

Azolyl Derivatives of Nitrohalobutadienes: V.* A New Route to Functionally Substituted Benzazetines**

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Abstract—Heating of 1-azolyl-1-(4-R-phenylamino)-2-nitro-3,4,4-trichloro-1,3-butadienes and 1-azolyl-1-(4-R-phenylamino)-2-nitro-3,4-dichloro-4-bromo-1,3-butadienes (R = BuO, EtO, MeO, Me; azolyl = 1-benzotriazolyl, 3,5-dimethyl-1-pyrazolyl, and 1,2,4-triazol-1-yl) in methanol or acetic acid gave the corresponding 2-(1-nitrotrihalopropenylidene)-4-R-benzazetines. The latter reacted with amines, sodium alkoxides, and sodium thiolates, affording salts of the *aci*-nitro form. The reactions with benzoyl chloride and chloroacetyl chloride in the presence of pyridine led to formation of mixed anhydrides.

Benzazetines are relatively poorly studied compounds. Their first representatives were synthesized in 1966 [2]. The most convenient methods for preparation of benzazetines include photochemical or thermal decomposition of benzotriazines [2, 3] and sultams [4] and reactions of triethylamine with anthranilium salts [5]. All known benzazetine derivatives contain a substituent on the nitrogen atom. Benzazetines having an unsubstituted NH group were not isolated in the pure form. In a few publications [6, 7] the possibility for formation of such compounds as unstable intermediates in some chemical processes was postulated.

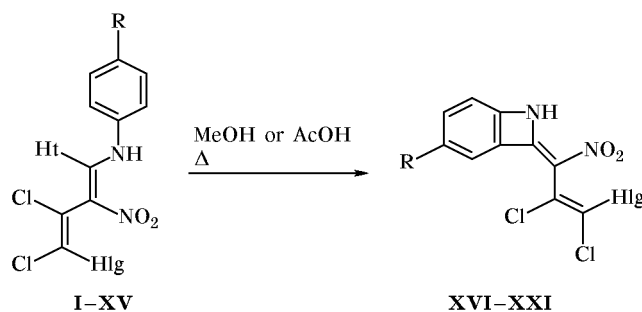
We previously reported on the synthesis and some reactions of 1-azolyl-1-arylamino-2-nitrotrichloro-1,3-butadienes and (*E*)-1-azolyl-1-arylamino-4-bromo-2-nitrodichloro-1,3-butadienes (azolyl = 1-benzotriazolyl, 3,5-dimethyl-1-pyrazolyl, 1,2,4-triazol-1-yl). We showed that the azolyl residues in these compounds can readily be replaced by various groups [1, 8]. The goal of the present work was to continue the study of chemical properties of 1-azolyl-1-arylamino-2-nitrotrihalo-1,3-butadienes and to develop new approaches to benzazetine systems on that basis.

We have found that heating of 1-azolyl-1-(4-R-phenylamino)-2-nitrotrihalo-1,3-butadienes **I–XV**

(R = BuO, EtO, MeO, Me) in methanol or acetic acid for 10 h at 55–60°C leads to formation of 2-(1-nitrotrihalo-2-propenylidene)-4-R-benzazetines **XVI–XXI** (Scheme 1). The yields of the products were 70–91%, except for methyl-substituted derivative **XIX** whose yield did not exceed 23%. In this case the reaction was accompanied by strong tarring.

The nature of the azolyl fragment has no appreciable effect on the process: the yields of the products obtained from triazolyl and pyrazolyl derivatives were lower by only 5–8% than those of the same products

Scheme 1.



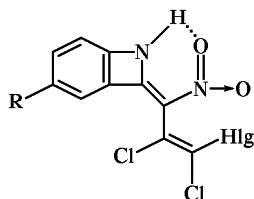
I–VII, Ht = 1-benzotriazolyl; **VIII–XIII**, Ht = 3,5-dimethyl-1-pyrazolyl; **XIV**, **XV**, Ht = 1,2,4-triazol-1-yl; **I–IV**, **VIII–X**, **XVI–XIX**, Hlg = Cl; **V–VII**, **XI–XV**, **XX**, **XXI**, Hlg = Br; **I**, **XVI**, R = BuO; **II**, **V**, **VIII**, **XI**, **XIV**, **XVII**, **XX**, R = EtO; **III**, **VI**, **IX**, **XII**, **XVIII**, **XXI**, R = MeO; **IV**, **VII**, **X**, **XIII**, **XV**, **XIX**, R = Me.

