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Synthesis and Structure of Phosphorylated Nitrocyclohexenes

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Abstract — Diene condensations of 2-nitro- and 2-bromo-2-nitroethenylphosphonates with 2,3-dimethyl-1,3-butadiene, as well as with 2,4-dihydro- and 3-methyl-2,4-dihydrothiophene 1,1-dioxides that generate 1,3-butadiene and isoprene under the reaction conditions were effected. (6-Nitrocyclohex-3-en-1-yl)phosphonates and their dehydrogenation and/or dehydrohalogenation products, namely nitrocyclohexadienyl- and nitrophenylphosphonates were prepared. The structure of the obtained compounds was proved by IR and ^{1}H and ^{31}P NMR spectroscopy, and independent synthesis.
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It is known that a lot of natural compounds, such as vitamins, terpenes, hormones, alkaloids, etc., contain the cyclohexane ring in their structures [1, 2]. For this reason, there is unrelenting interest of organic chemists in improving methods of synthesis of functionally substituted six-membered rings. One of these methods is the Diels–Alder reaction. The use of aliphatic dienes in this reaction allows formation of a six-membered ring, while the use of vicinal substituted nitroalkenes as dienophiles allows easily modified functional groups, such as NO_2, CO_2R, SO_2Ph, and others, to be introduced in the ring [3, 4]. Cyclohexenes with such functional groups hold promise as convenient reagents in the synthesis of biologically active compounds. Thus, for example, preparation of nitrocyclohexenes (or nitrocyclohexadienes) is the key stage in the synthesis of a natural analgesic epibatidine [5, 6], non-narcotic alkaloid mesembrane [7, 8], estrogenic hormones [9], morphine derivatives [10], and conduritols [11] which are important starting reagents for the design of anti-AIDS drugs.

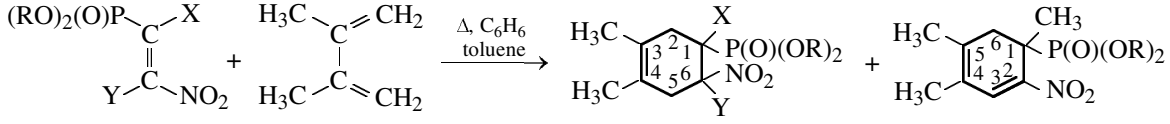
According to published data, nitroalkenes generally enter diene condensation with alkadienes under rigid conditions (prolonged heating in autoclave) [12-14]. Introduction of the second electron-acceptor substituent (CO_2R, CCl_3, or SO_2Ph) in the β position of nitroalkenes favors milder reaction conditions [3, 4].

Earlier we successfully reacted 2-nitroethenylphosphonates with some open-chain [15] and cyclic dienes [16–20]. In the present work we investigated reactions of nitroethenylphosphonates **I**–**III** with typical acyclic dienes, namely divinyl, isoprene, and 2,3-dimethylbuta-1,3-diene.

The reactions of nitroethenylphosphonates **I**, **II** with 2,3-dimethylbuta-1,3-diene were performed by refluxing the starting reagents in benzene for 1–2 h to obtain phosphorylated nitrocyclohexenes **IV**, **V** in 90–98% yields (Table 1).

Nitroalkene **III** containing a methyl group at the C^1 atom and an isopropoxy group at phosphorus failed to react with 2,3-dimethylbuta-1,3-diene under the same conditions. The reaction required more rigid conditions to occur: Refluxing in toluene for 10 h in the presence of aluminum chloride. The reaction was accompanied by dehydrogenation and gave 22% of phosphorylated nitrocyclohexane **VI** and 45% of nitrocyclohexadiene **VII**.

The formation of compound **VII** is probably favored by increased reaction temperature and duration [21, 22]. The much lower activity of the sterically shielded double bond is explained by heavy demands the Diels–Alder reaction imposes on mutual orientation of the starting reagents [23, 24].



I–III **IV–VI** **VII**

R = CH_2CH_2Cl, X = Y = H (**I, IV**), X = H, Y = Br (**II, V**); R = C_3H_7-*i*, X = CH_3, Y = H (**III, VI**).

Table 1. Yields, melting points, R_f, and elemental analyses of phosphorylated nitrocyclohexenes **IV**–**VI, VIII, XIII, XVa**, and **XVIa**, nitrocyclohexadienes **VII** and **XXIV**, and nitroarenes **X, XI**, and **XXV**

Comp. no.	Yield, %	mp, °C (R_f)	Found, %				Formula	Calculated, %			
			C	H	N	P		C	H	N	P
IV	90	86–87	39.81 39.85	5.73 5.75	3.94 3.95	8.53 8.55	$C_{12}H_{20}Cl_2NO_5P$	40.00	5.55	3.89	8.61
V	98	(0.46)	32.76 32.75	4.38 4.39	3.19 3.20	7.21 7.16	$C_{12}H_{19}BrCl_2NO_5P$	32.80	4.33	3.18	7.06
VI	22	(0.66)	54.15 54.19	8.33 8.35	4.38 4.39	9.25 9.28	$C_{15}H_{28}NO_5P$	54.05	8.41	4.20	9.31
VII	45	(0.59)	54.45 54.49	7.93 7.95	4.38 4.39	9.25 9.28	$C_{15}H_{26}NO_5P$	54.38	7.85	4.23	9.37
VIII	38	60–62	36.14 36.21	5.00 5.01	4.19 4.20	9.10 9.08	$C_{10}H_{16}Cl_2NO_5P$	36.14	4.82	4.22	9.34
X	37	0.24	36.50 36.52	4.21 4.25	4.30 4.31	9.22 9.28	$C_{10}H_{14}Cl_2NO_5P$	36.36	4.24	4.24	9.39
XI	45	(0.38)	36.50 36.55	3.21 3.25	4.30 4.31	9.58 9.28	$C_{10}H_{12}Cl_2NO_5P$	36.58	3.66	4.27	9.45
XIII	80	(0.46)	28.99 29.01	3.87 3.88	3.53 3.54	7.90 7.93	$C_{10}H_{15}BrCl_2NO_5P$	29.20	3.65	3.41	7.54
XVa	36	0.67	38.21 38.33	5.16 5.24	4.09 4.11	9.00 9.17	$C_{11}H_{18}Cl_2NO_5P$	38.15	5.20	4.05	8.96
XVIa	50	0.45	31.21 31.22	4.02 4.07	3.15 3.19	7.34 7.38	$C_{11}H_{17}BrCl_2NO_5P$	31.06	4.00	3.29	7.29
XXIV	39	(0.42)	40.45 40.50	5.21 5.25	3.80 3.81	8.58 8.62	$C_{12}H_{18}Cl_2NO_5P$	40.22	5.03	3.91	8.66
XXV	80	90–100	40.27 40.35	5.10 5.11	3.80 3.81	8.58 8.28	$C_{12}H_{16}Cl_2NO_5P$	40.44	4.49	3.93	8.71

