2), 3.63 (CH_2Cl). It should be noted that, according to [18], 9,10-dihydro-9,10-(etheno)anthracene is formed by reductive elimination of the nitro and phenylsulfonyl groups from 9,10-dihydro-9,10-(12-phenylsulfonyl-11-nitroethano)anthracene. The products of electrophilic substitution in anthracene, bis(2-chloroethyl) 1-(anthracen-9-yl)-2-nitroethylphosphonates **V** and **VI**, were obtained only in mixtures with other substances. Their structures were determined from the ^1H and ^{31}P NMR spectra. The molecules of these compounds contain cyclic and acyclic protons whose signals are well separated (Table 2); the protons of the aromatic rings of anthracenes are manifested in the range 7.0–7.5 ppm as two complex multiplets. The signals of the CH^1P protons in **V** and **VI** are observed at 4.82 and 5.00 ppm, and the signals of methylene (CH_2NO_2) and methine ($CHBrNO_2$) protons, at 5.20 and 6.37 ppm. In the spectrum of **VIII**, the signal of the nitroolefin proton (CH^2NO_2), as expected, is observed in a still lower field at 7.2 ppm among the multiplets of the aromatic ring protons (Table 2).

The IR spectra of **III**, **IV**, **VII**, and **VIII** contain the characteristic bands of all the functional groups. The alkoxyphosphoryl group gives three strong bands at 1025–1035, 1080, and 1260–1265 cm^{-1}. The nonconjugated nitro group is manifested at 1365–1370 and 1560–1565 cm^{-1} for **III** and **IV**, and the conjugated nitro group in **VII** and **VIII**, at 1535–1550 and 1350–1360 cm^{-1}.

Thus, 2-nitro- and 2-bromo-2-nitroethenylphosphonates react with anthracene along two pathways: [4+2] cycloaddition and electrophilic substitution in the *meso*-positions of anthracene. In the case of the bromo derivative, the adducts under the reaction conditions undergo dehydrobromination to form the corresponding nitroethenylphosphonates with antracene and dihydroanthracene substituents.

EXPERIMENTAL

The IR spectra were taken on an Infralyum FT-02 spectrometer (0.1–0.001 M solutions in $CHCl_3$). The ^1H and ^{31}P NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz, $CDCl_3$). The chemical shifts δ were determined relative to external HMDS (^1H) with an accuracy of ±0.5 Hz; for ^{31}P, the external reference was 85% H_3PO_4.

The purity of the compounds and the reaction progress were monitored by TLC on Silufol UV-254 plates with hexane–acetone (3 : 2) as eluent and iodine vapor as developer. The pure compounds were isolated by column chromatography on Chemapol 100/200 silica gel using the Trappe solvent series [24].

The starting nitro- and *gem*-bromonitroethenylphosphonates **I** and **II** were prepared according to [1, 25].

Bis(2-chloroethyl) 9,10-dihydro-9,10-(11-nitroethano)anthracen-12-ylphosphonate III and bis(2-chloroethyl) 1-(anthracen-9-yl)-2-nitroethylphosphonate V. Anthracene (0.32 g) was added to a solution of 0.50 g of bis(2-chloroethyl) 2-nitroethenylphosphonate **I** in 10 ml of absolute benzene. The mixture was refluxed for 17 h. After cooling, 20–30 ml of hot benzene was added; excess anthracene was filtered off. The filtrate was evaporated on a rotary evaporator, and the oily residue was chromatographed on silica gel. From the fraction eluted with chloroform, 0.20 g of a 1 : 5 mixture of **III** and **V** was isolated. From the fraction eluted with a 1 : 1 chloroform–diethyl ether mixture, 0.16 g (20%) of **III** was isolated as an oil, R_f 0.68. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1370, 1560 (NO_2), 1265 (P=O), 1035, 1080 (POC). Found, %: C 52.53, 52.56; H 4.91, 4.96; N 3.01, 3.04; P 6.73, 6.88. $C_{20}H_{20}Cl_2NO_5P$. Calculated, %: C 52.63; H 4.38; N 3.07; P 6.80.