* For communication IV, see [1].

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obtained from the corresponding benzotriazolyl-1-arylamino-2-nitrotrihalobutadienes. The main factor is the nature and position of substituent in the benzene ring of the 1-arylamino fragment. We failed to obtain benzazetines from aniline, *p*- and *m*-bromoaniline, *m*-toluidine, *p*-aminobenzoic acid, and 2,4-diaminotoluene derivatives. Replacement of the terminal halogen atom in the initial diene by an amino group [1] also hinders the process. In these cases, the reactions were accompanied by tarring, and we failed to separate the resulting product mixtures. No reaction occurred in diethyl ether, while in benzene strong tarring was observed.

The structure of the products was established on the basis of their IR, NMR, and mass spectra and elemental analyses (Tables 1, 2). Theoretically, compounds **XVI–XXI** can exist as *Z* and *E* isomers with respect to the nitrovinyl fragment. The data of ^1H and ^{13}C NMR spectroscopy together with TLC showed that these products were formed as a single isomer. Taking into account the possibility for formation of six-membered H-chelate ring involving the nitro and amino groups, which is typical of nitroenamines [9], benzazetine derivatives **XVI–XXI** are likely to be *Z* isomers:



This assumption is confirmed by the presence in the IR spectra of all compounds of a strong absorption band in the region $1610\text{--}1650\text{ cm}^{-1}$, which belongs to vibrations of the $\text{C}=\text{N}$ bond. The nitro group gives rise to absorption bands in the regions $1360\text{--}1393\text{ cm}^{-1}$ (symmetric vibrations) and $1526\text{--}1583\text{ cm}^{-1}$ (antisymmetric vibrations). Vibrations of the $\text{C}=\text{C}$ bonds are characterized by absorption bands at $1491\text{--}1494$ and $1550\text{--}1601\text{ cm}^{-1}$.

In the ^1H NMR spectra of compounds **XVI–XXI** (Table 1) aromatic protons of the benzazetine fragment appear as a multiplet at δ 7.3–8.2 ppm. The NH proton signal is observed as a broadened singlet in the region δ 11.3–12.9 ppm. Also, signals from the alkoxy groups were present.

The ^{13}C NMR spectra were recorded for trichloro derivatives **XVI–XVIII**. Apart from the upfield signals from alkoxy groups, all compounds showed in the spectra three signals from aromatic carbon atoms

at δ_{C} , ppm: 101.30, 118.67, 124.84 (**XVI**); 105.07, 121.84, 127.57 (**XVII**); 104.72, 122.20, 127.58 (**XVIII**). In addition, 7 signals were observed. Four of these belong to carbon atoms of the diene fragment, and the remaining three signals correspond to aromatic carbon atoms.

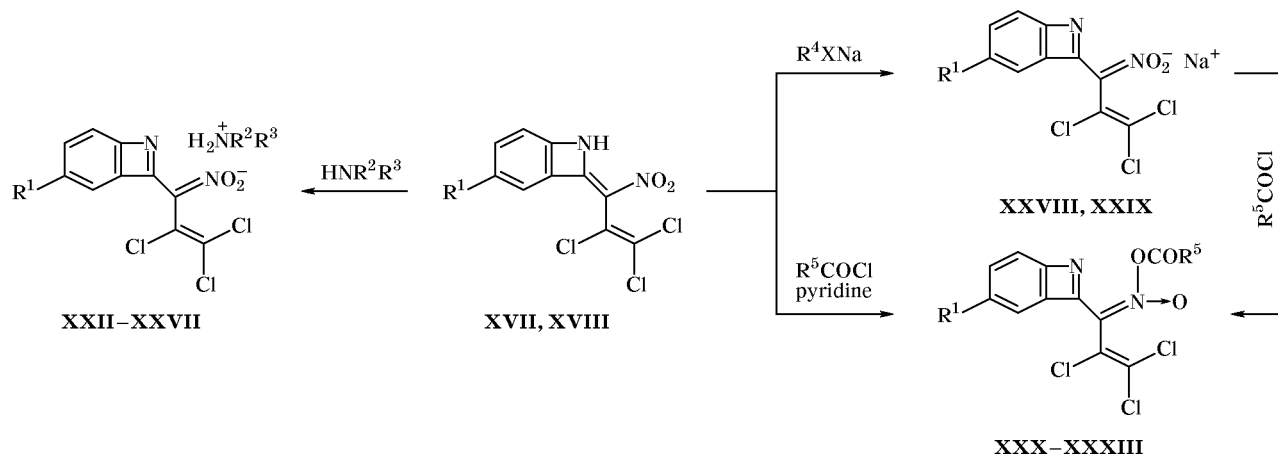
The mass spectra of **XVI–XXI** contain molecular ion clusters with isotope peak ratios 100:98:32:3.5 (**XVI–XIX**) and 61:100:46:6.4 (**XX**, **XXI**), which indicate the presence of three halogen atoms.