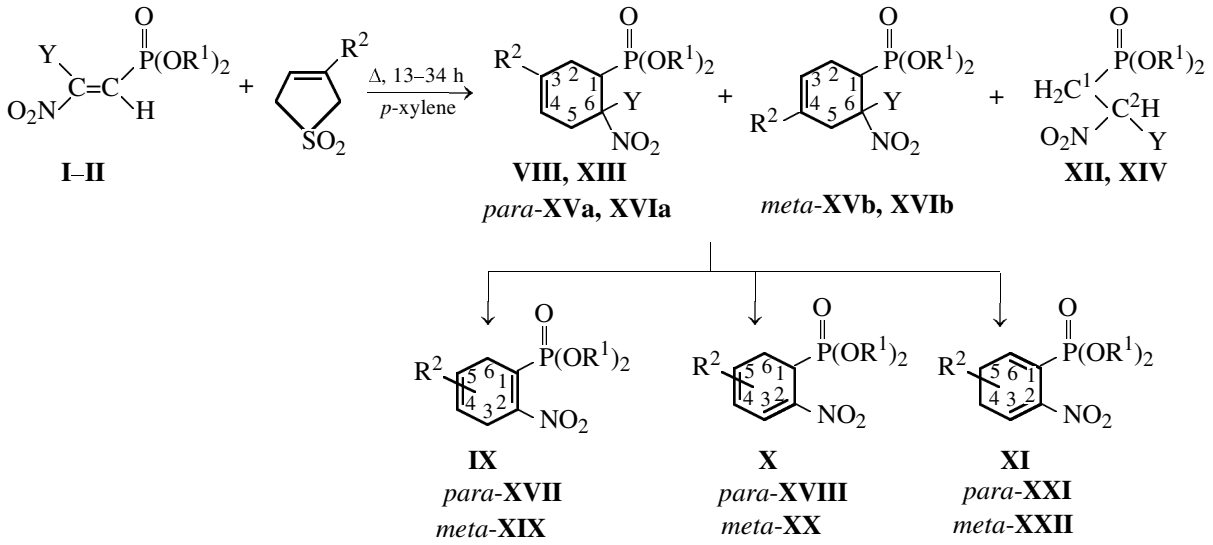
The condensation of nitroalkenes **I**, **II** with 2,4-dihydrothiophene 1,1-dioxides, synthetic precursors of aliphatic alka-1,3-dienes (divinyl, isoprene), required still more rigid conditions (refluxing in *p*-xylene for 18–34 h), because desulfonylation to generate dienes proceeds at an elevated temperature.

The reaction of nitroalkene **I** with unsubstituted 2,4-dihydrothiophene 1,1-dioxide leads to formation of bis(2-chloroethyl) (6-nitrocyclohex-3-en-1-yl)phosphonate (**VIII**). Therewith, like in the previous reaction, rigid reaction conditions favored dehydrogenation of cyclohexene **VIII** to form phosphorylated cyclohexa-1,4- and cyclohexa-2,4-dienes **IX**, **X,** as well as 2-nitrophenylphosphonate **XI**.

Along with the mentioned compounds, nitroethylphosphonate **XII** was isolated. Its formation can be explained by hydrogenation at the C≡C bond of nitroethenylphosphonate **I** that had no time to react with 2,4-dihydrothiophene 1,1-dioxide (or formed as a result of the retro process). The hydrogenation of nitroalkenes with hydrogen eliminated from the reaction product has also been reported by Itoh et al. [25].

gem-Bromonitroethenylphosphonate **II** reacted with 2,4-dihydrothiophene 1,1-dioxide by the same route to give, along with cyclohexene **XIII** (yield 80%), isomeric cyclohexa-1,4- and cyclohexa-2,4-dienes **IX**, **X**, nitrophenylphosphonate **XI**, and bis(2-chloroethyl) (2-bromo-2-nitroethyl)phosphonate (**XIV**).

It is known that nitroalkenes react with 2-substituted 1,3-dienes, yielding, as a rule, a mixture of *para*- and *meta*-substituted cyclohexenes [3, 4, 26, 27]. In our case, an unsymmetrical diene, isoprene, formed in situ from 3-methyl-2,4-dihydrothiophene 1,1-dioxide reacted with nitroalkenes **I**, **II** to form a mixture of regioisomers with the methyl group *para* or *meta* to the nitro group in the cyclohexene ring. The reaction was carried out at 140°C in *p*-xylene for 13–24 h and resulted in formation of mixtures of structural isomers **XVa**, **XVb** and **XVIa**, **XVIb** in total yields of 48 and 67%, respectively.



R^1 = CH_2CH_2Cl, Y = H (**I, XII**), Br (**II, XIV**); Y = H, R^2 = H (**VIII**), CH_3 (**XVa, XVb**); Y = Br, R^2 = H (**XIII**), CH_3 (**XVIa, XVIb**); R^2= H (**IX**–**XI**), CH_3 (**XVII**–**XXII**).

The formation of regioisomers is evidenced by doubled ring and methyl proton signals in the ^1H NMR spectra and phosphorus signals in the ^{31}P NMR spectra. The *para/meta* ratios determined by ^1H and ^{31}P NMR spectroscopy were equal to 4 : 1 (**XVa/XVb**) and 3 : 1 (**XVIa/XVIb**). By column chromatography we isolated individual *para* isomers **XVa** and **XVIa** only.

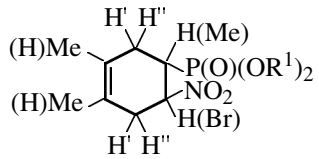
Rigid conditions of the condensation of isoprene with nitroalkenes **I**, **II** favor, like with divinyl, intramolecular transformation of nitrocyclohexenes **XVa, XVb, XVIa, XVIb**. The ^1H and ^{31}P NMR spectra of the reaction mixtures showed, together with signals of compounds **XVa, XVb, XVIa, XVIb**, signals of other unsaturated cyclic systems, namely conjugated and nonconjugated cyclohexadienes and benzene derivatives. Moreover, the reaction with isoprene is complicated by the fact that each nitrocyclohexene regioisomer undergoes intramolecular transformation, i.e. *para* and *meta* isomers each produce their corresponding pairs of nitrocyclohexadienes and nitroarenes. Thus, the reaction of nitroalkene **I** with isoprene (formed from 3-methyl-2,4-dihydrothiophene 1,1-dioxide) results in formation of not only phosphorylated nitrocyclohexenes **XVa**, **XVb**, but also of their dehydrogenation (nitrocyclohexadienylphosphonates **XVII**, **XVIII**, **XIX**, **XX**) and aromatization products (2-nitrophenylphosphonates **XXI**, **XXII**).

The structure of nitrocyclohexenes **IV**–**VI, VIII, XIII, XVa, XVb, XVIa, XVIb** was evidenced by IR, ^1H, and ^{31}P NMR spectroscopy (Table 2) and by comparison of their spectral data with the spectral characteristics of structurally related compounds, reported in [4, 38. 39].

The IR spectra of nitrocyclohexenylphosphonates, **IV**–**VI, VIII, XIII, XV, XVI** contain characteristic bands of all proposed functional groups. The phosphonate group gives strong stretching vibration bands in the ranges 1250–1240 (P=O), 1075–1110, and 1035–1010 cm^{-1} (P–O–C). Two bands (medium and strong) correspond to symmetrical and unsymmetrical vibrations of the nitro group (ν_s 1375–1320 and ν_{as} 1570–1560 cm^{-1}). The weak band at 1610 cm^{-1} in the spectrum of compound **XVa** corresponds to the double bond of the cyclohexene ring; for the majority of compounds of this series, especially those with a symmetrical C=C bond, this band is lacking.

