# Formation and thermal decomposition of adducts of phthalimidonitrene with spiro(1-pyrazolinecyclopropanes)

*Yu. V. Tomilov,[a]* I. V. Kostyuchenko,[a] E. V. Shulishov,[a] B. B. Averkiev,[b] M. Yu. Antipin,[b] and O. M. Nefedov[a]**

*[a]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 6390. E-mail: tom@ioc.ac.ru*

*[b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085.*

Oxidation of *N*-aminophthalimide with lead tetraacetate in the presence of spiro(1-pyrazolinecyclopropanes) at temperature from −20 °C to −30 °C resulted in the formal generation of phthalimidonitrene followed by its addition at the N=N bond of the pyrazoline ring to form 5(3)-substituted *N*-{spiro[1-pyrazolinio-3(5),1′-cyclopropane]}-*N*-phthalimidoamides (azimines), whose regioisomeric compositions were determined to a large extent by the nature of the substituents in the pyrazoline ring. The structures of phthalimidoazimines were established based on the NMR spectra and X-ray diffraction data. Thermal conversions of the resulting adducts, which proceeded either with retention or with opening of the spiro-fused cyclopropane ring, were studied.

**Key words:** spiro(1-pyrazolinecyclopropanes), *N*-pyrazolinio-*N*-phthalimidoamides (azimines), *N*-phthalimidonitrene, tetrahydropyrazolo[1,2-*b*]phthalazine-5,10-diones, thermolysis of azimines, NMR spectra, X-ray diffraction analysis.

The reactions of nitrenes with azo compounds were studied in close detail.[1] These reactions proceed generally when substituents in nitrene and azo compounds are of different electronic nature, to form stable 1,3-dipolar compounds, namely, azimines. The volumes of the substituents also affect the reactivity of azo compounds. The reactions with unsymmetrical azo compounds afforded two regioisomeric adducts, the sterically less hindered isomer being the major product.[1,2] The reactions of nitrenes (in particular, of aminonitrenes) with cyclic analogs of azoalkanes are less well studied, among which the addition of phthalimidonitrene to 2,3-diazabicyclo[2.2.1]hept-2-ene[3] and methyl-substituted 1-pyrazolines is worthy of note.[2,4]

In the present work, we studied the reactions of phthalimidonitrene and its formal precursor, *viz.*, *N*-acetoxyaminophthalimide,[5] with 1-pyrazolines **1**—**4**, including, on the one hand, the spiro-fused cyclopropane fragment and, on the other hand, substituents such as Ph, $N_3$, Br, or COOMe (Schemes 1 and 2). The starting spiro(pyrazolinecyclopropanes) **3** and **4** were synthesized by 1,3-dipolar cycloaddition of diazocyclopropane, which was generated *in situ*, to vinyl bromide[6] or methyl methacrylate.[7] Analogously, 5-phenylspiro(1-pyrazoline-3,1′-cyclopropane) (**1**) was prepared for the first time by the reaction of diazocyclopropane, which was generated *in situ*, with styrene (the yield was ~67%). Azide **2** was synthesized by the replacement of the bromine atom in pyrazoline **3** under the action of sodium azide.[6]

The reactions of generation and formal addition of *N*-phthalimidonitrene were carried out according to a standard procedure[4] by oxidation of *N*-aminophthalimide in $CH_2Cl_2$ with lead tetraacetate in the presence of an equimolar amount of 1-pyrazolines **1**—**4** and an excess of $K_2CO_3$ at a temperature from −20 to −30 °C. In all cases, the initial pyrazolines remained partially unconsumed (15—35%) and, according to the published data,[8] phthalimide, *N*-phthalimidophthalimide, and 1,4-bis-phthaloyltetrazene were obtained as by-products of oxidative conversions. Thus, the oxidation reaction of *N*-aminophthalimide with pyrazoline **1** resulted in the addition of the phthalimidonitrene fragment at the nitrogen atoms of the pyrazoline ring to form regioisomeric *N*-{5(3)-phenylspiro[1-pyrazolinio-3(5),1′-cyclopropane]}-*N*-phthalimidoamides (**5a** and **6a**) in a total yield of 70—75% (the ratio of the isomers was ~5.5 : 1). An analytically pure specimen of the major isomer **5a** was obtained by recrystallization from ethanol. The $^1$H NMR spectrum of this specimen has a characteristic set of signals of three protons of the pyrazoline ring (Table 1) and isolated signals of the cyclopropane ring (at δ 0.92 and 1.27), the phthalimide fragment (at δ 7.66 and 7.77), and the phenyl substituent (at δ 7.3—7.5).

