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Design and synthesis of pyrazolo[3,4-*d*]pyridazine 5,6-dioxides as novel NO-donors

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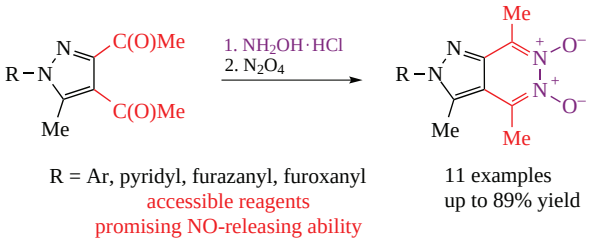
A simple and effective protocol for the synthesis of 2*H*-pyrazolo[3,4-*d*]pyridazine 5,6-dioxides includes a transformation of accessible 3,4-diacetyl-5-methyl-1*H*-pyrazoles into the corresponding 1,4-dioximes followed by their N_2O_4-mediated oxidative cyclization. All transformations proceed under mild conditions in good to high yields. According to the Griess assay, synthesized 2*H*-pyrazolo[3,4-*d*]pyridazine 5,6-dioxides showed promising NO-donor profiles producing NO in a wide range of concentrations.



Keywords: NO-donors, oxidative cyclization, pharmacologically oriented compounds, 1,2,5-oxadiazoles, pyrazolo[3,4-*d*]pyridazine 5,6-dioxides, dinitrogen tetraoxide.

One of the main trends in the design of potential drug candidates with improved pharmacokinetic profiles is a construction of new structures through a molecular hybridization of diverse compounds with known pharmacological activity.[1] In recent years, such approach has been widely used for the synthesis of hybrid molecules containing nitric oxide (NO) releasing structural motifs. Nitric oxide is a ubiquitous and crucial regulator of cellular metabolism, affecting various physiological processes.[2] Among the promising compounds capable of exogenous NO release under physiological conditions, 1,2,5-oxadiazole 2-oxides (furoxans) attract much attention.[3] Furoxan-based hybrid structures exhibit a number of pharmacological properties superior to those of the parent medications and furoxan precursors. Apparently, this fact may serve as an evidence to the synergistic effect of the NO-donor furoxan scaffold and hybridized pharmaceutical framework.[4] A wide series of promising drug candidates incorporating NO-donor furoxan subunit was successfully synthesized through a molecular hybridization approach.[5]

Previously, we have demonstrated that a combination of the furoxan ring with other NO-donor heterocyclic fragments (azasydnones,[6] pyridazine *N*,*N*′-dioxides[7]) resulted in enhanced NO-releasing ability compared to the parent compounds. This effect was especially relevant in the case of fused heterocyclic structures comprising a furoxan ring and pyridazine *N*,*N*′-dioxide moiety, namely, 4,7-dimethyl-1,2,5-oxadiazolo[3,4-*d*]pyridazine 1,5,6-trioxide **1** (Figure 1). Compound **1** was able to generate thiol-dependent amounts of NO and NO-like species and to relax noradrenaline-precontracted aortic rings at concentrations less than 0.1 mM. Deoxygenated furazan analogue, 4,7-dimethyl-1,2,5-oxadiazolo[3,4-*d*]pyridazine 5,6-dioxide **2**, was less active since the furazan subunit is unable to release NO. Nevertheless, compound **2** exhibited promising antiaggregant activity.[7]

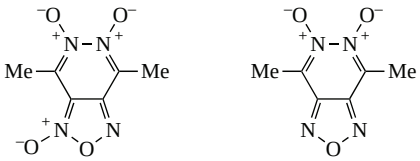


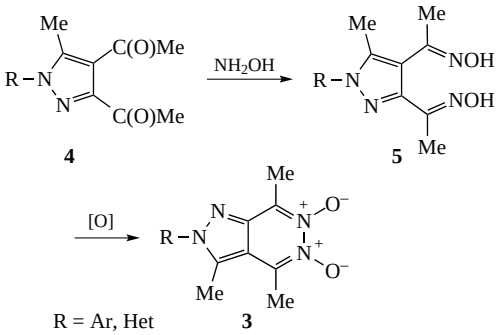
Figure 1 Previously synthesized structures comprising 1,2,5-oxadiazole and pyridazine *N*,*N*′-dioxide rings.