The ^1H and ^{31}P NMR spectra (Table 2, Fig. 1) demonstrate steric homogeneity of compounds **IV**–**VI, VIII, XIII, Va, XVIa** (their phosphorus signals are detected in the range 23.0–27.6 ppm). The formation of couples of *para* regioisomers **XVa**, **XVIa** and *meta* regioisomers **XVb**, **XVIb** is confirmed by doubled proton signals of the methyl group (1.70 and 1.75 ppm) and ring protons H^1 (3.0 and 3.58 ppm for *para* isomers **XVa**, **XVIa** and 3.25 and 3.50 ppm for the *meta* isomers, respectively) and H^6 (4.88 ppm for *para* isomer **XVa** and 4.70 ppm for *meta* isomer **XVb**). The methylene protons at C^2 in nitrocyclohexenes **IV, VI, VIII, XVa, XVb** appear as multiplets in the range 1.90–2.59 ppm. The nitro group affects the chemical shifts of the H^5 methylene proton signals, and they are observed downfield (2.32–2.78 ppm) from those of H^2 (2.50–2.59 ppm). These chemical

Table 2. ^{1}H and ^{31}P NMR spectral data for 6-nitrocyclohexenylphosphonates



IV–VI, VIII, XIII, XVa, XVb, XVIa, XVIb

Comp. no.	NMR spectra, δ, ppm ($CDCl_3$), *J*, Hz						
	^{1}H						^{31}P
	Me (H^3, H^4)	C^2H_2	C^5H_2	H^1 H^6	CH_2Cl (OCH)	PCH_2 (Me)	
IV	1.52 s 1.62 s	2.30 m, 2.40 m $J_{H^{2'}H^{2''}}$ 13.6, $J_{H^{2''}H^1}$ 10.2	2.66 m $J_{H^6H^{5'}}$ 7.3, $J_{H^6H^{5''}}$ 5.8	2.96 m 4.85 m $J_{H^1H^6}$ 8.8 J_{H^1P} 17.6, J_{H^6P} 7.3, $J_{H^1H^{2'}}$ 8.8 $J_{H^1H^{2''}}$ 11.8	3.70 m 4.30 m J_{HP} 6.3 J_{HP} 0 J_{HH} 7.2		27.5
V	1.48 s 1.60 s	2.46 m, 2.41 m $J_{H^{2'}H^{2''}}$ 9.7, $J_{H^{2'}H^1}$ 5.4, $J_{H^{2''}H^1}$ 8.3	3.19 m, 2.90 m $J_{H^{5'}H^{5''}}$ 17.6	3.41 – J_{H^1P} 19.2 $J_{H^1H^{2'}}$ 5.4 $J_{H^1H^{2''}}$ 8.3	3.67 m 4.26 m J_{HP} 6.5 J_{HP} 0 J_{HH} 7.1		23.0
VI	1.58 s 1.58 s	1.98 m, 1.90 m $J_{H^{2'}H^{2''}}$ 12.6, $J_{H^{2'}P}$ 4.5, $J_{H^{2''}P}$ 5.6	2.42 m, 2.32 m $J_{H^{5'}H^{5''}}$ 16.6, $J_{H^{5'}H^6}$ 5.0, $J_{H^{5''}H^6}$ 5.0	– 4.86 m J_{H^6P} 9.8 $J_{H^6H^{5'}}$ 5.0 $J_{H^6H^{5''}}$ 5.0	(4.61) (1.15) J_{HH} 7.0 J_{HP} 6.5 J_{HP} 1.2		26.0
VIII	(5.72 m)	2.59 m, 2.50 m $J_{H^{2'}H^{2''}}$ 11.2, $J_{H^1H^{2'}}$ 6.7, $J_{H^1H^{2''}}$ 7.5, $J_{H^{2'}P}$ 3.0, $J_{H^{2''}P}$ 3.7	2.78 m	3.00 4.90 $J_{H^1H^6}$ 7.5 $J_{H^1H^{2'}}$ 6.7, $J_{H^6H^{5'}}$ 6.3, $J_{H^1H^{2''}}$ 7.5, $J_{H^6H^{5''}}$ 7.3, J_{H^1P} 17.5 J_{H^6P} 6.7	3.72 m 4.35 m J_{HH} 7.2 J_{HP} 6.3 J_{HP} 0		27.0
XIII	(5.65 m, 5.85 m)	2.70 m	3.25 m	3.50 –	3.75 m 4.30 m		24.0
XVa	1.70 s (5.38 m)	2.50 m, 2.43 m $J_{H^{2'}H^{2''}}$ 11.2, $J_{H^1H^{2'}}$ 8.0, $J_{H^1H^{2''}}$ 6.5, $J_{H^{2'}P}$ 4.5, $J_{H^{2''}P}$ 5.3	2.73 m $J_{H^6H^5}$ 4.0, $J_{H^6H^{5'}}$ 6.0	3.00 4.88 $J_{H^1H^6}$ 7.2 J_{H^1P} 17.8, J_{H^6P} 7.1, $J_{H^1H^{2'}}$ 8.0 $J_{H^1H^{2''}}$ 6.5	3.67 m 4.26 m J_{HH} 7.2 J_{HP} 6.3 J_{HP} 0		27.0
XVb	1.75 s (5.30 m)	2.55 m	2.70 m	3.25 m 4.70 m	3.67 m 4.26 m J_{HH} 7.2 J_{HP} 6.3 J_{HP} 0		27.5
XVIa	1.70 s (5.32 m)	3.10 m	2.90 m	3.58 m –	3.71 m 4.32 m J_{HH} 7.1 J_{HP} 6.3 J_{HP} 0		23.0
XVIb	1.75 s (5.48 m)	2.62 m	3.20 m	3.50 m –	3.71 m 4.32 m J_{HH} 7.1 J_{HP} 6.3		23.5

shifts are fairly close to published data for related compounds [4].

The bromine atom in the *gem* position to NO_2 in **V, XIII, XVIa, XVIb** contributes to the downfield shift of the H^2 and H^5 methylene proton signals 0.5 ppm on average. The H^1 methine protons in the spectra of compounds **IV, VIII, XV** appear as a multiplet in the range 2.96–3.25 ppm, but in the case of compounds **V, XIII, XVI** bromine shifts this signal downfield to 3.41–3.58 ppm. The multiplet at 4.7–4.9 ppm in the spectra of compounds **IV, VI, VIII**, **XV** corresponds to H^6. The ring olefin protons in compounds **VIII, XIII, XV**, **XVI** give singlets

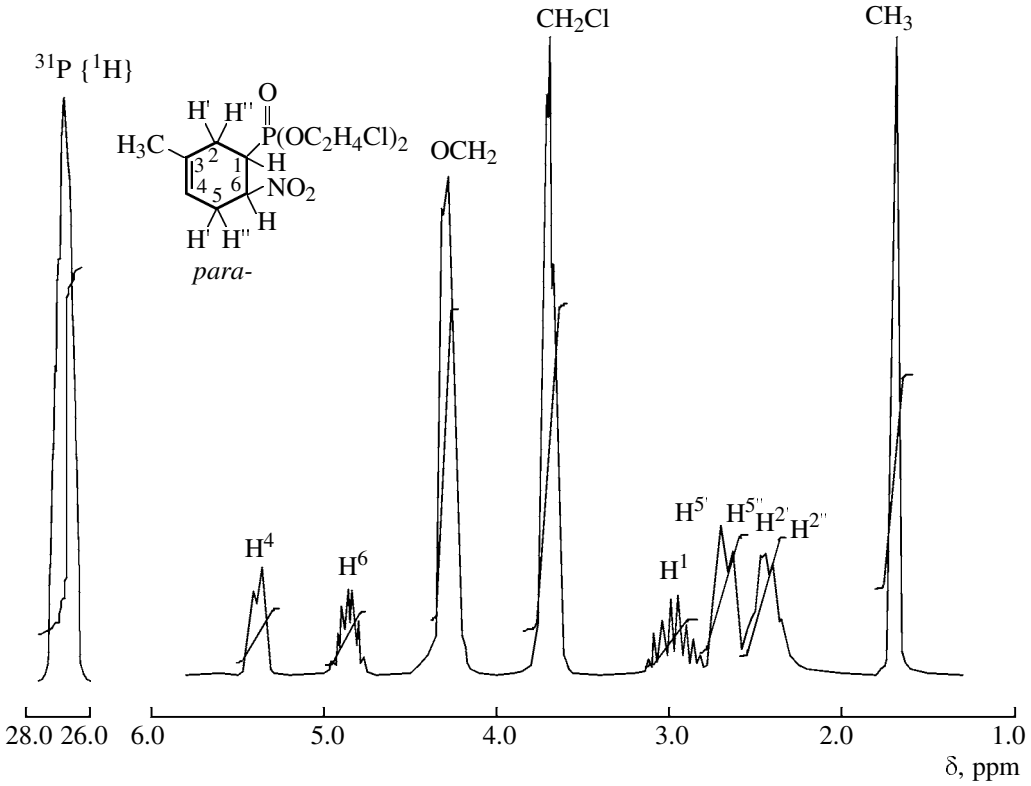
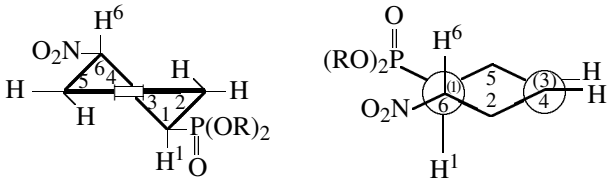