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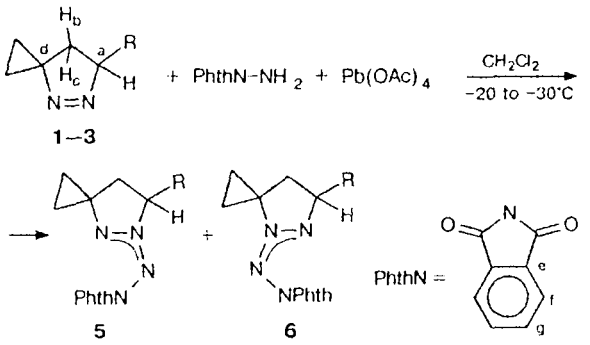
**Table 1.** $^1$H NMR spectra of the starting spiro(pyrazolinecyclopropanes), the resulting *N*-(1-pyrazolinio)-*N*-phthalimidoamides, and the products of their thermal conversions ($CDCl_3$, δ, *J*/Hz)

| Compound | $H_a$ (dd) | $H_b$ (dd) | $H_c$ (dd) | $CH_2CH_2$ (m) | $C_6H_4$ (m, 2×2 H) | Other H atoms | $J_{ab}$ | $J_{ac}$ | $J_{bc}$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 5.63 | 2.25 | 1.79 | 1.84, 1.73, 1.18, 1.10 (4×1 H) | | 7.22—7.40 (Ph) | 9.7 | 7.0 | 12.3 |
| **2** | 5.81 | 2.09 | 1.61 | 1.80 (2 H), 1.19 (2 H) | | | 8.7 | 5.5 | 13.4 |
| **3** | 6.39 | 2.50 | 2.12 | 1.84 (2 H), 1.27 (2 H) | | | 8.0 | 3.0 | 14.5 |
| **4** | | 2.30 d | 1.62 d | 1.74 (2 H), 1.11 (2 H) | | 1.60 (Me), 3.79 (OMe) | | | 12.2 |
| **5a** | 5.98 | 2.92 | 2.28 | 1.27 (2 H), 0.92 (2 H) | 7.80 and 7.67 | 7.35—7.54 (Ph) | 9.6 | 4.9 | 12.4 |
| ***Z*-5b** | 6.16 | 2.66 | 2.09 | 1.22 (2 H), 0.91 (2 H) | 7.84 and 7.72 | | 8.1 | 4.0 | 13.4 |
| ***Z*-5c** | 6.44 | 3.14 | 2.48 | 1.30 (2 H), 1.20, 0.92 (2×1 H) | 7.82 and 7.70 | | 7.4 | 1.6 | 13.9 |
| **6a** | 5.30 | 2.83 | 2.39 | 2.21, 2.03, 1.39, 1.11 (4×1 H) | 7.81 and 7.68 | 7.27—7.51 (Ph) | 8.2 | 6.6 | 12.2 |
| **6b** | 5.63 | 2.82 | 2.28 | 2.08 (2 H), 1.23 (2 H) | 7.85 and 7.75 | | 7.2 | 3.0 | 13.0 |
| ***Z*-7** | | 2.75 d | 2.38 d | 1.21 (2 H), 0.90 (2 H) | 7.81 and 7.70 | 2.09 (Me), 3.93 (OMe) | | | 12.7 |
| **9** | 5.89 | 3.19 | 2.05 | 2.83, 2.04 (2×1 H), 0.84 (2 H) | 8.25 and 7.77 | 7.22—7.41 (Ph) | 8.5 | 1.2 | 12.5 |
| **12** | | 2.88 d | 2.12 d | 2.63, 2.17 (2×1 H), 0.89 (2 H) | 8.25 and 7.78 | 1.92 (Me), 3.82 (OMe) | | | 12.5 |
| **14** | 7.76 d | 6.08 d | | 3.52 t, 3.11 t ($^3J$ = 7.4) | 7.89 and 7.78 | 8.48 br.s (NH) | 2.3 | | |

**Scheme 1**




R = Ph (**1**, **5a**, **6a**), $N_3$ (**2**, **5b**, **6b**), Br (**3**, **5c**)

We failed to isolate the minor azimine **6a** in the individual state. However, its content in the specimen was increased to ~75% by TLC. The $^1$H NMR spectrum of azimine **6a** has a set of signals identical with that observed for the major isomer. However, the signal of the methine proton is substantially shifted upfield (Δδ 0.68; see Table 1). This fact suggests, by analogy with other unsymmetrically substituted 1-pyrazolines,[4] the presence of two regioisomers. In this case, isomer **5a**, which was formed by the addition of phthalimidonitrene to the sterically less hindered N(1) atom of the initial pyrazoline **1**, was obtained as the major product. This is also confirmed by the chemical shifts of the protons of the spiro-fused cyclopropane ring directed toward the nitrogen atoms of the pyrazoline ring. Thus, these signals in the NMR spectra of azimines **5a** and **6a** are observed at δ 1.2—1.3 and 2.0—2.2, respectively, which is associated with the deshielding effect of the substituent at the N atom adjacent to the cyclopropane ring. Interestingly, the signals of the same protons of the cyclopropane rings in spiro(1-pyrazoline-3,1′-cyclopropanes), including those in pyrazoline **1**, are observed at δ 1.8—1.9, while the signals of these protons in spiro(2-pyrazoline-5,1′-cyclopropanes) are observed at δ 0.9—1.0.[9]

The addition of phthalimidonitrene to azidopyrazoline **2** proceeded analogously to compound **1** to give azide-containing azimines **5b** and **6b** in a total yield of up to 65%. In this case (according to the data of $^1$H and $^{13}$C NMR spectroscopy; Tables 1 and 2), the sterically less hindered regioisomer **5b** is the major product (the **5b** : **6b** ratio was approximately 3.3 : 1). The latter isomer was isolated in analytically pure form by crystallization from benzene. The fact that the resulting compound has the structure of regioisomer **5b** with the *Z* configuration of the phthalimide substituent was established by X-ray diffraction analysis (Table 3, Fig. 1, *a*). The principal geometric parameters of the molecule are given in Table 4. Unfortunately, we failed to isolate the minor isomer in the individual form either by TLC or by crystallization from benzene or ethanol. Boiling (4 h) of benzene solutions of pure azimine **5b** as well as of its mixture with isomer **6b** did not lead to interconversions of these isomers. This fact, along with the NMR spectral data, supports the conclusion that the resulting azimines are regioisomers rather than stereoisomers.