Therefore, a search for new effective NO-donors comprising pyridazine *N*,*N*′-dioxide moiety fused with other pharmacophoric heterocycles remains highly urgent.

There are two synthetic routes to the formation of a pyridazine *N*,*N*′-dioxide framework. The first one is based on a direct oxidation of the pyridazine scaffold. However, this approach usually suffers from low reaction yields of the target products.[8] Later, utilization of one of the strongest oxidizers HOF enabled a preparation of these compounds in much higher yields, albeit considerable amounts of pyridazine *N*-oxides were still formed.[9] The second approach to the assembly of a pyridazine *N*,*N*′-dioxide core includes an oxidative cyclization of 1,4-dioximes.[10] Interestingly, only several examples of fused heterocyclic systems comprising a pyridazine *N*,*N*′-dioxide moiety annulated to the 1,2,5-oxadiazole ring synthesized by this approach are known so far.[7,11] At the same time, bicyclic structures incorporating pyridazine *N*,*N*′-dioxide scaffold fused with a pyrazole ring, which is a known pharmacophore in various medications,[12] are completely unknown. Herein, we present our research on the design and synthesis of 2*H*-pyrazolo[3,4-*d*]-pyridazine 5,6-dioxides incorporating additional aromatic and heterocyclic (pyridine, furazan, furoxan) moieties. A construction of the target biheteroaryl derivatives containing a furoxan motif

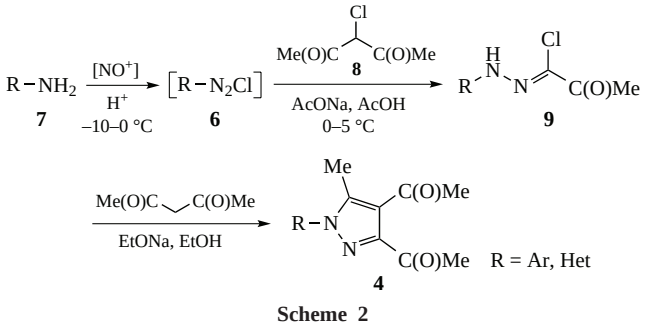
as another structural scaffold capable of NO release was especially emphasized. Since pyridazine dioxide derivatives correspond to valuable NO-donor prodrug candidates, their NO-releasing ability was estimated *in vitro*.

A simple two-step approach for an assembly of the target bicyclic systems **3** starting from readily available reagents has been herein proposed. This route involves a transformation of diacetylpyrazoles **4** into the corresponding dioximes **5** with subsequent oxidative cyclization into the final structures **3** (Scheme 1).



Scheme 1

The initial diacetylpyrazoles **4** were synthesized according to a standard procedure[13] by an azo coupling of (het)arenediazonium salts **6** (prepared by diazotization of the corresponding amines **7**) with chloroacetylacetone **8**. Thus formed chlorohydrazones[14] **9** underwent cyclocondensation with acetylacetone resulting in diacetylpyrazoles **4** (Scheme 2). Arguably, this reaction occurs *via* an *in situ* generation of nitrile imine intermediates.[14(b),(c)]