We have studied some chemical properties of benzazetines **XVII** and **XVIII**. In a basic medium, e.g., in alcoholic solutions of alkali, sodium alkoxides, or sodium thiolates, as well as by the action of amines in diethyl ether or benzene, the benzazetine system is transformed into benzazete, and the nitro group is converted into *aci*-nitro with formation of the corresponding salts **XXII–XXIX** (Scheme 2) in 70–80% yield. These salts are stable compounds which are readily soluble in water, alcohol, acetone, and chloroform and poorly soluble in hexane and other hydrocarbons. Treatment of salts **XXII–XXIX** with hydrochloric acid quantitatively gives initial compounds **XVII** and **XVIII**.

Benzazetines **XVII** and **XVIII** were brought into reactions with benzoyl and chloroacetyl chlorides. No reaction occurred on prolonged heating of the reactants in boiling ether or benzene. In the presence of pyridine, from equimolar amounts of the reactants we obtained the corresponding mixed anhydrides **XXX–XXXIII** in 60–65% yield (Scheme 2). Presumably, the NH proton in initial compounds **XVII** and **XVIII** is strongly deactivated by formation of intramolecular hydrogen bond with the nitro group, and addition of pyridine to the reaction mixture favors transformation of the benzazetine system into benzazete and proton transfer from the NH group to the nitro group. The resulting *aci*-nitro group reacts with acyl chloride, and liberated hydrogen chloride is bound by pyridine.

The structure of compounds **XXII–XXXIII** was determined from their IR, ^1H NMR and mass spectra and elemental analyses (Tables 1, 2). The IR spectra of **XXII–XXXIII** contained strong absorption bands at $1626\text{--}1650\text{ cm}^{-1}$, which are typical of $\text{C}=\text{N}$ bonds. Symmetric and antisymmetric vibrations of $\text{N}-\text{O}$ bonds in the nitro groups were observed at $1345\text{--}1385$ and $1519\text{--}1531\text{ cm}^{-1}$, respectively. The double $\text{C}=\text{C}$ bonds in the side chain and aromatic rings gave rise to absorption bands in the regions $1470\text{--}1490$ and $1575\text{--}1628\text{ cm}^{-1}$. Stretching vibrations of the carbonyl groups in mixed anhydrides **XXX–XXXIII** were characterized by strong absorption bands at 1750 , 1736 , 1746 , and 1733 cm^{-1} , respectively.

Scheme 2.



XXVII, XXII-XXIV, XXVIII, XXX, XXXI, $\text{R}^1 = \text{OEt}$; **XXVIII, XXV-XXVII, XXIX, XXXII, XXXIII**, $\text{R}^1 = \text{OMe}$; **XXII, XXV**, $\text{R}^2 = \text{H}$, $\text{R}^3 = t\text{-Bu}$; **XXIII, XXIV**, $\text{R}^2 = \text{R}^3 = \text{Et}$; **XXIV, XXVII**, $\text{R}^2\text{R}^3 = (\text{CH}_2)_5$; **XXX-XXXIII**, $\text{X} = \text{O}$, $\text{R}^4 = \text{Me, Et}$; $\text{X} = \text{S}$, $\text{R}^4 = \text{Ph, CH}_2\text{Ph}$; **XXX, XXXII**, $\text{R}^5 = \text{Ph}$; **XXXI, XXXIII**, $\text{R}^5 = \text{ClCH}_2$.

