1720 (C=O); 1610, 1520. ^{1}H NMR ($CDCl_3$), δ: 3.18 (s, 6 H, Me_2N); 7.00 (d, 1 H, CH=, J = 13.5 Hz); 7.12 (s, 1 H, CH=); 7.50—7.90 (m, 10 H, 2 Ph); 8.30 (d, 1 H, NCH=).

2-Benzyl-5-cyano-8-phenacyl-6-phenyl-2,7-naphthyridin-1-one (5a). A mixture of enamine **4** (0.22 g, 0.5 mmol) and benzylamine (0.20 g, 1.8 mmol) in 3 mL of pyridine was refluxed for 5 h. The precipitate was filtered off, washed with MeOH (5 mL) and ether (2×5 mL), and dried *in vacuo* (10 Torr, 50 °C) to give 0.15 g (50%) of 2,7-naphthyridine **5a**, m.p. 277—278 °C. MS (EI, 70 eV), m/z: 455 $[M]^+$. IR (KBr), ν/cm^{-1}: 2210 (C≡N); 1660, 1612, 1550 (C=C, C=O). ^{1}H NMR ($CDCl_3$), δ: 5.30 (s, 2 H, CH_2); 6.78 (d, 1 H, CH=); 7.40—8.10 (m, 15 H, 3 Ph + 1 H, CH=); 8.53 (s, 1 H, CH=); 16.63 (br.s, 1 H, OH).

5-Cyano-8-phenacyl-6-phenyl-2-propyl-2,7-naphthyridin-1-one (5b) was prepared similarly to compound **5a**. The yield of 2,7-naphthyridine **5b** was 58%, m.p. 258—260 °C. MS (EI, 70 eV), m/z: 407 $[M]^+$. ^{1}H NMR ($CDCl_3$), δ: 1.08 (t, 3 H, Me); 1.88 (m, 2 H, CH_2); 4.00 (t, 2 H, NCH_2); 6.70 (d, 1 H,CH=); 7.49—8.00 (m, 10 H, 2 Ph + 1 H, CH=); 8.46 (s, 1 H, CH=); 16.63 (s, 1 H, OH).

8-Benzoyl-6-benzyl-3-cyano-4-(2-dimethylaminovinyl)-2-phenyl-1,6-naphthyridin-5-one (6). A mixture of compound **3** (0.3 g, 0.88 mmol) and benzylamine (0.5 g, 4.6 mmol) in 3 mL of EtOH was refluxed for 5 h. The precipitate was filtered off, washed with EtOH (3 mL) and ether (2 mL), and dried *in vacuo*. Benzene (5 mL) and DMF DMA (0.2 g, 1.7 mmol) were added, and the mixture was refluxed for 20 h. The precipitate was filtered off, washed with ether (2×5 mL), and dried *in vacuo* (10 Torr, 50 °C) to give 0.2 g (74%) of 1,6-naphthyridine **6**, m.p. 238—239 °C. MS (EI, 70 eV), m/z: 510 $[M]^+$. IR (KBr), ν/cm^{-1}: 2205 (C≡N); 1663, 1630, 1605, 1500 (C=C, C=O). ^{1}H NMR ($CDCl_3$), δ: 3.15 (s, 6 H, Me_2N); 5.23 (s, 2 H, NCH_2); 7.22—7.88 (m, 15 H, 3 Ph + 1 H, CH= + 1 H, CH=); 8.00 (d, 1 H, CH=).

The results of elemental analysis of compounds **4**, **5a,b**, and **6** correspond to the results of calculations.

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A new approach to synthesis of 1-aryl-2-nitrozodiazene 1-*N*-oxides

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We recently obtained 1-aryl-2-nitrodiazene 1-oxides (NDO) by nitration of 1-aryl-2-acetyldiazene 1-oxides[1]; however, the imperfection of the method of their synthesis due to thermal and chemical instability of the starting compounds hinders investigation of this new class of compounds.

This publication investigates the possibility of NDO synthesis (Scheme 1) by substitutive nitration of stable 1-aryldiazene 1-oxides **2** that include *tert*-butyl (**2a—c**), *tert*-butoxycarbonyl (**2d**), and carbamoyl (**2e**) groups at the distal N atom.

In nitration with nitronium tetrafluoroborate in MeCN, the best results were obtained for *tert*-butyldiazene oxides **2a—c**; the yields of corresponding NDO **3a—c** were ≥75% (Table 1). Apparently, this reaction proceeds *via* formation of intermediate **5** with subsequent elimination of the *tert*-butyl cation.

