OL Organic Letters

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Nucleophilic Catalyzed Structural Binary Cleavage of a Fused [5,5]-Bicyclic Compound

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Cite This: *Org. Lett.* 2021, 23, 9408−9412 Read Online

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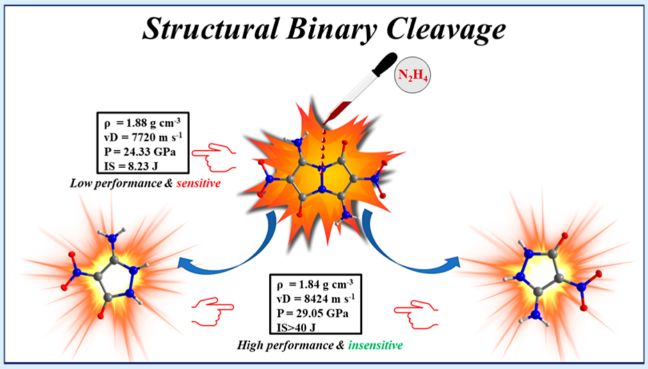
ABSTRACT: Structural binary cleavage of 3,7-diamino-2,6-dinitro-1*H*,5*H*-pyrazolo-[1,2-*a*]pyrazole-1,5-dione **3**, under nucleophilic conditions, leads to the formation of a monocyclic pyrazole unit of 5-amino-4-nitro-1,2-dihydro-3*H*-pyrazol-3-one, **4**. Additionally, various salts of the pyrazole ring were synthesized and fully characterized. Detonation properties and mechanical sensitivities of **4** and other new compounds are remarkably improved compared to **3**. This simple and efficient strategy is highly desirable for future studies on the development of insensitive and high performing materials.



Over the years, synthesis and development of fused bicyclic compounds have been focused on structurally fascinating and biologically active compounds.[1,2] Because of unique structural features, including inherent planarity and high conjugation in heteroaromatic skeletons, materials with fused bicyclic rings are in high demand in the field of high-energy-density materials (HEDMs).[3] Fused heterocyclic compounds have large ring-strain energies and high enthalpies of formation, while the heteroaromatic bonds result in high density and oxygen balance, high thermostability, and low sensitivity.[4] Several new designs and synthetic methods have been developed as routes to fused compounds by the introduction of energetic groups (e.g., $-NO_2$, $NHNO_2$, $-ONO_2$, $C(NO_2)_3$, etc.). These have been extensively studied in order to increase thermostabilities and decrease sensitivities with concomitantly high detonation properties.[5−8]

Fused [5,5]-bicyclic heterocycles are the simplest fused rings for building highly thermostable materials (Figure 1).[9−12] In recent years, pyrazole-based [5,5]-bicyclic heterocycles have been frequently encountered in the synthesis of high performing HEDMs. In this context, 3,7-diamino-2,6-dinitro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole-1,5-dione, **3**, was found to be a very interesting [5,5]-bicyclic compound with an "N——N" bridge between the two pyrazole rings.[13,14] The synthesis of compound **3** is achieved in four simple synthetic steps from inexpensive starting materials.[12] Compound **3** contains two carbonyl moieties followed by *trans* amino and nitro groups on the [5,5]-bicyclic skeleton. Due to the presence of extensive intermolecular and intramolecular hydrogen bonding between the NO_2 and NH_2 groups, the molecule is planar. Additionally, the $\pi-\pi$ bond interactions between the two molecules lead to high thermostability (T_{dec} = 328.8 °C) and high density at 1.88 g·cm^{-3}.[14] However, it is relatively sensitive to impact (IS = 8.2 J) and the detonation properties are only slightly better than those of the heat-resistant high explosive, hexanitrostilbene (HNS) (IS = 5 J; FS = 240 N). The presence of the azo bond between the two rings leads to high sensitivity and low performance.[15] When compound **3** was subjected to various electrophilic reagents in an effort to obtain high performing