In the ^1H NMR spectra of salts **XXII-XXVII**, broadened singlets at δ 5.20–6.30 and 7.90–9.20 ppm correspond to protons of the NH_2^+ and NH_3^+ groups, respectively. Such signals are not observed in the spectra of anhydrides **XXX-XXXIII** and sodium salts **XXVIII** and **XXIX**. Also, multiplet signals from the benzazete fragments (δ 7.1–7.8 ppm) and alkyl and alkoxy groups were present.

The mass spectra of salts **XXII-XXIX** contained no molecular ion peaks. The main fragment ions are formed by elimination of amine molecule from compounds **XXII-XXIX**, of NaCl from products **XXVIII** and **XXIX**, and also of chlorine atoms and nitro group. Anhydrides **XXX-XXXIII** showed in the mass spectra the molecular ion peaks and fragment ion peaks resulting from elimination of the acyl fragment, alkyl groups, and chlorine atoms.

Mixed anhydrides **XXX-XXXIII** were also synthesized by the action of chloroacetyl chloride and benzoyl chloride on the corresponding sodium salts **XXVIII** and **XXIX**. This reaction provides an additional support to the proposed structure of compounds **XXX-XXXIII**.

EXPERIMENTAL

The IR spectra were recorded on a Protege-460 spectrometer in KBr. The ^1H NMR spectra were obtained on a Tesla BS-567A instrument (100 MHz) in CDCl_3 , and the ^{13}C NMR spectra were run on a Tesla BS-587A spectrometer (20 MHz) in acetone- d_6 . The chemical shifts were measured relative to TMS. The

mass spectra (50 eV) were recorded on an MKh-1320 mass spectrometer.

Compounds **II-XV** were synthesized by the procedures reported in [1, 8].

1-(1-Benzotriazolyl)-1-(4-butoxyphenylamino)-3,3,4-trichloro-2-nitro-1,3-butadiene (I). To a suspension of 4.83 g (10 mmol) of 1,1-bis(1-benzotriazolyl)-3,3,4-trichloro-2-nitro-1,3-butadiene in 100 ml of diethyl ether at 20°C we added over a period of 10 min a solution of 1.82 g (11 mmol) of *p*-butoxyaniline in 15 ml of ether, and the mixture was stirred for 4 h. The precipitate was filtered off, washed with ether (3×10 ml), and recrystallized from methanol. Yield 4.11 g (85%), mp 119–120°C. IR spectrum, ν , cm^{-1} : 1375, 1582 (NO_2); 1494, 1509, 1619 ($\text{C}=\text{C}$, $\text{C}=\text{N}$); 3256 (NH). ^1H NMR spectrum, δ , ppm: 0.92 t (3H, CH_3), 1.48 m (2H, CH_2C), 1.65 m (2H, CH_2C), 3.85 t (2H, CH_2O), 6.71 d (2H, H_{arom}), 7.02 d (2H, H_{arom}), 7.65 m (3H, CH, benzotriazole), 8.08 d (1H, CH, benzotriazole), 11.75 br.s (1H, NH). Found, %: C 49.95; H 3.88; Cl 21.90; N 14.44. M^+ 481. $\text{C}_{20}\text{H}_{18}\text{Cl}_3\text{N}_5\text{O}_3$. Calculated, %: C 49.76; H 3.76; Cl 22.03; N 14.51. M 482.75.

4-Butoxy-2-(2,3,3-trichloro-1-nitro-2-propenyli-dene)benzazetine (XVI). A mixture of 4.83 g (10 mmol) of butadiene **I** and 30 ml of glacial acetic acid was stirred for 10 h at 60°C. It was then poured onto ice, and the precipitate was filtered off, washed with water and ether, and dried in a vacuum. Recrystallization from chloroform–hexane (5:1) gave 2.55 g (70%) of product **XVI**, mp 169–171°C. ^{13}C NMR spectrum, δ_{C} , ppm: 13.76 (CH_3), 19.15 (CH_2C), 30.92

Table 1. Yields, melting points, and IR and ¹H NMR spectra of compounds **XVI–XXXIII**