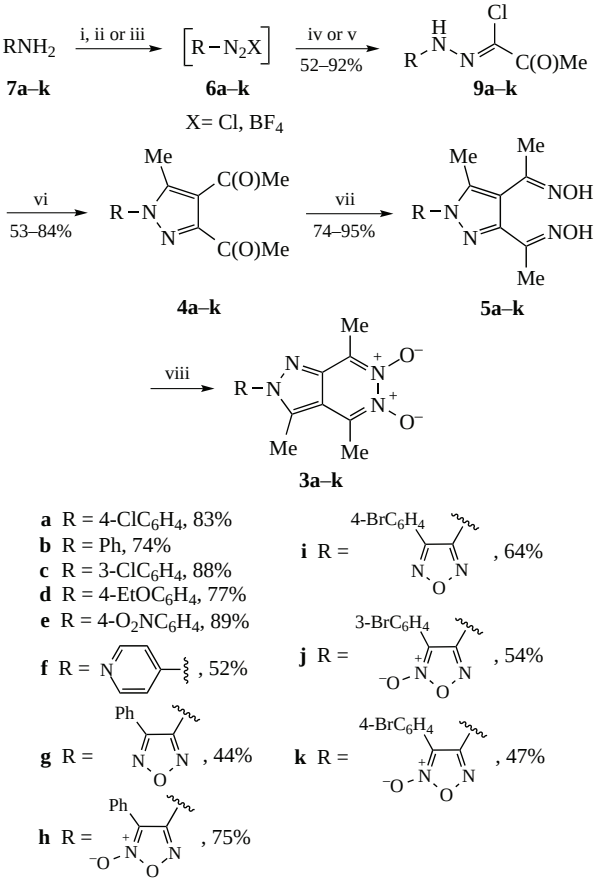
Scheme 2

Dioximes **5** were obtained upon treatment of diketones **4** with $NH_2OH \cdot HCl$ in EtOH under elevated temperatures in the absence of any bases. Since the most unexplored step in the presented strategy is an oxidation of 1,4-dioximes **5** into the target bicyclic systems **3**, representative 4-chlorophenyl substituted substrate **5a** was synthesized to optimize oxidation conditions (Scheme 3, Table 1). A treatment of dioxime **5a** with 100% HNO_3 in CF_3CO_2H resulted in a decomposition of the starting material (entries 1, 2). No reaction occurred when the $K_3Fe(CN)_6$/NaOH system was applied (entry 3). Target pyridazine 5,6-dioxide **3a** was formed in moderate yield with the use of excess of N_2O_4 in Et_2O in the presence of $NaHCO_3$ (entry 4). A higher yield of compound **3a** was achieved upon treatment of dioxime **5a** with N_2O_4 without any additives (entry 5). A replacement of Et_2O with $CHCl_3$ resulted in a significant drop of the yield along with a formation of substantial amounts of unidentified by-products (entry 6). The yield of the target product **3a** did not depend on the molar excess of N_2O_4 (entries 5, 7–9). Therefore, the optimal conditions for the oxidative cyclization of dioxime **5a** into pyridazine *N*,*N'*-dioxide **3a** were the treatment of dioxime **5a** with two equivalents of N_2O_4 in Et_2O at 20 °C for 1 h (entry 8).

Table 1 Optimization of the reaction conditions for the synthesis of 2-(4-chlorophenyl)-2*H*-pyrazolo[3,4-*d*]pyridazine 5,6-dioxide **3a**.[a]

Entry	Oxidant (equiv.)	Solvent	*T*/°C	*t*/h	Yield of **3a** (%)[b]
1	100% HNO_3 (24)	CF_3CO_2H	–20	0.25	–[c]
2	100% HNO_3 (12)	CF_3CO_2H	–20	0.25	–[c]
3	$K_3Fe(CN)_6$ (2)[d]	H_2O	20	2	–[e]
4	N_2O_4 (5)[f]	Et_2O	20	1	53
5	N_2O_4 (5)	Et_2O	20	1	85
6	N_2O_4 (5)	$CHCl_3$	20	1	35[g]
7	N_2O_4 (3)	Et_2O	20	1	84
8	N_2O_4 (2)	Et_2O	20	1	83
9	N_2O_4 (2)	Et_2O	20	2	80

[a] Reagents and conditions*:* dioxime **5a** (1 mmol), oxidant, solvent (1–5 ml), stirring at specified temperature. [b] Isolated yields. [c] Decomposition of the starting material was observed. [d] NaOH (2 mmol) was also added. [e] No reaction. [f] $NaHCO_3$ (0.05 mmol) was added. [g] A complex mixture of products was formed.