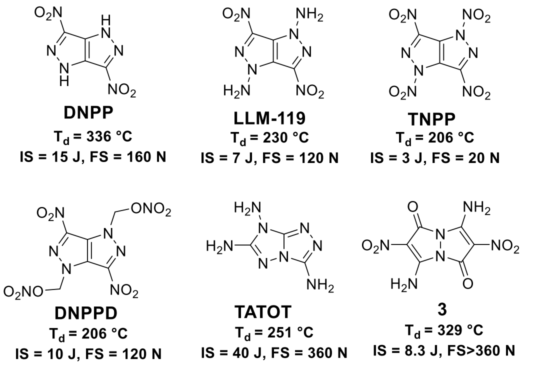
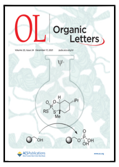


Figure 1. Selected fused [5,5]-bicyclic heterocycles.

Received: October 20, 2021
Published: November 30, 2021



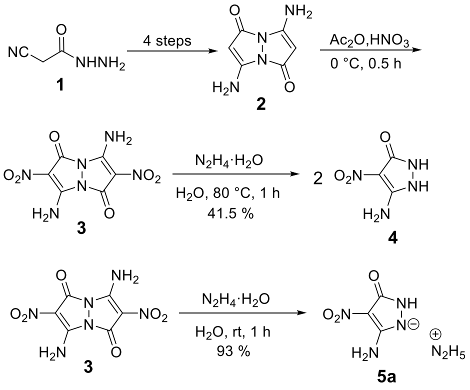
https://doi.org/10.1021/acs.orglett.1c03534
Org. Lett. 2021, 23, 9408−9412

materials, all efforts were unsuccessful.[14] Therefore, we were stimulated to study its nucleophilic reactivity.

In general, azo-bridged fused bicyclic ketones are very sensitive to nucleophiles (hydroxides or alkoxides), which lead to ring opening to form corresponding carboxylic acids or esters.[16] With this in mind, we were encouraged to study the reactivity of **3** with a series of amine-based nucleophiles. Surprisingly, the fused [5,5]-bicyclic **3** was converted into a monocyclic pyrazole ring, **4**, in the presence of nucleophiles in aqueous medium. Requiring a very large number of steps, the syntheses of **4** and its ammonium salt mixtures had been studied in 1915. Later their crystal structures were reported in 1991. However, no further studies with respect to **4** have been conducted.[17,18] Now with fewer steps and as a product of an elegant cleavage reaction, we have synthesized the pyrazole ring (**4**) and its various salts. Very interestingly, the sensitivity and detonation properties of **4** were improved compared with **3**, and some of its salts have better detonation properties which approach those of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX).

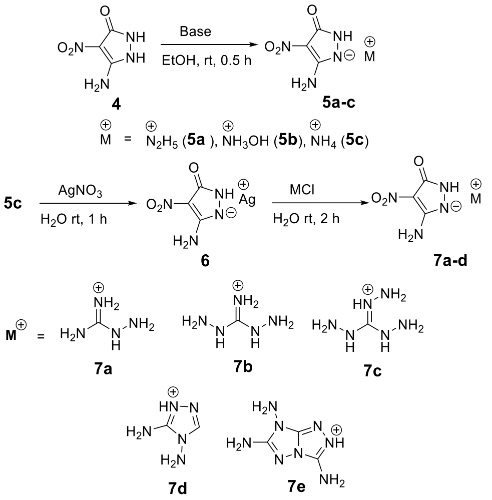
The fused [5,5]-bicyclic compound **3** was treated with 2 equiv of hydrazine monohydrate in an aqueous solution at 80 °C for 1 h. Then, the reaction mixture was cooled to room temperature and treated with a few drops of glacial acetic acid to give brown crystals of pyrazole, **4** in 41.5% yield. This reaction led to the hydrazinium salt (**5a**, 93%) when **3** was reacted with hydrazine monohydrate for 1 h in an aqueous solution at room temperature. Then the reaction mixture was concentrated by air, and the hydrazinium salt **5a** was purified by crystallization from hot water (Scheme 1).