Fig. 1. ^{1}H and ^{31}P NMR spectra of bis(2-chloroethyl) (*para*-3-methyl-6-nitrocyclohex-3-en-1-yl)phosphonate (**XVa**) in $CDCl_3$.

and multiplets at 5.30–5.85 ppm. The H^3 and H^4 signals of compound **VIII** overlap (5.72 ppm), whereas in compound **XIII** these proton signals are resolved: 5.65 (H^3) and 5.85 ppm (H^4). The chemical shifts of methyl protons vary depending on the position of the methyl group. Thus, the methyl groups at saturated carbon atoms and isopropyl methyl groups in compound **VI** appear at 1.25 ppm, while the methyl groups at the ring C=C bond in compounds **IV**–**VI, X, XV**, at 1.48–1.75 ppm.

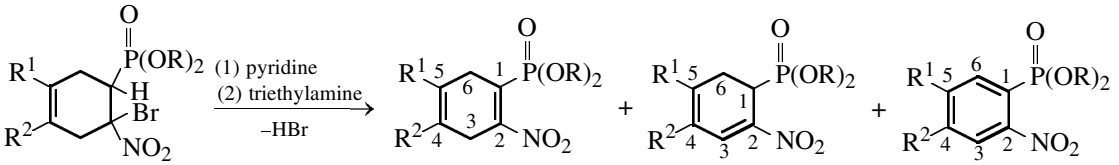


To establish mutual arrangement of the nitro and phosphonate groups and conformational characteristics of the six-membered ring in nitrocyclohexenylphosphonates, we used as analytical criterion the value of the spin-spin coupling constant of the vicinal protons H^1 and H^6. For the investigated compounds the $^{3}J_{1,6}$ values span the range 7.2–8.8 Hz, which corresponds to the dihedral angle between the vicinal protons of about 180° or to their axial arrangement [30, 31]. Hence, the six-membered ring in compounds **IV, VIII, XV** has a *half-chair* conformation with equatorial arrangement of bulky substituents [NO_2 and $P(O)(OR)_2$] and *anti* orientation of the vicinal protons along the C^1–C^6 bond in the Newman projection.

For elucidation of the structure of nitrocyclohexadienyl- and nitroarylphosphonates isolated from the mixture of the Diels–Alder reaction products, we tried to synthesize these compounds directly from bromonitrocyclohexanes **V, XIII, XXIa, XXIb** by dehydrohalogenation. In was found that halonitrocyclohexene **V**, when refluxed in benzene in the presence of triethylamine, splits off HBr to form a mixture of nitrocyclohexa-1,4- and -1,2-dienes **XXIII** and **XXIV**. The use of pyridine as dehydrohalogenating agent and prolonged (48 h) heating in benzene induced formation of aromatic derivative **XXV**, along with cyclohexadienes **XXIII**, **XXIV**.

The splitting off of HBr from bromonitrocyclohexene **XIII** (under reflux in benzene for 48 h in the presence of pyridine) also gave a mixture of nitrocyclohexadienylphosphonates **IX**, **X** and nitrophenylphosphonate **XI**.

Dehydrobromination of cyclohexenes **XVIa**, **XVIb** occurred in a more intricate fashion. The ^{1}H and ^{31}P



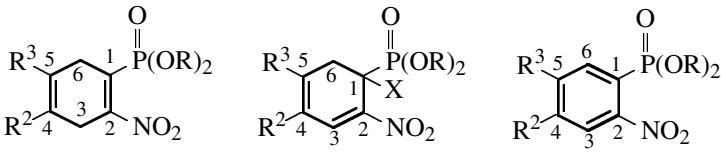
V, XIII, XVIa, XVIb **IX, XVII, XIX, XXIII** **X, XVIII, XX, XXIV** **XI, XXI, XXII, XXV**

$R^1 = R^2 = CH_3$ (**V, XXIII–XXV**); $R^1 = R^2 = H$ (**XIII, IX–XI**); $R^1 = CH_3$, $R^2 = H$ (**XVI–XVIII, XXI**); $R^1 = H$, $R^2 = CH_3$ (**XIX, XX, XXII**).

NMR spectra of the reaction mixture after 46-h refluxing in toluene in the presence of pyridine revealed formation of regioisomeric *para*- and *meta*-nonconjugated **XVII**, **XIX** and conjugated **XVIII**, **XX** cyclohexadienes and corresponding arenes **XXI**, **XXII**. However, we failed to isolate individual compounds from this multicomponent mixture.

The structure of nitroaromatic compounds **XI, XXI, XXII, XXV** was elucidated on the basis of their spectral characteristics (Table 3). For example, in the ^1H

Table 3. ^1H and ^{31}P NMR spectral data for nitrocyclohexadienylphosphonates **VII, IX, X, XVII–XXIV** and nitroarylphosphonates **XI, XXI, XXII, XXV**



IX, XVII, XIX, XXIII **VII, X, XVIII, XX, XXIV** **XI, XXI, XXII, XXV**

Comp. no.	NMR spectra, δ, ppm ($CDCl_3$), *J*, Hz							
	^{31}P	C^1H, (CH_3)	C^5H	C^4H, (CH_3)	C^5H, (CH_3)	C^6H	CH_2Cl, (CH_3)	OCH_2, (OCH)
Nitrocyclohexadienylphosphonates								
IX	12	3.50 m	2.70 m	6.40 m	5.40 m	2.50 m	3.72 m	4.30 m
XVII	15.5	–	2.45 m	5.50 m	(1.75 s)	2.40 m	3.70 m	4.35 m
XIX	17.5	–	2.41 m	(1.78 s)	5.45 m	2.45 m	3.70 m	4.45 m
XXIII	13	–	2.50 m	(1.68 s)	(1.63 s)	2.40 m	3.70 m	4.45 m
VII[a]	–	(1.33) J_{CH_3P} 17	7.50 J_{H^3P} 16.5	(2.30 s)	(2.22 s)	3.75, J_{CH_2P} 16	(1.33 m)	(4.75 m)
X	28	–	8.00 m	7.10 m	7.30 m	2.50 m	3.71 m	4.38 m
XVIII	27	3.50	8.02 m	7.40 m	(2.32 s)	2.50 m	3.68 m	4.35 m
XX	24	3.50 m	7.80 J_{H^3P} 8.00	(2.42 s)	7.50 m	2.55 m	3.70 m	4.38 m
XXIV	23	3.60 m	7.80 J_{H^3P} 8.00	(2.38 s)	(2.30 s)	2.50 m	3.70 m	4.30 m
Nitroarylphosphonates								
XI	15	–	8.20 m	7.35 m	7.50 m	6.31 m	3.71 m	4.40 m
XXI	14	–	8.15 m	7.15 m	(2.25 s)	6.30 m	3.70 m	4.45 m
XXII	15	–	8.00 J_{H^3P} 9.00	(2.50 s)	7.20 m	6.50 m	3.71 m	4.38 m
XXV	17	–	8.12 J_{H^3P} 15.8	(2.42 s)	(2.30 s)	6.18 J_{H^6P} 6.00	3.71 J_{HH} 7.20, J_{HP} 1.20	4.38 J_{HP} 6.80

[a] In compound **VII**, $R^1 = i\text{-}C_3H_7$ and $X = CH_3$; in the other compounds, $R^1 = CH_2CH_2Cl$ and X = H.