Nitrodiazene oxide **3a** is also produced in good yield from carbamoyldiazene oxide **2e**, but the reaction rate in this case is substantially slower. The most easily substituted group is the *tert*-butoxycarbonyl group in

Table 1. Synthesis of 1-aryl-2-nitrodiazene 1-oxides **3a—c** (see Scheme 1)

Reaction	T/°C (t/h)	Yield of product **3** (%)
2a → **3a**	20 (0.7)	91
2b → **3b**	1) −20 (0.5), 2) −20 → +10 (0.2)	81
2c → **3c**	20 (6)	75
2d → **3a**	−20 → +20 (0.2)	45
2e → **3a**	20 (7)	85

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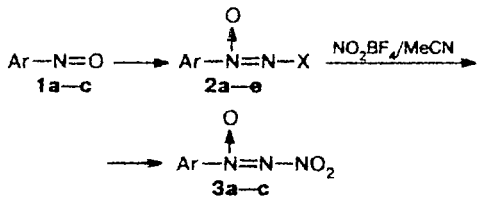
Table 2. Melting points and spectral parameters of compounds **2a,d,e**, **3a**, and **4**

Compound	M.p./°C (solvent)	Found / Calculated (%) C	H	N	Cl	Molecular formula	IR (KBr), ν/cm^{-1}	^{1}H NMR, δ[a]	^{14}N NMR, δ[a,b] [Δν$_{1/2}$/Hz]	MS,[c] *m/z*
2a	83—84 (hexane)	42.96 / 42.66	3.81 / 3.94	9.61 / 9.95	37.98 / 37.77	$C_{10}H_{11}Cl_3N_2O$	1510 (N(O)=N)	1.50 (s, 9 H, Bu^t); 7.40 (s, 2 H, Ar)	−60 (N→O) [70]	280 [M]$^+$
2d	104—104.5 (hexane)	40.75 / 40.58	3.39 / 3.41	8.30 / 8.60	32.47 / 32.67	$C_{11}H_{11}Cl_3N_2O_3$	1510 (N(O)=N); 1770 (C=O)	1.62 (s, 9 H, Bu^t); 7.46 (s, 2 H, Ar)	−56 (N→O) [70]	324 [M]$^+$
2e	135—137 (CCl_4)	31.17 / 31.32	1.48 / 1.50	15.31 / 15.65	39.45 / 39.61	$C_7H_4Cl_3N_3O_2$	1492 (N(O)=N); 2708 (C=O)	5.90 (br.s, 2 H, NH_2); 7.48 (s, 2 H, Ar)	−53 (N→O) [85]	267 [M]$^+$
3a	80—81 (hexane)	26.73 / 26.65	0.72 / 0.75	15.38 / 15.54	39.46 / 39.33	$C_6H_2Cl_3N_3O_3$	1495 (N(O)=N); 1287, 1622 (NO_2)	7.53 (s, 2 H, Ar)	−39 (NO_2) [25] −55 (N→O) [50]	269 [M]$^+$
4	104—105 (hexane)	33.62 / 33.57	0.81 / 0.80	16.38 / 16.76	42.59 / 42.46	$C_7H_2Cl_3N_3O$	1487 (N(O)=N); 2205 (CN)	7.53 (s, 2 H, Ar)	−33 (N→O) [90]	249 [M]$^+$

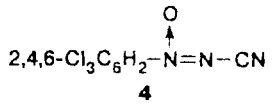
[a] In $CDCl_3$.
[b] Chemical shifts relative to nitromethane.
[c] EI, 70 eV; reported peaks with ^{35}Cl isotope.

Scheme 1

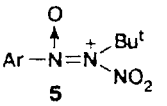


Ar = 2,4,6-$Cl_3C_6H_2$ (**1a**, **2a**, **2d**, **2e**, **3a**), Ph (**1b**, **2b**, **3b**), 2-$NO_2C_6H_4$ (**1c**, **2c**, **3c**); X = Bu^t (**2a,b,c**), COOBu^t (**2d**), $CONH_2$ (**2e**)

Reagents and conditions: 1. **2a** from **1a**: Br_2NBu^t, CH_2Cl_2, 20 °C, 3 h (91%); 2. **2d** from **1a**: NH_2COOBu^t, dibromoisocyanuric acid (DBI), CH_2Cl_2, 20 °C, 2 h (98%); 3. **2e** from **1a**: H_2NCN, DBI, CH_2Cl_2/Et_2O, 0 → 20 °C (compound **4**, 87%), then HCl/H_2O/dioxane, 20 °C, 4 h (87%).



4



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compound **2d**; however, the yield of NDO **3a** does not exceed 45%, and this is due to formation of side products.

To the best of our knowledge, the carbamoyl group, as well as the *tert*-butoxycarbonyl one, were not used previously as leaving groups in substitute nitration reactions.

The starting diazene oxides **2a**, **2b**,[2] **2c**,[3] and **2d** were prepared from nitroso compounds **1** and *N,N*-dibromo derivatives according to the Kovacic[2] procedure, and **2e** — by hydrolysis of cyanodiazene **4***.

The structures of compounds **2a,d,e**, **3a** and **4** are confirmed by spectral methods (see Table 2). NDO **3b** and **3c** are identical with the previously known samples[1].

* About synthesis and hydrolysis of cyanodiazene oxides see Ref. 4.

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