a R = 4-ClC_6H_4, 83%
b R = Ph, 74%
c R = 3-ClC_6H_4, 88%
d R = 4-$EtOC_6H_4$, 77%
e R = 4-$O_2NC_6H_4$, 89%
f R = , 52%
g R = , 44%
h R = , 75%
i R = , 64%
j R = , 54%
k R = , 47%

Scheme 3 *Reagents and conditions*: i, $NaNO_2$, 6 M HCl, 0–5 °C (for **7a–e**); ii, $NaNO_2$, 40% HBF_4, –5 °C (for **7f**); iii, $NOBF_4$, TFA, –10–0 °C (for **7g–k**); iv, **8**, AcONa, EtOH, 0–5 °C (for **9a–f**); v, **8**, MeOH or MeOH–AcOH, –10 °C (for **9g–k**); vi, $CH_2(COMe)_2$, EtONa, EtOH; vii, $NH_2OH \cdot HCl$, EtOH, 75–80 °C; viii, N_2O_4, Et_2O, 20 °C.

Next, a substrate scope for the synthesis of various 2*H*-pyrazolo[3,4-*d*]pyridazine 5,6-dioxides was investigated (see Scheme 3). Aside from compound **3a**, a set of aryl substituted compounds **3b–e** were synthesized in 74–89% yields. In the case of heteroaryl substituted derivatives some modifications for the generation of intermediates **5f–k** and **9f–k** were required. In particular, diazotization of 4-aminopyridine **7f** was conducted in 40% HBF_4,[15] while 1,2,5-oxadiazolyl diazonium tetrafluoroborates **6g–k** were prepared using $NOBF_4$ in CF_3CO_2H.[3(a)] Also, azo coupling of thus obtained diazonium salts **6g–k** was performed at lower temperature in the absence of any bases due to their high reactivity and low stability in solutions. Nevertheless, the presented protocol proved to be suitable for the synthesis of

2*H*-pyrazolo[3,4-*d*]pyridazine 5,6-dioxides **3f–k** incorporating an additional pyridine, furazan or furoxan subunits (see Scheme 3).

Intermediate compounds **4**, **5**, **9** as well as target bicyclic systems **3a–k** were fully characterized by IR, ^{1}H, ^{13}C NMR spectroscopy and HRMS or elemental analysis (see Online Supplementary Materials). The structures of diacetyl derivative **4h** and 2*H*-pyrazolo[3,4-*d*]pyridazine 5,6-dioxide **3h** were additionally confirmed by single-crystal X-ray diffraction studies (Figure 2).†

NO-donor ability of the synthesized 2*H*-pyrazolo[3,4-*d*]-pyridazine 5,6-dioxides **3a–k** was estimated according to Griess assay (Figure 3). The formation of nitrite-anion as a result of NO oxidation may serve as a reliable tool for measuring the amount of NO release.[3(*a*),(*e*),6] The amounts of NO_2^- produced by the

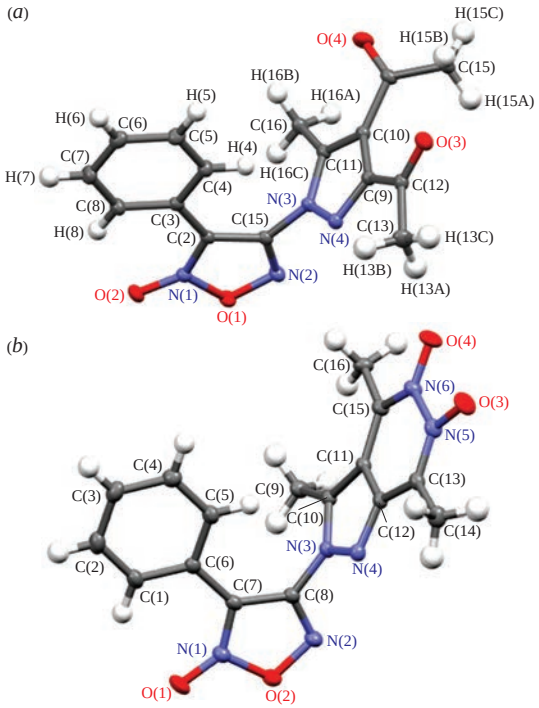


Figure 2 Molecular structures of (*a*) **4h** and (*b*) **3h** in crystals (probability ellipsoids for non-hydrogen atoms at $p = 0.5$ level).