Unlike pyrazolines **1** and **2**, the oxidation reactions of *N*-aminophthalimide with bromopyrazoline **3** proceeded less efficiently. In this case, although the reaction conditions were somewhat varied (the temperature was varied from −10 to −30 °C; the time of addition of $Pb(OAc)_4$ was varied from 20 to 90 min; alternate addition of small amounts of *N*-aminophthalimide and $Pb(OAc)_4$), ~30—45% of the initial bromopyrazoline **3** remained unchanged. Treatment of the reaction mixture with a small amount of ether and recrystallization of the precipitate that formed from benzene afforded *N*-{5-bromospiro[1-pyrazolinio-3,1′-cyclopropane]}-*N*-phthalimidoamide (**5c**) in 30—35% yield. The $^1$H NMR spectrum of the azimine obtained has the expected set of

**Table 2.** $^{13}C$ NMR spectra of the starting spiro(pyrazolinecyclopropanes), the resulting *N*-(1-pyrazolinio)-*N*-phthalimidoamides, and the products of their thermal conversions ($CDCl_3$, δ)

| Compound | $C_a$ | $C_b$ | $C_d$ | $CH_2CH_2$ | CO | $C_e$ | $C_f$ | $C_g$ | Other C atoms |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 90.0 | 33.2 | 69.5 | 14.1 (2 C) | | | | | 139.5, 128.8, 127.7, 127.2 (Ph) |
| **2** | 96.0 | 30.6 | 69.6 | 14.6, 14.3 | | | | | |
| **3** | 78.6 | 35.3 | 68.2 | 14.8, 12.9 | | | | | |
| **4** | 92.6 | 35.1 | 69.1 | 14.1, 13.3 | | | | | 171.2 (CO), 52.4 (OMe), 22.0 (Me) |
| **5a** | 79.7 | 38.6 | 53.9 | 14.2, 12.3 | 164.0 | 131.2 | 123.2 | 133.9 | 137.9, 129.1, 128.8, 126.6 (Ph) |
| ***Z*-5b** | 88.1 | 35.2 | 53.6 | 13.8, 12.4 | 164.2 | 131.1 | 123.4 | 134.0 | |
| ***Z*-5c** | 67.6 | 40.8 | 54.5 | 13.5, 10.0 | 164.2 | 131.1 | 123.4 | 134.0 | |
| **6a** | 70.4 | 38.5 | 55.0 | 15.0, 13.9 | | 131.2 | 123.3 | 133.8 | 140.8, 127.8, 126.8, 126.5 (Ph) |
| **6b** | 80.5 | 35.5 | 56.1 | 16.6, 13.9 | 164.1 | 131.3 | 123.6 | 134.1 | |
| ***Z*-7** | 83.7 | 42.0 | 52.7 | 13.0, 12.6 | 164.2 | 131.2 | 123.2 | 133.8 | 169.0 (CO), 53.7 (OMe), 23.2 (Me) |
| **9** | 59.1 | 40.4 | 46.3 | 12.3, 7.0 | 155.0 | 130.6 | 127.3 | 133.3 | 139.5, 129.0, 128.0, 125.8 (Ph) |
| | | | | | 154.8 | 129.2 | 127.1 | 133.0 | |
| **12** | 65.6 | 44.4 | 45.3 | 10.8, 8.1 | 155.1 | 130.6 | 127.1 | 133.3 | |
| | | | | | 154.9 | 129.2 | 127.0 | 132.9 | |
| **14** | 130.8 | 104.5 | 149.2 | 32.2, 31.1 | 164.6 | 129.9 | 124.1 | 134.8 | |

**Table 3.** Principal crystal-structural data for compounds **5b**, **5c**, and **7**

| Parameter | *Z*-5b | *Z*-5c | *Z*-7 |
|---|---|---|---|
| Molecular formula | $C_{13}H_{11}N_7O_2$ | $C_{16}H_{14}BrN_4O_2$ | $C_{16}H_{16}N_4O_4$ |
| M | 297.29 | 374.22 | 328.33 |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1$ |
| *a*/Å | 13.101(3) | 7.228(2) | 7.805(5) |
| *b*/Å | 7.902(2) | 9.970(2) | 10.001(4) |
| *c*/Å | 14.620(3) | 22.595(6) | 10.265(5) |
| β/deg | 116.44(3) | 98.00(2) | 93.37(5) |
| *V*/Å$^3$ | 1355.2(5) | 1612.6(6) | 799.9(7) |
| *Z* | 4 | 4 | 2 |
| $d_{calc}$/g cm$^{-3}$ | 1.457 | 1.541 | 1.363 |
| Diffractometer | CAD-4 | Siemens P3/PC | Siemens P3/PC |
| Radiation (λ/Å) | | Mo-Kα (0.71073) | |
| Scanning technique | θ/2θ | ω | ω |
| $2\theta_{max}$/deg | 44 | 50 | 55 |
| Number of independent reflections | 1661 | 2830 | 1933 |
| $R_1$ (based on *F* for reflections with $I > 2\sigma(I)$) | 0.0679 | 0.0895 | 0.0752 |
| | 1040 | 1521 | 852 |