Bis(2-chloroethyl) 9,10-dihydro-9,10-(11-bromo-11-nitroethano)anthracen-12-ylphosphonate IV, bis(2-chloroethyl) 1-(anthracen-9-yl)-2-bromo-2-nitroethylphosphonate VI, bis(2-chloroethyl) 9,10-dihydro-9,10-(11-nitroetheno)anthracen-12-ylphosphonate VII, and bis(2-chloroethyl) 1-(anthracen-9-yl)-2-nitroethenylphosphonate VIII. *a. In benzene.* Anthracene (1.20 g) was added to a solution of 1.20 g of bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonate **II** in 20 ml of benzene. The mixture was refluxed for 17 h. After cooling, excess anthracene was filtered off, and the filtrate was evaporated on a rotary evaporator. The oily residue was chromatographed on silica gel. From the fraction eluted with CCl_4, we isolated 0.32 g (18%) of **IV** as a green oil, R_f 0.51. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1370, 1565 (NO_2), 1262 (P=O), 1025, 1080 (POC). Found, %: C 44.81, 44.82; H 3.19, 3.21; N 2.93, 2.94; P 5.73, 5.88. $C_{20}H_{19}BrCl_2NO_5P$. Calculated, %: C 44.85; H 3.55; N 2.62; P 5.79. From the fraction eluted with ether, we isolated 0.28 g of a 5 : 2 mixture of **IV** and **VI**.

b. In toluene. Anthracene (1.20 g) was added to a solution of 1.20 g of bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonate **II** in 10 ml of toluene. The mixture was refluxed for 21 h. After cooling, the mixture was extracted with ether (5 × 20 ml). The ether extracts were evaporated, and the oily residue was chromatographed on silica gel. From the fraction eluted with CCl_4, we isolated 1.00 g of a 6 : 1 mixture of **IV** and **VII**, and from the fraction eluted with $CHCl_3$, 0.36 g of a 1 : 2 : 2 mixture of **VI**–**VIII**. By repeated chromatography of the latter mixture, we isolated the following compounds. From the fraction eluted with chloroform, we obtained 0.11 g (7%) of **VII** as a light yellow oil, R_f 0.65. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1360, 1550 (NO_2), 1285 (P=O), 1022, 1084 (POC). Found, %: C 52.81, 52.82; H 3.79, 3.81; N 3.03, 3.04; P 6.73, 6.75. $C_{20}H_{18}Cl_2NO_5P$. Calculated, %: C 52.86; H 3.96; N 3.08; P 6.83. From the fraction eluted with ether, we obtained 0.10 g (6%) of **VIII** as a yellow oil, R_f 0.85. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1350, 1595 (NO_2), 1270 (P=O), 1025, 1080 (POC). Found, %: C 52.43, 52.46; H 3.90, 3.94; N 3.01, 3.04; P 6.73, 6.78. $C_{20}H_{18}Cl_2NO_5P$. Calculated, %: C 52.86; H 3.96; N 3.08; P 6.83.

Bis(2-chloroethyl) 9,10-dihydro-9,10-(11-nitroetheno)anthracen-12-ylphosphonate VII. Pyridine (0.45 g) was added to a solution of 0.60 g of 9,10-dihydro-9,10-(11-bromo-11-nitroethano)anthracene **IV** in 10 ml of absolute benzene. The mixture was refluxed for 90 h. The precipitate of pyridine hydrobromide was filtered off, the filtrate was evaporated, and the oily residue was chromatographed on alumina. From the fraction eluted with chloroform, we isolated 0.13 g (25%) of **VII** as an oil, R_f 0.65. The product was identical in R_f and spectral characteristics to the sample isolated from a mixture of products of the Diels–Alder reaction of **II** with anthracene.

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