† *Crystal data for* **4h**. $C_{16}H_{14}N_4O_4$ (M_r = 326.31), triclinic, space group $P\bar{1}$, a = 8.0831(4), b = 9.0099(4) and c = 11.4421(5) Å, V = 728.85(6) Å^3, Z = 2, d_x = 1.487 g cm^{-3}, absorption coefficient: 0.110 mm^{-1}, $F(000)$ = 340, the final R = 0.0438, wR = 0.1012 for 3936 observed reflections with $I > 2\sigma(I)$.

Crystal data for **3h**. $C_{16}H_{14}N_6O_4$ (M_r = 354.33), monoclinic, space group $P2_1/c$, a = 10.5233(2), b = 17.6418(3) and c = 8.28210(10) Å, V = 1529.11(4) Å^3, Z = 4, d_x = 1.539 g cm^{-3}, absorption coefficient: 0.115 mm^{-1}, $F(000)$ = 736, the final R = 0.0671, wR = 0.1454 for 4087 observed reflections with $I > 2\sigma(I)$.

X-ray diffraction data for **4h** and **3h** were collected at 100 K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using MoK$_\alpha$-radiation (0.71073 Å). The intensity data were integrated by the SAINT program and corrected for absorption and decay using SADABS. The structure was solved by direct methods using SHELXS-2013 and refined on F^2 using SHELXL-2018. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters.

Crystal data and structure refinement parameters are given in Online Supplementary Materials.

CCDC 2021356 and 2021357 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

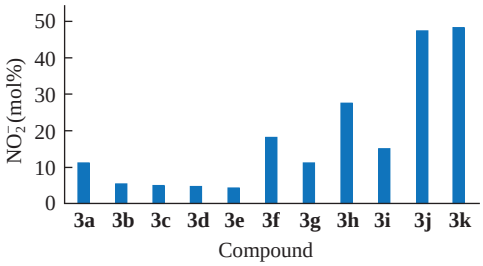


Figure 3 NO release data for compounds **3a–k**.

synthesized pyridazine dioxides under physiological conditions (pH 7.4; 37 °C) after 1 h incubation were measured *via* the Griess reaction using a spectrophotometric technique. It was found that aryl substituted 2*H*-pyrazolo[3,4-*d*]pyridazine 5,6-dioxides **3a–e** produced low amounts of NO (4.2–10.5%). Heteroaryl substituted derivatives **3f**,**g**,**i** released higher fluxes of NO (11.0–18.1%), while compounds **3h**,**j**,**k** comprising NO-donor furoxan and pyridazine dioxide subunits demonstrated the highest NO-releasing ability (27.7–48.3%).

In summary, a general approach to an assembly of the 2*H*-pyrazolo[3,4-*d*]pyridazine 5,6-dioxide scaffold bearing additional aromatic or heterocyclic moieties was developed. This protocol involves diazotization of initial amines followed by one-pot azo coupling with chloroacetylacetone. Cyclo-condensation of thus formed chlorohydrazones with acetyl-acetone affords diacetylpyrazoles which are easily converted to the corresponding dioximes. Subsequent oxidative cyclization furnishes the formation of target 2-aryl(hetaryl)-2*H*-pyrazolo[3,4-*d*]pyridazine 5,6-dioxides in good and high yields. The synthesized fused heterocyclic systems demonstrated good NO-donor profiles releasing NO in a wide range of concentrations, which seems useful for various biomedical insights. To the best of our knowledge, this is the first general protocol for the construction of NO-releasing 2*H*-pyrazolo[3,4-*d*]pyridazine 5,6-dioxide framework.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.01.012.

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