signals (see Table 1). It is highly probable that the signals of the protons of the cyclopropane ring observed at δ 0.9—1.3 are indicative of the structure of azimine **5c**, which was formed by the addition of the phthalimidonitrene fragment to the N(1) atom of bromopyrazoline **3**, remote from the spirocyclopropane ring. X-ray diffraction analysis of the azimine obtained confirmed the validity of the assignment made and demonstrated that the azimine has the structure of isomer *Z*-**5c** (see Fig. 1,*b*, Tables 3 and 4).

**Table 4.** Principal geometric parameters of molecules *Z*-**5b**, *Z*-**5c**, and *Z*-**7**

| Bond | *d*/Å | | | |
|---|---|---|---|---|
| | *Z*-5b | *Z*-5c | *Z*-7 | **8*** |
| N(1)–N(2) | 1.270(5) | 1.277(10) | 1.251(7) | 1.272 |
| N(2)–N(3) | 1.317(5) | 1.305(10) | 1.326(8) | 1.314 |
| N(3)–N(4) | 1.410(5) | 1.406(9) | 1.412(8) | 1.401 |
| N(1)–C(11) | 1.454(6) | 1.460(11) | 1.453(9) | 1.474 |
| N(2)–C(13) | 1.525(5) | 1.517(10) | 1.523(8) | 1.519 |
| C(9)–C(10) | 1.508(7) | 1.47(2) | 1.496(12) | |
| C(9)–C(11) | 1.492(6) | 1.503(14) | 1.526(11) | |
| C(10)–C(11) | 1.488(6) | 1.46(2) | 1.479(10) | |
| C(11)–C(12) | 1.519(6) | 1.520(13) | 1.512(10) | |
| C(12)–C(13) | 1.515(6) | 1.499(13) | 1.523(9) | |
| C(13)–Y** | 1.452(6) | 1.933(10) | 1.521(9) | |
| N(5)–N(6) | 1.247(6) | | | |
| N(6)–N(7) | 1.129(6) | | | |
| **Angle** | **ω/deg** | | | |
| | *Z*-5b | *Z*-5c | *Z*-7 | **8*** |
| N(1)–N(2)–N(3) | 130.1(4) | 129.9(7) | 129.8(6) | 127.5 |
| N(1)–N(2)–C(13) | 116.5(4) | 116.1(7) | 118.1(5) | 117.1 |
| N(3)–N(2)–C(13) | 113.4(4) | 114.0(7) | 112.2(5) | 115.4 |
| N(2)–N(3)–N(4) | 109.3(4) | 108.5(7) | 108.3(5) | 109.1 |
| N(2)–N(1)–C(11) | 106.8(4) | 106.9(7) | 107.1(5) | 106.5 |
| N(1)–C(11)–C(12) | 108.0(4) | 107.0(8) | 108.6(6) | |
| C(11)–C(12)–C(13) | 102.7(4) | 103.4(7) | 104.2(5) | |
| N(2)–C(13)–C(12) | 100.2(4) | 99.9(7) | 99.8(5) | |
| C(9)–C(11)–C(10) | 60.8(3) | 59.3(7) | 59.7(5) | |
| C(10)–C(9)–C(11) | 59.5(3) | 58.9(7) | 58.6(5) | |
| C(9)–C(10)–C(11) | 59.7(3) | 61.8(7) | 61.7(5) | |

* The data on *Z*-*N*-(5,5-dimethyl-1-pyrazolinio)-*N*-phthalimidoamide (**8**)[10] are given for comparison.

** Y = $N_3$ (**5b**), Br (**5c**), or COOMe (**7**).

Unfortunately, one cannot speak about the high selectivity of addition of phthalimidonitrene to pyrazoline **3**, unlike pyrazolines **1** and **2**, because the $^1H$ NMR