Comp. no.	Yield, %	mp, °C	IR spectrum, ν , cm^{-1}		¹ H NMR spectrum, δ , ppm
			NO ₂	C=C, C=N)	
XVI	70	169–171	1361, 1529	1493, 1599, 1642	0.99 t (3H, CH ₃), 1.41–1.61 m (2H, CH ₂ CH ₃), 1.74–1.91 m (2H, CH ₂ CH ₂ CH ₃), 4.07 t (2H, CH ₂ O), 7.33–7.75 m (3H, C ₆ H ₃), 12.95 br.s (1H, NH)
XVII	91	209–210	1360, 1530	1492, 1601, 1648	1.35–1.55 (3H, CH ₃), 4.00–4.25 q (2H, CH ₂ O), 7.30–7.70 m (3H, C ₆ H ₃), 12.70 br.s (1H, NH)
XVIII	83	195–196	1365, 1532	1492, 1601, 1650	3.90 s (3H, CH ₃ O), 7.35–7.80 m (3H, C ₆ H ₃), 12.80 br.s (1H, NH)
XIX	25	190–191	1393, 1518	1546, 1593, 1680	2.50 s (3H, CH ₃), 7.5–8.2 m (3H, C ₆ H ₃), 12.5 br.s (1H, NH)
XX	79	202–204	1360, 1533	1493, 1600, 1650	1.33–1.52 t (3H, CH ₃), 4.08–4.28 q (2H, CH ₂ O), 7.35–7.71 (3H, C ₆ H ₃), 11.30 br.s (1H, NH)
XXI	76	198–200	1360, 1526	1492, 1600, 1648	3.92 s (3H, CH ₃ O), 7.40–7.75 m (3H, C ₆ H ₃), 11.45 br.s (1H, NH)
XXII	78	201–203	1345, 1531	1458, 1514, 1571, 1626	1.22 s (9H, CH ₃), 1.38–1.50 t (3H, CH ₃), 4.00–4.22 q (2H, CH ₂ O), 5.20 br.s (3H, $\overset{+}{\text{N}}\text{H}_3$), 7.15–7.75 m (3H, C ₆ H ₃)
XXIII	76	187–189	1362, 1519	1455, 1569, 1599, 1630	1.23–1.60 m (9H, CH ₃), 2.95–3.20 two q (4H, CH ₂ N), 4.00–4.25 q (2H, CH ₂ O), 7.15–7.75 m (3H, C ₆ H ₃), 9.20 br.s (2H, $\overset{+}{\text{N}}\text{H}_2$)
XXIV	73	108–110	1385, 1529	1455, 1600, 1648	1.35–1.45 t (3H, CH ₃), 1.50–1.90 m (6H, CH ₂ C), 3.05–3.30 m (4H, CH ₂ N), 4.00–4.20 q (2H, CH ₂ O), 7.15–7.75 m (3H, C ₆ H ₃), 7.90 br.s (2H, $\overset{+}{\text{N}}\text{H}_2$)
XXV	80	192–193	1345, 1529	1458, 1571, 1628	1.27 s (9H, CH ₃ C), 3.90 s (3H, CH ₃ O), 6.28 br.s (3H, $\overset{+}{\text{N}}\text{H}_3$), 7.20–7.80 m (3H, C ₆ H ₃)
XXVI	77	197–198	1351, 1521	1455, 1567, 1627	1.25–1.40 two t (6H, CH ₃), 2.93–3.15 two q (4H, CH ₂ N), 3.90 s (3H, CH ₃ O), 7.16–7.80 m (3H, C ₆ H ₃), 8.15 br.s (2H, $\overset{+}{\text{N}}\text{H}_2$)
XXVII	70	102–104	1383, 1529	1489, 1569, 1650	1.50–1.90 m (6H, CH ₂ C), 3.10–3.40 m (4H, CH ₂ N), 3.90 s (3H, CH ₃ O), 7.10–7.80 m (3H, C ₆ H ₃), 9.00 br.s (2H, $\overset{+}{\text{N}}\text{H}_2$)
XXVIII	80	168–170	1351, 1529	1460, 1570, 1625	1.20–1.45 t (3H, CH ₃), 3.70–4.05 q (2H, CH ₂ O), 6.95–7.50 m (3H, C ₆ H ₃)
XXIX	74	172–174	1352, 1531	1459, 1571, 1626	3.78 s (3H, CH ₃ O), 7.12–7.48 m (3H, C ₆ H ₃)
XXX	65	129–131	1369, 1503	1575, 1599, 1621	1.40–1.60 t (3H, CH ₃), 4.10–4.36 q (2H, CH ₂ O), 7.45–8.20 m (8H, C ₆ H ₅ and C ₆ H ₃)
XXXI	60	183–185	1368, 1530	1482, 1598, 1648	1.40–1.55 t (3H, CH ₃), 4.05–4.25 m (4H, CH ₂ O and CH ₂ Cl), 7.30–7.80 m (3H, C ₆ H ₃)
XXXII	64	137–139	1376, 1504	1575, 1600, 1622	4.00 s (3H, CH ₃ O), 7.45–8.30 m (8H, C ₆ H ₅ and C ₆ H ₃)
XXXIII	62	188–190	1365, 1532	1490, 1600, 1650	3.90 s (3H, CH ₃ O), 4.12 s (2H, CH ₂ Cl), 7.25–7.85 m (3H, C ₆ H ₃)