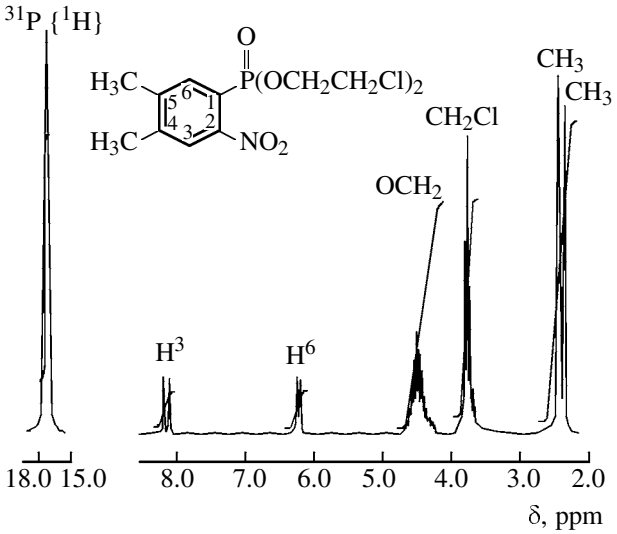


Fig. 2. ^1H and ^{31}P NMR spectra of bis(2-chloroethyl) (4,5-dimethyl-2-nitrophenyl)phosphonate (**XXV**) in $CDCl_3$.

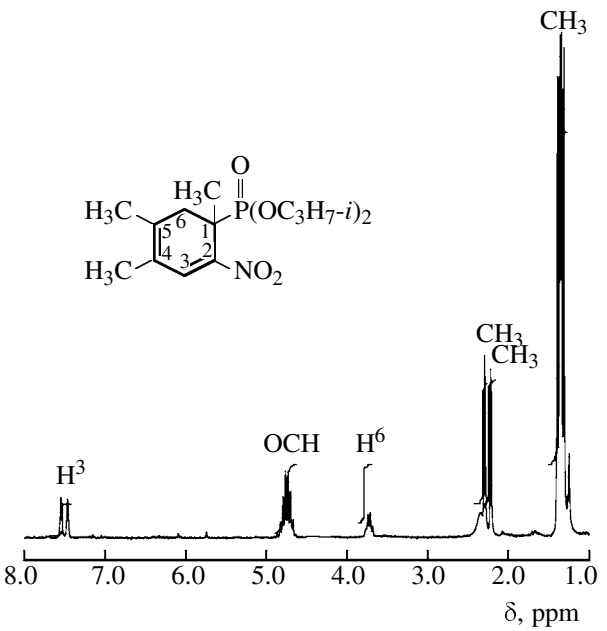


Fig. 3. ^1H NMR spectra of diisopropyl (1,4,5-trimethyl-2-nitrocyclohexa-2,4-dien-1-yl)phosphonate (**VII**) in $CDCl_3$.

NMR spectrum of compound **XXV** the H^6 signal is at 6.18 ppm and the H^3 signal, due to the action of the electron-acceptor NO_2 group, is shifted downfield to 8.12 ppm. Both signals are doublets (Fig. 2), on account of the spin–spin coupling of H^3 and H^6 with phosphorus.

The same pattern of benzene proton signals is observed in the ^1H NMR spectra of compounds **XI**, **XXI**, **XXII**, which allows these compounds, too, to be related to aromatic derivatives. The phosphorus signals of compounds **XI, XXI, XXII, XXV** are in the range 14.0–17.0 ppm. The IR spectra of nitroarylphosphonate **XXV** contain characteristic absorption bands of the functional groups present in the molecule: The phosphonate group gives three bands at 1250 ($\nu_{P=O}$) and 1085 and 1025 cm^{-1} (ν_{P-O-C}), and the conjugated nitro group, two bands at 1550 and 1360 cm^{-1}.

The assignment of nitrocyclohexadienylphosphonates to conjugated (**VII, X, XVIII, XX, XXIV**) and nonconjugated (**IX, XVII, XIX, XXIII**) systems was carried out by analysis of their ^1H and ^{31}P NMR spectral characteristics and comparison with the corresponding characteristics of model nitrocyclohexadienes [4]. Nonconjugated cyclohexadienes **IX, XVII, XIX, XXIII** are characterized by the presence in the ^1H NMR spectra of signals of methylene protons at C^3 and C^6 (2.40–2.40 ppm) and olefin protons at an isolated C=C bond (5.45–5.50 ppm), in accordance with the corresponding parameters of structurally related compounds [4, 33].

The two conjugated C=C bonds in the six-membered ring causes a downfield shift of the methylene and olefin proton signals compared to the respective signals of the starting cyclohexenes and nonconjugated cyclohexadienes [33] (Tables 2, 3). Thus, in the ^1H NMR spectra of cyclohexadiene **VII** the H^3 olefin proton gives a doublet at 7.5 ppm, and ring methylene protons, a signal at 3.7 ppm (Fig. 3).

Compounds **X, XVIII, XX, XXIV** show similar ^1H NMR spectral pictures, which allows these compounds to be related to conjugated cyclohexadienes (Table 3).

An important criterion in the structural analysis of the investigated compounds is the value of the chemical shift of methyl protons. The signals of the methyl group at C^1 and isopropoxy methyl groups in compound **VII** almost coincide and occur at 1.33–1.35 ppm. The signals of the CH_3 group at the C=C bond in nonconjugated dienes **XVII, XIX, XXIII** are detected in the range 1.63–1.74 ppm, but the respective signals of conjugated **VI, XVIII, XX, XXIV** and aromatic **XXI, XXII, XXV** structures are shifted downfield (2.22–2.50 ppm).

The position of methyl proton signals was used to identify the *para* and *meta* isomers of nitrocyclohexadienes. The downfield CH_3 signal at 2.42 ppm cor-

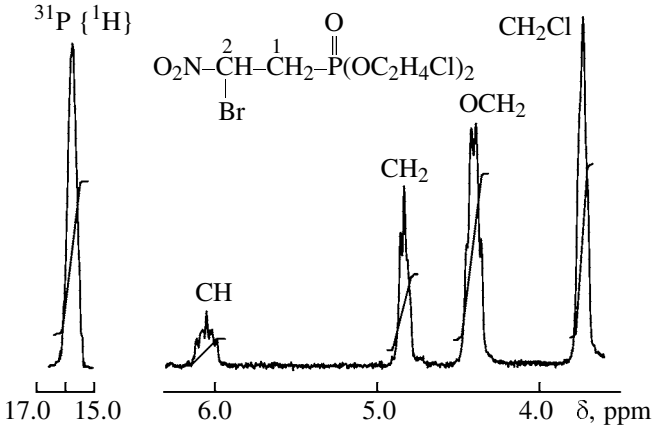


Fig. 4. ^{1}H and ^{31}P NMR spectra of bis(2-chloroethyl) (2-bromo-2-nitroethyl)phosphonate (**XIV**) in $CDCl_3$.

responds to proximate arrangement of the methyl and nitro groups in *meta* isomer **XX**. At the same time, the CH_3 group in *para* isomer **XVIII** experiences a weaker effect from the electron-acceptor nitro group, and, as a result, its signal is shifted upfield (2.32 ppm).

The phosphorus signals of conjugated dienes **VII, X, XVIII, XX, XXIV** appear at 23.0–28.0 ppm and those of nonconjugated dienes **IX, XVII, XIX, XXIII** and aromatic structures **XI, XXI, XXII, XXV**, at 12.0–17.5 ppm, providing evidence showing that the phosphonate group is located at the sp^3- and sp^2-carbon atoms, respectively.