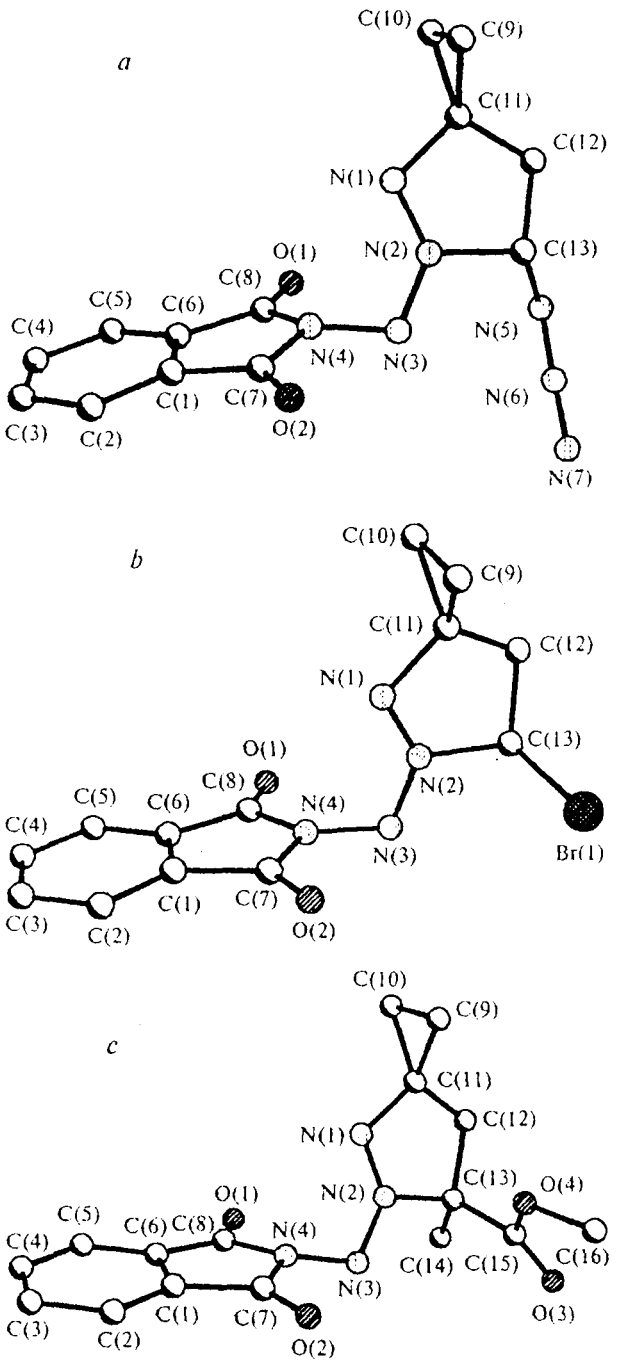
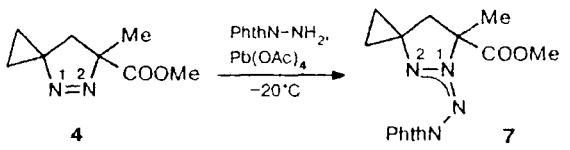



**Fig. 1.** Overall views of molecules *Z*-**5b** (*a*), *Z*-**5c** (*b*), and *Z*-**7** (*c*).

spectrum of the reaction mixture contains an additional set of signals with lower intensities compared to the signals of *Z*-**5c**, which are also typical of the three-spin system of the pyrazoline ring. We failed to isolate and identify the compound formed. However, it is highly improbable that this compound is a regioisomer corresponding to structure **6** because the signal of the methine proton of the CHR group (δ 6.61) is observed in a lower field compared to the analogous signal of *Z*-**5c** (δ 6.44), which is inconsistent with the spectral data for regioisomers **5a,b** and **6a,b**.

Pyrazoline **4** formally containing two tertiary substituents at the azo group also added the phthalimidonitrene fragment. However, in this case azimine was formed as the only isomer in ~52% yield. Since the $^1$H NMR spectrum of the latter compound (see Table 1) has signals of the protons of the methyl group at very low field (δ 2.09) and signals of the protons of the cyclopropane ring at higher field (δ 1.21) compared to the initial pyrazoline **4**, it can be suggested that in this case, the addition of the phthalimidonitrene fragment also occurred at the nitrogen atom that is more remote from the cyclopropane fragment (N(2)) in spite of the fact that the sterically more hindered regioisomer **7** was formed.

**Scheme 2**



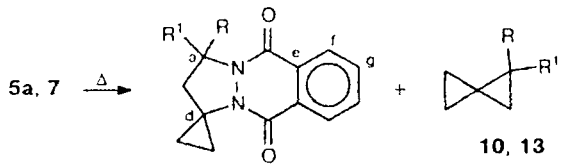

To confirm the structure of azimine **7**, we studied this compound by X-ray diffraction analysis (see Fig. 1,*c*, Tables 3 and 4). It was established that the phthalimidoimine fragment is attached to the nitrogen atom that is remote from the cyclopropane ring and the phthalimide fragment has the *Z* configuration with respect to the exocyclic N(2)—N(3) bond. An analogous configuration of the azimine fragment has been established previously[10] in *Z*-*N*-[5,5-dimethyl-1-pyrazolinio]-*N*-phthalimidoamine (**8**), which was the minor product of addition of phthalimidonitrene to 3,3-dimethyl-1-pyrazoline. However, since this reaction afforded the sterically less hindered regioisomer, *viz.*, *N*-[3,3-dimethyl-1-pyrazolinio]-*N*-phthalimidoamide, as the major isomer (the ratio of the isomers was 3.7 : 1),[2] the regioselective formation of azimine **7** should be considered taking into account the electronic factors rather than steric hindrances caused by the substituents. It should be noted that the 1,5-addition of acyl chlorides to compound **4** also proceeded exclusively at the N(2) atom.[11]

In all the structures (**5b**, **5c**, and **7**) studied by X-ray diffraction analysis, the heterocycle adopts an envelope conformation with the C(12) atom deviating from the mean plane through the remaining atoms of the heterocycle, on the average, by 0.3 Å. The azimine system is virtually planar. The sum of the bond angles at the central N(2) atom is 360° and the maximum deviations from the mean N(1)N(2)N(3)N(4)C(11)C(13) plane in

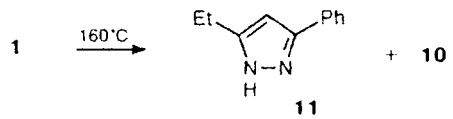
all the compounds under consideration are less than 0.05 Å.