Table 2. Elemental analyses of compounds XVI–XXXIII

Comp. no.	Found, %				Formula	Calculated, %				<i>M</i>	
	C	H	Hlg	N		C	H	Hlg	N	found ^a	calcd.
XVI	46.35	3.87	29.46	7.51	C ₁₄ H ₁₃ Cl ₃ N ₂ O ₃	46.25	3.60	29.25	7.70	362	363.63
XVII	42.87	2.53	31.61	8.44	C ₁₂ H ₉ Cl ₃ N ₂ O ₃	42.95	2.70	31.70	8.35	334	335.57
XVIII	41.32	2.36	32.83	8.83	C ₁₁ H ₇ Cl ₃ N ₂ O ₃	41.09	2.20	33.08	8.71	320	321.55
XIX	43.44	2.61	34.50	9.05	C ₁₁ H ₇ Cl ₃ N ₂ O ₂	43.24	2.31	34.81	9.17	304	305.55
XX	37.69	2.58	39.91	7.45	C ₁₂ H ₉ BrCl ₂ N ₂ O ₃	37.93	2.39	39.69	7.37	378	380.02
XXI	35.99	2.22	41.52	7.84	C ₁₁ H ₇ BrCl ₂ N ₂ O ₃	36.10	1.93	41.21	7.65	364	366.00
XXII	47.12	5.06	25.86	10.25	C ₁₆ H ₂₀ Cl ₃ N ₃ O ₃	47.02	4.93	26.02	10.28	–	408.72
XXIII	47.06	4.61	25.60	9.83	C ₁₆ H ₂₀ Cl ₃ N ₃ O ₃	47.02	4.93	26.02	10.28	–	408.72
XXIV	48.93	4.98	25.40	10.20	C ₁₇ H ₂₀ Cl ₃ N ₃ O ₃	48.53	4.79	25.28	9.99	–	420.73
XXV	45.50	4.74	27.03	10.68	C ₁₅ H ₁₈ Cl ₃ N ₃ O ₃	45.65	4.60	26.95	10.65	–	394.69
XXVI	45.84	4.76	26.50	10.56	C ₁₅ H ₁₈ Cl ₃ N ₃ O ₃	45.65	4.60	26.95	10.65	–	394.69
XXVII	47.58	4.08	25.84	10.08	C ₁₆ H ₁₈ Cl ₃ N ₃ O ₃	47.25	4.46	26.15	10.39	–	406.70
XXVIII	40.07	2.48	29.71	7.94	C ₁₂ H ₈ Cl ₃ N ₂ NaO ₃	40.31	2.25	29.75	7.83	–	357.56
XXIX	38.06	1.49	30.63	8.62	C ₁₁ H ₆ Cl ₃ N ₂ NaO ₃	38.46	1.76	30.96	8.15	–	343.54
XXX	51.67	3.10	24.05	6.41	C ₁₉ H ₁₃ Cl ₃ N ₂ O ₄	51.90	2.98	24.19	6.37	438	439.68
XXXI	41.05	2.63	34.27	6.74	C ₁₄ H ₁₀ Cl ₄ N ₂ O ₄	40.81	2.45	34.42	6.80	410	412.06
XXXII	50.44	2.74	25.18	6.97	C ₁₈ H ₁₁ Cl ₃ N ₂ O ₄	50.79	2.61	24.99	6.58	424	425.66
XXXIII	39.44	2.04	35.55	7.43	C ₁₃ H ₈ Cl ₄ N ₂ O ₄	39.23	2.03	35.63	7.04	396	398.02