The IR and ^{1}H and ^{31}P NMR spectral characteristics of nitro- and bromonitroethylphosphonates **XII**, **XIV** completely correspond to the proposed structures. Thus, the methylene proton signals of compound **XII** are at 4.69 (C^1H_2) and 4.88 ppm (C^2H_2). The bromine atom in compound **XIV** contributes to the downfield shift of the C^1H_2 signals to 4.82 ppm, and the C^2H methine proton resonates at 6.05 ppm (Fig. 4). The phosphorus signals are singlets in the range of 16.0–20.0 ppm.

Thus, we developed conditions for the reaction of 2-nitro- and 2-bromo-2- nitroethenylphosphonates with 2,3-dimethylbuta-1,3-diene, as well as with 2,4-dihydrothiophene and 3-methyl-2,4-dihydrothiophene 1,1-dioxides, synthetic precursors of alka-1,3-dienes. We found that nitro- phosphorylated cycloadducts show enhanced tendency for intermolecular transformations under their preparation conditions (dehydrobromination, dehydrogenation, and aromatization), and the highest reactivity is characteristic of bromine-containing nitrocycloalkenylphosphonates.

We found that the Diels-Alder reactions with 2-nitroethenylphosphonates and acyclic alka-1,3-dienes provides a convenient synthetic route to nitrocyclohexenylphosphonates, nitro precursors of potentially biologically active compounds [32], specifically β-aminophosphonic acids of the cyclohexane series. The synthesis of one of such compounds we described in [34].

EXPERIMENTAL

The IR spectra were recorded on an Infra-LYUM FT-02 spectrometer in chloroform (*c* 0.1–0.001 M). The ^{1}H and ^{31}P NMR spectra were registered on a Brucker AC-200 spectrometer (200 MHz) in $CDCl_3$ against external HMDS (^{1}H; accuracy ±0.5 Hz, δ scale) or external 85% phosphoric acid (^{31}P). Individual compounds were isolated by column chromatography on silica gel (Chemapol 100/200). Purity and reaction control was performed TLC on Silufol-254 plates, eluent hexane–acetone (3 : 2), developer iodine vapor. Compound ratios were determined by ^{1}H and ^{31}P NMR spectroscopy after column chromatography.

The starting nitro- and *gem*-bromonitroethenylphosphonates **I**–**III** were prepared by published procedures [35–37].

Bis(2-chloroethyl) (3,4-dimethyl-6-nitrocyclohex-3-en-1-yl)phosphonate (IV). To a solution of 1.10 g of bis(2-chloroethyl) 2-nitroethenylphosphonate (**I**) in 6 ml of absolute benzene, 1.50 ml of 2,3-dimethylbuta-1,3-diene in 1 ml of anhydrous benzene was added, and the reaction mixture was heated under reflux for 1 h. The solvent was then removed on a rotary evaporator to give 1.25 g (90%) of compound **IV**, mp 86–87°C (from hexane–benzene, 5 : 1).

Bis(2-chloroethyl) (6-bromo-3,4-dimethyl-6-nitrocyclohex-3-en-1-yl)phosphonate (V). To a solution of 1.00 g of bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonate (**II**) in 5 ml of anhydrous benzene, 0.90 ml of 2,3-dimethylbuta-1,3-diene in 1 ml of absolute benzene was added, and the reaction mixture was refluxed for 1 h. The solvent was then removed on a rotary evaporator. The residual yellow oil was purified by chromatography on silicic acid, eluent benzene, to obtain 1.20 g (98%) of compound **V** as an oil, R_f 0.46.

Diisopropyl (6-nitro-1,3,4-trimethylcyclohex-3-en-1-yl)phosphonate (VI) and diisopropyl (2-nitro-1,4,5-trimethylcyclohexa-2,4-dien-1-yl)phosphonate (VII). To a solution of 0.80 g of diisopropyl 1-methyl-2-nitroethenylphosphonate (**III**) in 6 ml of toluene, 0.05 g of aluminum chloride and 2.55 ml of 2,3-dimethylbuta-1,3-diene were added. The reaction mixture was heated under reflux for 10 h and held for

3 days at 20°C. Aluminum chloride was filtered off, the solvent was removed on a rotary evaporator, and the oily residue was purified by chromatography on alumina. From the benzene fraction, 0.45 g (45%) of compound **VII** was isolated as a light yellow oil, R_f 0.59. From the ether fraction, 0.22 g (22%) of compound **VI** was isolated as a light yellow oil, R_f 0.66.

Bis(2-chloroethyl) (6-nitrocyclohex-3-en-1-yl)-phosphonate (VIII), bis(2-chloroethyl) (2-nitrocyclohexa-1,4-dien-1-yl)phosphonate (IX), bis-(2-chloroethyl) (2-nitrocyclohexa-2,4-dien-1-yl)-phosphonate (X), bis(2-chloroethyl) 2-nitrophenylphosphonate (XI), and bis(2-chloroethyl) 2-nitroethylphosphonate (XII). To a solution of 1.52 g of bis(2-chloroethyl) 2-nitroethenylphosphonate (**I**) in 10 ml of *p*-xylene, 0.78 g of 2,4-dihydrothiophene 1,1-dioxide was added, and the reaction mixture was refluxed for 34 h. The solvent was removed on a rotary evaporator, and the residual oil was subjected to chromatography on silica gel. From the first benzene fraction (ca. 200 ml), 0.69 g (38%) of compound **VIII** was isolated, mp 60–62°C. From the second benzene portion (ca. 200 ml), 0.20 g of a mixture of compounds **IX**, **X**, and **XI** (1 : 3 : 1) was isolated as a yellow oil. From the ether fraction, 0.22 g of a mixture of compounds **XI** and **XII** (1 : 10) was isolated as a yellow oil. The latter mixture was subjected to repeated chromatography to isolate, from the ether fraction, 0.20 g (13%) of compound **XII** as an oil crystallizing on storage, mp 80–81°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1560, 1375 (NO_2), 1220 (P=O), 1030, 1090 (P–O–C). ^1H NMR spectrum, ($CDCl_3$), δ, ppm (*J*, Hz): 4.69 m (2H, $CH_2P(O)(OR)_2$) ($^3J_{HH}$ 5.8, J_{H^1P} 3.4); 4.88 m (2H, CH_2NO_2) ($^3J_{HH}$ 5.8, J_{H^2P} 6.8); 3.75 m (4H, $2CH_2Cl$), 4.43 m (4H, $2OCH_2$). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 20.00. Found, %: C 25.79, 25.71; H 4.45, 4.38; N 5.04, 5.16; P 11.12, 11.28. $C_6H_{12}Cl_2NO_5P$. Calculated, %: C 25.71; H 4.28; N 5.00; P 11.07.

Bis(2-chloroethyl) (6-bromo-6-nitrocyclohex-3-en-1-yl)phosphonate (XIII), bis(2-chloroethyl) 2-nitrophenylphosphonate (XI), and bis(2-chloroethyl) 2-bromo-2-nitroethylphosphonate (XIV). To a solution of 1.00 g of bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonate (**II**) in 10 ml of *p*-xylene, 0.40 g of 2,4-dihydrothiophene 1,1-dioxide was added, and the reaction mixture was refluxed for 18 h. The solvent was removed on a rotary evaporator, and the residual oil was subjected to chromatography on silica gel. From the chloroform fraction, 0.92 g (80%) of compound **XIII** was isolated as an oil, R_f 0.46. From the ether fraction, 0.17 g of a mixture of compounds **XIV** and **XI** (1 : 1) was isolated as a yellow oil. From the ether fraction after repeated chromatography, 0.09 g (10%) of compound **XIV** was isolated as an oil crystallizing on storage, mp 51–53°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1570, 1375 (NO_2), 1270 (P=O), 1025, 1080 (P–O–C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.82 m (2H, $CH_2P(O)(OR)_2$) ($^3J_{HH}$ 3.24, J_{H^1P} 3.5); 6.05 m (1H, $CHBrNO_2$) ($^3J_{HH}$ 3.24, J_{H^2P} 2.00); 3.70 m (4H, $2CH_2Cl$), 4.40 m (4H, $2OCH_2$). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 16.00. Found %: C 20.25, 20.27; H 4.18, 4.20; N 4.18, 4.20.; P 8.40, 8.48. $C_6H_{11}BrCl_2NO_5P$. Calculated %: C 20.05; H 3.06; N 3.90; P 8.64.