A comparison of the N—N bond lengths (see Table 4) is indicative of the presence of conjugation between the double N(1)—N(2) bond and the lone electron pair of the N(3) atom. The N(2)—N(3) bond has a one-and-a-half order, while the N(1)=N(2) bond is slightly elongated compared to the typical value (1.25—1.26 Å).

We also studied thermal conversions of azimines **5a—c** and **7** isolated in individual form. Thermolysis of azimine **5a** in an *o*-dichlorobenzene solution at 170 °C (~10 h) proceeded with elimination of nitrogen and resulted in complete conversion of **5a** (according to the data of TLC and $^1$H NMR spectroscopy). After removal of the solvent *in vacuo* and treatment of the residue with ether, tetrahydropyrazolo[1,2-*b*]phthalazinedione **9** was obtained in ~28% yield. Compound **9** was identified by NMR spectroscopy (see Tables 1 and 2) and mass spectrometry. The $^1$H NMR spectrum of the portion of the solvent distilled off had high-field signals typical of phenylspiropentane **10** (*cf.* Ref. 12) along with intense signals of *o*-dichlorobenzene. Interestingly, thermolysis of pyrazoline **1** proceeded differently. In this case (*o*-dichlorobenzene, 160 °C, 0.5 h), isomerization of pyrazoline **1** to 5(3)-ethyl-3(5)-phenylpyrazole (**11**) was the major process (the yield of **11** was ~67%), accompanied by the formation of phenylspiropentane, which was distilled off together with the solvent. The absence of pyrazole **11** among the thermolysis products of azimine **5a** indicates that the thermal decomposition of spirocyclopropane-containing 1-pyrazolinioamides to form spiropentane derivatives proceeded without the participation of spiro(1-pyrazolinecyclopropanes), in particular, of compound **1**.

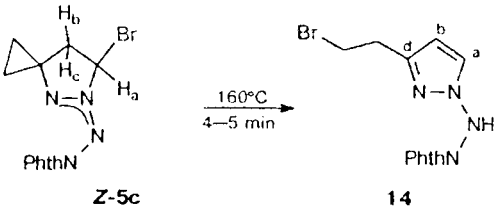



R = H, R¹ = Ph (**5a**, **9**, **10**); R = Me, R¹ = COOMe (**7**, **12**, **13**)




Thermolysis of azimine **7** (*o*-dichlorobenzene, 170 °C, 16 h) proceeded analogously. After removal of the solvent, tetrahydropyrazolo[1,2-*b*]phthalazinedione **12** was isolated from the reaction mixture in ~30% yield. In the solvent distilled off, spiropentanecarboxylic ester **13** was detected. The latter compound has been synthesized previously by pyrolysis of pyrazoline **4**.[7] The compositions of the resulting heterocyclic compounds, which differ from the initial azimines **5a** and **7** by $N_2$, were established based on the data of elemental analysis and mass spectra, which have intense molecular ion peaks. In the $^1$H NMR spectra of compounds **9** and **12**, the signals of the protons of the cyclopropane ring that are directed toward the condensed heterocycle are shifted downfield compared to those of azimines **6a,b** and have different chemical shifts due to the nonequivalence of the substituents in the pyrazolidine ring (see Table 1).

Unlike azimines **5a** and **7**, thermolysis of bromopyrazolinioamide **5c** proceeded differently. In this case, elimination of nitrogen was virtually not observed and isomerization, which was accompanied by opening of the cyclopropane ring and migration of the bromine atom, was the major process. Thus, heating of azimine **5c** in *o*-dichlorobenzene over a short period (160 °C, 4—5 min) afforded *N*-(pyrazol-1-yl)phthalimidoamine **14** in 65% yield.




*Z*-**5c** **14**

The results obtained demonstrated that the addition of the phthalimidonitrene fragment to spiro(1-pyrazolinecyclopropanes) proceeded predominantly (or exclusively) at the nitrogen atom that is remote from the cyclopropane fragment to form *Z*-*N*-(pyrazolinio)-*N*-phthalimidoamides (azimines) that are stable under normal conditions. Thermolysis of azimines, which do not contain highly reactive substituents, was accompanied by elimination of nitrogen to yield spiropentane derivatives and condensed heterocycles (tetrahydropyrazolo[1,2-*b*]phthalazinediones), which retain the spiro-fused cyclopropane fragment. Thermolysis of bromine-containing azimine *Z*-**5c** can serve as a new procedure for the preparation of amines containing several N—N bonds.