^a The molecular weights of compounds XVI–XXI and XXX–XXXIII were determined from the mass spectra; given are *m/z* values corresponding to the ³⁵Cl and ⁷⁹Br isotopes. The mass spectra of compounds XXII–XXIX contained no molecular peak ions; determination of their molecular weights by cryoscopy in dioxane, water, benzene, and nitrobenzene gave underestimated values.

(CH₂C), 68.67 (CH₂O); 101.30, 118.67, 124.84 (CH_{arom}); 126.41, 127.70, 131.83, 134.18, 143.70, 155.78, 156.87 (C_{arom}, C_{diene}).

4-Ethoxy-2-(2,3,3-trichloro-1-nitro-2-propenylidene)benzazetine (XVII). A mixture of 4.55 g (10 mmol) of butadiene II and 50 ml of methanol was stirred for 15 h at 55°C, and the precipitate was filtered off, washed with water and ether, and dried in a vacuum. Recrystallization from chloroform–hexane (5:1) gave 3.05 g (91%) of benzazetine XVII, mp 209–210°C. ¹³C NMR spectrum, δ_C, ppm: 18.35 (CH₃); 67.93 (CH₂O); 105.07, 121.84, 127.57 (CH_{arom}); 123.05, 129.30, 130.72, 133.93, 137.21, 156.85, 158.70 (C_{arom}, C_{diene}).

Compounds XVIII–XXI were synthesized in a similar way from butadienes III–XV. Their yields, melting points, spectral parameters, and elemental analyses are given in Tables 1 and 2.

4-Methoxy-2-(2,3,3-trichloro-1-nitro-2-propenylidene)benzazetine (XVIII). ¹³C NMR spectrum, δ_C, ppm: 59.86 (CH₃O); 104.72, 122.20, 127.58 (CH_{arom}); 123.33, 129.67, 131.13, 134.29, 137.56, 157.30, 159.92 (C_{arom}, C_{diene}).

***tert*-Butylammonium salt of 1-*aci*-nitro-2,3,3-trichloro-1-(4-ethoxybenzazet-2-yl)-2-propene (XXII).** To a solution of 0.67 g (2 mmol) of benzazetine XVII in 100 ml of benzene we added a solution of 0.16 g (2.2 mmol) of *tert*-butylamine in 10 ml of benzene, and the mixture was stirred for 20 h at 45°C. The precipitate was filtered off, washed with benzene and hexane, and dried in vacuo. Yield of XXVIII 0.64 g (78%).

Compounds XXIII–XXVII were synthesized in a similar way from benzazetines XVII and XVIII and appropriate amines. Their yields, melting points, spectral parameters, and elemental analyses are given in Tables 1 and 2.

Sodium salt of 1-*aci*-nitro-2,3,3-trichloro-1-(4-ethoxybenzazet-2-yl)-2-propene (XXVIII). To a solution of 0.05 g (2.2 mmol) of sodium in 50 ml of anhydrous methanol we added 0.67 g (2 mmol) of benzazetine XVII, and the mixture was stirred for 4 h at 20–25°C. Chloroform was added to the mixture, the extract was filtered and concentrated under reduced pressure, and the product was precipitated with ether, washed with hexane, and dried in a vacuum. Yield of XXVIII 0.57 g (80%).