Bis(2-chloroethyl) [3(4)-methyl-6-nitrocyclohex-3-en-1-yl]phosphonates (XVa, XVb), bis(2-chloroethyl) [5(4)-methyl-2-nitrocyclohexa-1,4-dien-1-yl]-phosphonates (XVII, XIX), bis(2-chloroethyl) [5(4)-methyl-2-nitrocyclohexa-2,4-dien-1-yl]phosphonates (XVIII, XX), bis(2-chloroethyl) [5(4)-methyl-2-nitrophenyl]phosphonates (XXI, XXII), and bis(2-chloroethyl) 2-nitroethylphosphonate (XII). To a solution of 1.00 g of bis(2-chloroethyl) 2-nitroethenylphosphonate (**I**) in 10 ml of *p*-xylene, 1.32 g of 3-methyl-2,4-dihydrothiophene 1,1-dioxide was added, and the reaction mixture was heated under reflux for 24 h. The solvent was removed on a rotary evaporator, and the residue was subjected to chromatography on silica gel. From the first benzene fraction (ca. 100 ml), 0.14 g of a mixture of compounds **XVII**, **XIX**, and **XXI** (2 : 1 : 1) was isolated as a yellow oil, and from the second benzene fraction (ca. 100 ml), 0.22 g of a mixture of compounds **XVII**, **XX**, and **XXII** (2 : 1 : 2) as a yellow oil. From the chloroform fraction, 0.6 g (48%) of compound **XV** as a mixture of structural isomers **XVa** and **XVb** (4 : 1), R_f 0.67 and 0.55, respectively. From the ether fraction, 0.15 g (15%) of compound **XII** was isolated as an oil crystallizing on storage, mp 80–81°C. Repeated chromatography of the mixture of isomers **XVa** and **XVb**, eluent chloroform, gave 0.45 g (36%) of *para* isomer **XVa**, R_f 0.67.

Bis(2-chloroethyl) [6-bromo-3(4)-methyl-6-nitrocyclohex-3-en-1-yl]phosphonate (XVIa, XVIb), bis(2-chloroethyl) [5(4)-methyl-2-nitrocyclohexa-1,4-dien-1-yl]phosphonates (XVII, XIX), bis(2-chloroethyl) [5(4)-methyl-2-nitrocyclohexa-2,4-dien-1-yl]phosphonates (XVIII, XX), bis(2-chloroethyl) [5(4)-methyl-2-nitrophenyl]phosphonates (XXI, XXII), and bis(2-chloroethyl) 2-bromo-2-nitroethylphosphonate (XIV). To a solution of 1.00 g of bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonate (**II**) in 10 ml of *p*-xylene, 1.11 g of 3-methyl-2,4-dihydrothiophene 1,1-dioxide was added, and the reaction mixture was refluxed for 13 h. The solvent was removed on a rotary evaporator, and the residue was subjected to chromatography on silica gel.

From the first benzene fraction (ca. 100 ml), 0.08 g of a mixture of compounds **XVII**, **XIX**, and **XXII** (3 : 1 : 1) was isolated as a yellow oil. From the second benzene fraction (ca. 100 ml), 0.06 g of a mixture of compounds **XVIII**, **XX**, and **XXI** (1 : 0.5 : 1) was isolated as a yellow oil. From the chloroform fraction, 0.80 g (67%) of compound **XVI** as a mixture of structural isomers **XVIa** and **XVIb** (3 : 1), R_f 0.45 and 0.32, respectively, was isolated. From the ether fraction, 0.10 g (10%) of compound **XVI** was isolated as an oil crystallizing on storage, mp 51–53°C. Repeated column chromatography of the mixture of isomers **XVIa** and **XVIb**, eluent chloroform, gave 0.6 g (50%) of *para* isomer **XVIa**, R_f 0.45.

Bis(2-chloroethyl) (4,5-dimethyl-2-nitrocyclohexa-1,4-dien-1-yl)phosphonate (XXIII), bis(2-chloroethyl) (4,5-dimethyl-2-nitrocyclohexa-2,4-dien-1-yl)phosphonate (XXIV), and bis(2-chloroethyl) (4,5-dimethyl-2-nitrophenyl)phosphonate (XXV). *a*. To a solution of 0.50 g of bis(2-chloroethyl) (6-bromo-3,4-dimethyl-6-nitrocyclohex-3-en-1-yl)phosphonate (**V**) in 4 ml of anhydrous benzene, 0.16 ml of triethylamine was added, and the reaction mixture was refluxed for 4 h. After cooling, the triethylamine hydrobromide formed was filtered off, 20 ml of benzene was added to the filtrate, and the resulting solution was washed with water. The benzene solution was separated, dried over magnesium sulfate, and the solvent was removed on a rotary evaporator. The residue was subjected to chromatography on silica gel. From the ether fraction, 0.15 g (39%) of compound **XXIV** was isolated as an oil, R_f 0.42. From the methanol fraction, 0.12 g of a mixture of compounds **XXIII** and **XXIV** (2 : 5) was isolated as a yellow oil, R_f 0.68 and 0.42.

b. To a solution of 0.50 g of compound **V** in 4 ml of anhydrous benzene, 1.00 ml of pyridine was added, and the reaction mixture was refluxed for 48 h. After cooling, the pyridine hydrobromide formed was filtered off, and the filtrate was evaporated on a rotary evaporator. The residue was extracted with ether, and the solvent was removed to obtain 0.32 g (80%) of compound **XXV**, mp 99–100°C (from CCl_4). The residue after extraction with ether was subjected to repeated chromatography. From the methanol fraction, 0.06 g of a mixture of compounds **XXIII** and **XXIV** (1 : 3) was isolated, R_f 0.68 and 0.42, respectively.

Bis(2-chloroethyl) (2-nitrocyclohexa-1,4-dien-1-yl)phosphonate (IX), bis(2-chloroethyl) (2-nitrocyclohexa-2,4-dien-1-yl)phosphonate (X), and bis-(2-chloroethyl) 2-nitrophenylphosphonate (XI). To a solution of 0.50 g of bis(2-chloroethyl) (6-bromo-6-nitrocyclohex-3-en-1-yl)phosphonate (**XIII**) in 10 ml of anhydrous benzene, 0.48 ml of pyridine was added, and the reaction mixture was refluxed for 48 h. The pyridine hydrobromide formed was filtered off, the filtrate was evaporated on a rotary evaporator, and the residue was subjected to chromatography on a silica gel. From the benzene fraction, 0.20 g of a mixture of compounds **IX** and **X** (1 : 6) was isolated as a yellow oil. From the methanol fraction, 0.18 g (45%) of compound **XI** was isolated as a yellow oil, R_f 0.38. Repeated chromatography of the mixture of compounds **IX** and **X** gave 0.15 g (37%) of compound **X** as a yellow oil, R_f 0.24.