## Experimental

The $^1$H and $^{13}$C NMR spectra were recorded on Bruker AC-200 (200 and 50.3 MHz) and Bruker AM-300 (300 MHz) spectrometers in $CDCl_3$ solutions containing 0.05% $Me_4Si$ as the internal standard. The mass spectra were measured on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct introduction of the sample). The IR spectra were obtained on a Bruker IFS-113v spectrometer in thin layers. The initial spiro(1-pyrazolinecyclopropanes) **2—4** were prepared according to procedures reported previously.[6,7] X-ray diffraction studies of single crystals of compounds **5b**, **5c**, and **7** were performed on Siemens P3/PC (**5c** and **7**) and CAD-4 (**5b**) diffractometers using Mo-Kα radiation. The principal crystal-structural data for the crystals studied are given in Table 3. The structures were solved by direct methods and refined anisotropically by the full-matrix least-squares method. The positions of the hydrogen atoms in compounds **5c** and **7** were

placed in geometrically calculated positions and were included in the refinement using the riding model. In the structure of **5b**, the positions of the hydrogen atoms were located from the difference electron density synthesis and refined isotropically. The experimental data sets for compounds **5b** and **7** were processed with the use of the PROFIT program for profile analysis.[13] All crystal-structural calculations were performed using the SHELXTL PLUS program package.[14] The atomic coordinates and the complete crystal-structural data for compounds **5b**, **5c**, and **7** were deposited with the Cambridge Structural Database. The principal geometric parameters of the compounds under study are given in Table 4.

**5-Phenylspiro(1-pyrazoline-3,1′-cyclopropane) (1).** *N*-Nitroso-*N*-cyclopropylurea (2.58 g, 20 mmol) was added portionwise to an intensively stirred mixture of MeONa (1.40 g, 26 mmol) in MeOH (4 mL), $CH_2Cl_2$ (20 mL), and styrene (2.08 g, 20 mmol) at a temperature from −25 to −20 °C during 15 min. The reaction mixture was stirred for 10 min. Then the temperature was increased to 10 °C and water (~0.5 mL) was added. The transparent organic layer was separated and the solid residue was washed with $CH_2Cl_2$ (10 mL) and dried with $Na_2SO_4$. The solvent together with the unconsumed styrene was removed *in vacuo*. The residue (2.45 g) was dissolved in benzene and passed through a layer of silica gel. After evaporation of the solvent, a viscous slightly yellowish liquid (2.30 g) was obtained, which corresponded to pyrazoline **1** (the yield was 67%). According to the data of TLC and $^1H$ and $^{13}C$ NMR spectroscopy (see Tables 1 and 2), this product was rather pure. The partial mass spectrum, *m/z* ($I_{rel}$ (%)): 172 (52) $[M]^+$, 171 (34), 157 (45), 129 (48), 128 (52), 39 (100).

**Synthesis of phthalimidoazimines (general procedure).** A solution of $Pb(OAc)_4$ (0.66 g, 1.5 mmol) in $CH_2Cl_2$ (20 mL) was added dropwise to a suspension containing pyrazolines **1**—**4** (1.5 mmol), *N*-aminophthalimide (0.24 g, 1.5 mmol), and $K_2CO_3$ (1.4 g, 10 mmol) in $CH_2Cl_2$ (20 mL) at a temperature from −30 to −20°C during 0.5 h. The reaction mixture was stirred for 1.5 h, filtered through a thin layer of silica gel, and washed with $CH_2Cl_2$ (15 mL). The solvent was removed *in vacuo*. Then the residue was treated with ether (20 mL) and the precipitate of azimines that formed was filtered off and recrystallized. The major isomers **5a**—**c** or **7** were isolated. The filtrate was concentrated and the solid residue was separated by TLC (silica gel, a 3.5 : 1 benzene—AcOEt mixture). The initial pyrazolines, *viz.*, 1,4-bisphthalyltetrazene[8] ($R_f$ = 0.75, the partial mass spectrum, *m/z* ($I_{rel}$ (%)): 320 (47) $[M]^+$, 292 (17), 174 (25), 146 (58), 104 (100)) and phthalimidoazimines **6a,b** with an admixture of isomers **5a,b** (in the case of pyrazolines **1** and **2**), were isolated. The compositions of the resulting compounds were analyzed at all stages by $^1H$ NMR spectroscopy.

***N*-{5-Phenylspiro[1-pyrazolinio-3,1′-cyclopropane]}-*N*-phthalimidoamide (5a).** The yield was 58—60%, m.p. 216—218°C (from EtOH). The partial mass spectrum, *m/z* ($I_{rel}$ (%)): 332 (2.1) $[M]^+$, 303 (1.7), 104 (100), 76 (56). Found (%): C, 68.97; H, 4.95; N, 16.58. $C_{19}H_{16}N_4O_2$. Calculated (%): C, 68.66; H, 4.85; N, 16.86. The $^1H$ and $^{13}C$ NMR spectra are given in Tables 1 and 2, respectively.

***Z*-*N*-{5-Azidospiro[1-pyrazolinio-3,1′-cyclopropane]}-*N*-phthalimidoamide (*Z*-5b).** The yield was ~50%, m.p. 173—174°C (from benzene). The partial mass spectrum, *m/z* ($I_{rel}$ (%)): 297 (3.6) $[M]^+$, 255 (2), 146 (17), 104 (100), 90 (46), 76 (60). Found (%): C, 52.23; H, 3.65; N, 33.18. $C_{13}H_{11}N_7O_2$. Calculated (%): C, 52.52; H, 3.73; N, 32.98. The $^1H$ and $^{13}C$ NMR spectra are given in Tables 1 and 2, respectively.