Sodium salt of 1-*aci*-nitro-(4-methoxybenzazet-2-yl)-2,3,3-trichloro-2-propene (XXIX). To a solution of 0.05 g (2.2 mmol) of sodium in 50 ml of anhydrous ethanol we added 0.24 g (2.2 mmol) of benzenethiol, and the mixture was kept for 1 h. To the resulting solution we added 0.67 g (2 mmol) of benzazetine **XVIII**, and the mixture was stirred for 3 h at 20–25°C. The solvent and benzenethiol were removed under reduced pressure, the oily residue was dissolved in 30 ml of chloroform, and the solution was filtered and diluted with 50 ml of hexane. The precipitate was filtered off and was purified by reprecipitation from chloroform with hexane. Yield of **XXIX** 0.51 g (74%).

O-Benzoyl-1-*aci*-nitro-2,3,3-trichloro-1-(4-ethoxybenzazet-2-yl)-2-propene (XXX). *a.* A mixture of 0.67 g (2 mmol) of benzazetine **XVII**, 0.34 g (2.4 mmol) of benzoyl chloride, and 0.19 g (2.4 mmol) of pyridine in 100 ml of benzene was stirred for 10 h at 60°C. The mixture was filtered, the filtrate was evaporated to dryness, and the residue was washed with hexane and treated with ether. The extract was diluted with hexane, and the precipitate was filtered off, washed with hexane, and dried in a vacuum. Yield of product **XXX** 0.57 g (65%).

b. Benzoyl chloride, 0.31 g (2.2 mmol), was added to a mixture of 0.72 g (2 mmol) of sodium salt **XXVIII** and 30 ml of benzene, and the mixture was stirred for 12 h at 50°C. The precipitate was filtered off, the filtrate was evaporated to dryness, and the residue was washed with hexane and was dissolved in CH₂Cl₂. The product was precipitated with hexane and dried in a vacuum. Yield 0.55 g (62%).

Mixed anhydrides **XXXI–XXXIII** were obtained from benzazetines **XVII** and **XVIII** and benzoyl or chloroacetyl chloride, following the above procedure,

method *a.* Their yields, melting points, spectral parameters, and elemental analyses are given in Tables 1 and 2.

REFERENCES

1. Potkin, V.I., Zapol'skii, V.A., Knizhnikov, V.A., and Kaberdin, R.V., *Russ. J. Org. Chem.*, 2000, vol. 36, no. 6, pp. 877–883.
2. Burgess, E.M. and Milne, G., *Tetrahedron Lett.*, 1966, no. 1, pp. 93–96; Burgess, E.M. and McCullagh, L.M., *J. Am. Chem. Soc.*, 1966, vol. 88, no. 7, pp. 1580–1581.
3. Ege, G., *Chem. Ber.*, 1968, vol. 101, no. 9, pp. 3079–3089; Ege, G. and Pasedach, F., *Chem. Ber.*, 1968, vol. 101, no. 9, pp. 3089–3095; Bashir, N. and Gilchrist, T., *J. Chem. Soc., Perkin Trans. 1*, 1973, no. 8, pp. 868–872.
4. Lancaster, M. and Smith, D.J.H., *J. Chem. Soc., Chem. Commun.*, 1980, no. 11, pp. 471–472.
5. Olofson, R.A., van der Meer, R.K., Hoskin, D.H., Bernheim, M.Y., Stournas, S., and Morrison, D.S., *J. Org. Chem.*, 1984, vol. 49, no. 18, pp. 3367–3372.
6. Rees, C.W., Starr, R.C., and Whittle, R.J., *Tetrahedron Lett.*, 1976, no. 50, pp. 4647–4650.
7. Pfister-Guillouzo, G., Gracian, F., Senio, A., Letulle, M., and Ripoll, J.-L., *Tetrahedron Lett.*, 1992, vol. 33, no. 39, pp. 5753–5756.
8. Zapol'skii, V.A., Potkin, V.I., Nechai, N.I., Kaberdin, R.V., and Pevzner, M.S., *Russ. J. Org. Chem.*, 1997, vol. 33, no. 10, pp. 1461–1467; Zapol'skii, V.A., Potkin, V.I., Nechai, N.I., Kaberdin, R.V., and Pevzner, M.S., *Russ. J. Org. Chem.*, 1997, vol. 33, no. 11, pp. 1632–1637.
9. Perekalin, V.V., Sopova, A.S., and Lipina, E.S., *Nepredel'nye nitrosoedineniya* (Unsaturated Nitro Compounds), Leningrad: Khimiya, 1982.