Bis(2-chloroethyl) [5(4)-methyl-2-nitrocyclohexa-1,4-dien-1-yl]phosphonates (XVII, XIX), bis-(2-chloroethyl) [5(4)-methyl-2-nitrocyclohexa-2,4-dien-1-yl]phosphonates (XVIII, XX), and bis(2-chloroethyl) (5-methyl-2-nitrophenyl)phosphonate (XXI). *a*. To a solution of 0.48 g of bis(2-chloroethyl) [6-bromo-3(4)-methyl-6-nitrocyclohex-3-en-1-yl]-phosphonates (**XVIa**, **XVIb**) in 4 ml of absolute toluene, 0.45 ml of pyridine was added, and the reaction mixture was refluxed for 46 h. The pyridine hydrobromide formed was filtered off, the filtrate was evaporated on a rotary evaporator, and the residue was subjected to chromatography on silica gel. From the chloroform fraction, 0.30 g of a mixture of compounds **XVII** and **XIX** (3 : 1) was isolated as a yellow oil. From the methanol fraction, 0.12 g of a mixture of compounds **XVIII**, **XX**, and **XXI** (2 : 1 : 3) was isolated as a yellow oil.

b. To a solution of 0.60 g of bis(2-chloroethyl) [6-bromo-3(4)-methyl-6-nitrocyclohex-3-en-1-yl]-phosphonates (**XVIa**, **XVIb**) in 10 ml of anhydrous benzene, 0.58 ml of pyridine was added, and the reaction mixture was heated under reflux for 84 h. The pyridine hydrobromide formed was filtered off, the filtrate was evaporated on a rotary evaporator, and the residue was subjected to chromatography on silica gel. From the first chloroform fraction (ca. 100 ml), 0.20 g of a mixture of compounds **XVII** and **XIX** (3 : 1) was isolated as a yellow oil. From the second chloroform fraction (ca. 100 ml), 0.35 g of a mixture of compounds **XVIII**, **XX**, and **XXI** (2 : 1 : 5) was isolated as a yellow oil.

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REFERENCES

1. Ono, N., *The Nitro Group in Organic Synthesis,* New York: VCH, 2001.
2. Perekalin, V.V., Lipina, E.S., Berestovitskaya, V.M., and Efremov, D.A., *Nitroalkenes* (Conjugated Nitro Compounds), London: Wiley, 1994.
3. Burkett, H., and Wright, W., *J. Org. Chem.,* 1960, vol. 25, no 2, p. 276.
4. Ono, N., Kamimura, A., and Kaji, A., *J. Org. Chem.,* 1988, vol. 53, no. 2, p. 251.
5. Albertini, E., Barco, S., and Benneti, S., *Tetrahedron Lett.,* 1994, vol. 35, no. 49, p. 929.
6. Habermann, J., Ley, S., and Scon, J., *J. Chem. Soc. Perkin Trans. 1,* 1999, no. 10, p. 1253.
7. Jwamatsi, S., Matsubara, K., and Nagashima, H., *J. Org. Chem.,* 1999, vol. 64, no. 26, p. 9625.
8. Arce, E., Carreno, M. C., Cid, M.B., and Ruano, J.L., *J. Org. Chem.,* 1994, vol. 59, no. 12, p. 3421.
9. Cere, V., Peri, F., and Pollicino, S., *Tetrahedron Lett.,* 1997, vol. 38, no. 44, p. 7797.
10. Barltrop, B.J., and Nicholson, J.S., *J. Chem. Soc.,* 1951, p. 2524.
11. Cere, V., Montovani, G., Peri, F., Pollicino, S., and Ricci, A.A., *Tetrahedron,* 2000, vol. 56, no. 9, p. 1225.
12. Alder, K., Ferdinand, H., and Windemuth, E., *Ber.,* 1938, no. 12, p. 2451.
13. Dudinskaya, A.A., Shvekhgeimer, G.A., Novikov, S.S., and Solovetskii, V.V., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1961, no. 3, p. 524.
14. Kataev, E.F., and Matveeva, P.S., *Zh. Obshch. Khim.,* 1953, vol. 23, no. 3, p. 405.
15. Kuzhaeva, A.A., Berestovitskaya, V.M., Deiko, L.I., Anisimova, N.A., and Berkova G.A., *Zh. Obshch. Khim.,* 2002, vol. 72, no. 10, p. 1752.
16. Kuzhaeva, A.A., Anisimova, N.A., Deiko, L.I., Berkova, G.A., and Berestovitskaya, V.M., *Khim. Geterotsikl. Soedin.,* 2003, no. 8, p. 1264.
17. Berestovitskaya, V.M., Anisimova, N.A., Litvinov, I.A., Kuzhaeva, A.A., Berkova, G.A., Gubaidullin, A.T., and Deiko L.I., *Zh. Obshch. Khim.,* 2004, vol. 74, no. 4, p. 574.
18. Anisimova, N.A., Kuzhaeva, A.A., Berkova, G.A., Berestovitskaya, V.M., and Deiko L.I., *Zh. Obshch. Khim.,* 2005, vol. 75, no. 11, p. 1833.
19. Anisimova, N.A., Kuzhaeva, A.A., Berkova, G.A., Deiko, L.I., and Berestovitskaya V.M., *Zh. Obshch. Khim.,* 2005, vol. 75, no. 7, p. 1106.
20. Anisimova, N.A., Kuzhaeva, A.A., Berkova, G.A., Deiko, L.I., and Berestovitskaya V.M., *Zh. Obshch. Khim.,* 2005, vol. 75, no. 5, p. 729.
21. Dudinskaya, A.A., Shvekhgeimer, G.A., and Novikov, S.S., *Izv. Akad. Nauk USSR, Ser. Khim.,* 1961, no. 3, p. 522.
22. Ono, N., Miyake, H., and Kaji, A., *J. Chem. Soc., Chem. Commun.,* 1982, no. 1, p. 33.
23. Gilchrist, T.L. and Storr, R.C., *Organic Reactions and Orbital Symmetry,* Cambridge: Cambridge Univ., 1972.
24. Gilchrist, T.L., *Heterocyclic Chemistry,* Harlow: Longman Scientific & Technical, 1992, 2nd ed.
25. Itoh, K., Ishida, H., and Chikaschita, H., *Chem. Lett.,* 1982, no. 7, p. 1117.
26. Wildman, W.C., Wildman, R.B., Norton, W.T., and Fine, J.B., *J. Am. Chem. Soc.,* 1953, vol. 75, p. 1912.
27. Nazarov, I.N., Kuznetsova, A.I., and Kuznetsov, N.V., *Zh. Obshch. Khim.,* 1950, vol. 20, no. 2, p. 68.
28. Ono, N., Miyake, H., Kamimura, A., and Kaji, A., *J. Chem. Soc., Perkin Trans. 1,* 1987, no. 9, p. 1929.
29. Shin, C., Jamaura, M., Nui, E., Jshida, Y., Inui, E., and Yochimura, J., *Bull. Chem. Soc. Jpn.,* 1978, vol. 51, no. 9, p. 2618.
30. Ionin, B.I., Ershov, B.A., and Kol'tsov, A.I., *YaMR-spektroskopiya v organicheskoi khimii* (NMR Spectroscopy in Organic Chemistry), Leningrad: Khimiya, 1983.
31. Ionin, B.I., and Timofeeva, T.N., *Usp. Khim.,* 1972, vol. 41, no. 4, p. 758.
32. Uziel, J. and Genet, J., *Zh. Org. Khim.,* 1997, vol. 33, no. 11, p. 1605.
33. Brand, J.C.D. and Eglinton, G., *Applications of Spectroscopy to Organic Chemistry,* London: Oldbourne, 1965.
34. Anisimova, N.A., Kuzhaeva, A.A., Deiko, L.I., Berkova, G.A., and Berestovitskaya, V.M., *Zh. Obshch. Khim.,* 2003, vol. 73, no. 9, p. 1575.
35. Baranov, G.M. and Perekalin, V.V., *Zh. Obshch. Khim.,* 1987, vol. 57, no. 4, p. 793.
36. Mastryukova, T.A., Baranov, G.M., Perekalin, V.V., and Kabachnik, M.I., *Dokl. Akad. Nauk SSSR,* 1966, vol. 171, no. 6, p. 1341.
37. Botata, Zh.E., Deiko, L.I., Kostina, T.K., Baranov, G.M., and Berestovitskaya, V.M., *Zh. Obshch. Khim.,* 1995, vol. 65, no. 1, p. 160.