***Z*-*N*-{5-Bromospiro[1-pyrazolinio-3,1′-cyclopropane]}-*N*-phthalimidoamide (*Z*-5c).** The yield was ~30%, m.p. 141—142°C (from benzene). The partial mass spectrum, *m/z* ($I_{rel}$ (%)): 336 and 334 (2.4) $[M]^+$, 255 (0.8), 227 (1.9), 213 and 211 (1.6), 104 (100), 76 (41). Found (%): C, 46.17; H, 3.05; Br, 23.28. $C_{13}H_{11}BrN_4O_2$. Calculated (%): C, 46.59; H, 3.31; Br, 23.84. The $^1H$ and $^{13}C$ NMR spectra are given in Tables 1 and 2, respectively.

***Z*-*N*-{5-Methyl-5-methoxycarbonylspiro[1-pyrazolinio-3,1′-cyclopropane]}-*N*-phthalimidoamide (*Z*-7).** The yield was ~52%, m.p. 210—211°C (from EtOH). The partial mass spectrum, *m/z* ($I_{rel}$ (%)): 328 (1.8) $[M]^+$, 241 (2.2), 200 (12), 104 (100), 76 (56). Found (%): C, 58.77; H, 4.95; N, 16.80. $C_{16}H_{16}N_4O_4$. Calculated (%): C, 58.53; H, 4.91; N, 17.06. The $^1H$ and $^{13}C$ NMR spectra are given in Tables 1 and 2, respectively.

**Thermolysis of phthalimidoazimines (general procedure).** Solutions of phthalimidoazimines **5a** and **7** (~0.3 mmol) in *o*-dichlorobenzene (1 mL) were heated at ~170 °C for 10 and 16 h, respectively, until gas evolution ceased. Then the solvent was removed *in vacuo* and condensed phthalazinediones **9** and **12** were obtained by recrystallization of the solid residue from a 1 : 2 benzene : hexane mixture. The $^1H$ NMR spectrum of the fraction that was distilled off revealed the presence of phenyl- (**10**)[12] or 1-methyl-1-methoxycarbonylspiropentanes (**13**),[7] which virtually did not contain admixtures of other compounds.

**Spiro{5,10-dioxo-3-phenyl-2,3,4,5,10,11-hexahydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,1′-cyclopropane} (9).** The yield was ~28%, m.p. 147—148°C (from ether). The partial mass spectrum, *m/z* ($I_{rel}$ (%)): 304 (98) $[M]^+$, 236 (18), 227 (10), 200 (16), 156 (40), 104 (100), 76 (53). The $^1H$ and $^{13}C$ NMR spectra are given in Tables 1 and 2, respectively.

**Spiro{3-methoxycarbonyl-3-methyl-5,10-dioxo-2,3,4,5,10,11-hexahydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,1′-cyclopropane} (12).** The yield was ~30%, m.p. 152—153°C (from ether). The partial mass spectrum, *m/z* ($I_{rel}$ (%)): 300 (100) $[M]^+$, 241 (86), 200 (88), 148 (50), 130 (48), 104 (91), 76 (94). The $^1H$ and $^{13}C$ NMR spectra are given in Tables 1 and 2, respectively.

**5(3)-Ethyl-3(5)-phenylpyrazole (11).** A solution of pyrazoline **1** (60 mg, 0.35 mmol) in *o*-dichlorobenzene (1 mL) was heated in a sealed tube at 170°C for 3 h. The solvent was removed by microdistillation *in vacuo* (1 Torr, the temperature of the bath was 70 °C). In the distillate, phenylspiropentane (**10**) was detected by $^1H$ NMR spectroscopy (*cf.* Ref. 12). The residue was dissolved in a 3 : 1 benzene—AcOEt mixture and passed through a short layer of silica gel. After removal of the solvents, compound **11** was obtained as an oily slightly yellowish liquid in a yield of 40 mg (~68%). The partial mass spectrum, *m/z* ($I_{rel}$ (%)): 172 (100) $[M]^+$, 171 (62), 157 (32). $^1H$ NMR, δ: 10.0 (br.s, 1 H, NH), 7.74 and 7.29 (both m, 2+3 H, Ph), 6.37 (s, 1 H, H-4), 2.65 (q, 2 H, $CH_2$, $J$ = 7.3 Hz), 1.20 (t, 3 H, Me, $J$ = 7.3 Hz). $^{13}C$ NMR, δ: 149.5 and 149.2 (C-3, C-5), 132.5, 128.7, 127.6, and 125.6 (Ph), 100.3 (C-4), 19.5 ($CH_2$), 13.4 (Me).

***N*-[3-(2-Bromoethyl)pyrazol-1-yl]-*N*-phthalimidoamine (14).** A solution of azimine **5c** (55 mg, 0.16 mmol) in *o*-dichlorobenzene (1.5 mL) was heated at 160 °C for 4—5 min. Then the solvent was removed *in vacuo* and the residue was recrystallized from a 1 : 4 benzene—hexane mixture. Compound **14** was obtained as yellow crystals in a yield of 35 mg (~65%), m.p. 161—163°C. The partial mass spectrum, *m/z* ($I_{rel}$ (%)): 336 and 334 (0.5) $[M]^+$, 279 and 277 (0.8), 252 and 250 (0.4), 199 (1.1), 183 (13), 104 (100), 76 (30). The $^1H$ and $^{13}C$ NMR spectra are given in Tables 1 and 2, respectively.

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