Scheme 1. Syntheses of 4 and Its Salt 5a



The pyrazole **4** and its hydrazinium salt **5a** are very thermostable (>290 °C) and insensitive to mechanical stimuli. Because of the high thermostability and lower sensitivities of the energetic salt,[19] we have reacted compound **4** with nitrogen-rich bases in ethanol to give salts **5a**−**c**. Additionally, the ammonium salt **5c** was treated with silver nitrate in water and stirred at room temperature for 2 h. The insoluble silver salt, **6**, precipitated. Compound **6** was treated with various chlorides in water and stirred at room temperature for 6 h to give a series of nitrogen-rich energetic salts (**7a**−**e**) (Scheme 2).

Scheme 2. Syntheses of Energetic Salts 5a−c, 6, and 7a−e



To understand the nucleophilic reactivity of **3**, it was treated with various amine bases including aqueous ammonia (28%), hydroxylamine (50 wt % water), hydrazine (80% wt. water), ethylamine, diethylamine, and triethylamine. Interestingly, under all reaction conditions, the fused [5,5]-bicyclic compound **3** was converted into varying amounts of the monocyclic pyrazole **4**. Significant yields of the product were obtained in the presence of hydroxylamine or aqueous ammonia, but inseparable mixtures of products were obtained with all alkylamine bases. A high yield (with 2 equiv of **4**) was obtained in the presence of hydrazine due to its stronger nucleophilicity compared to the other bases (Table 1). This provides an interesting example of a chemical binary cleavage of a fused [5,5]-bicyclic compound **3** in a nonmetal catalyzed reaction. A plausible mechanism pathway for a binary cleavage of a fused [5,5]-bicyclic compound in the presence of hydrazine is shown in Scheme 3.

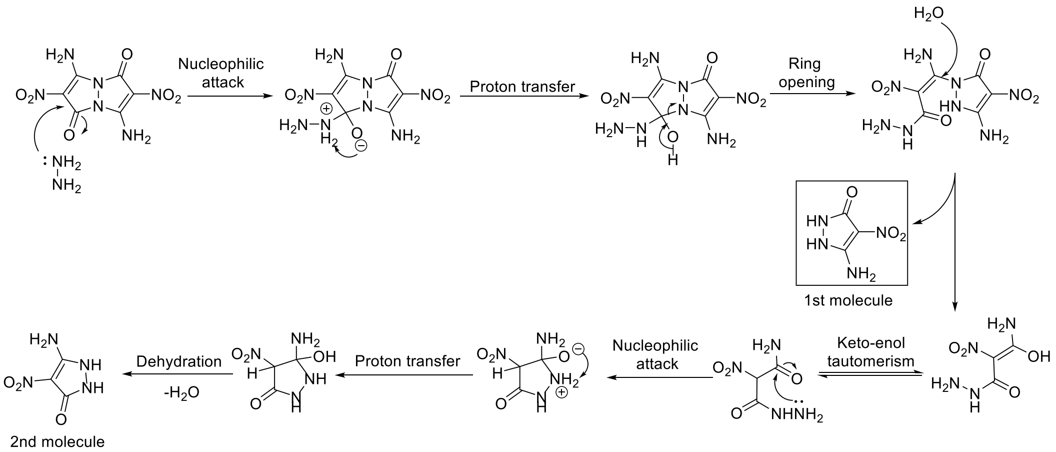
Table 1. Reactivity of Compound 3 with Nucleophiles

Entry	Nucleophiles	Time (h)	Temp (°C)	Yield of **4** (%)
1	NH_3 (30%)	1.5	80	68
2	NH_2OH (50%)	1.5	80	65
3	NH_2NH_2 (80%)	1	80	41.5
4	$EtNH_2$	2	80	mixture
5	Et_2NH	2	80	mixture
6	Et_3N	2	80	mixture

Pyrazole **4** and all the new salts (**5a**−**c** and **7a**−**e**) were fully characterized by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy, and elemental analysis. The ^{15}N NMR spectra were recorded for **3**, **4**, **5a**, and **7e** in DMSO-d_6, and the assignments were made by comparison with similar compounds (Figure S23).[20,21]

Single yellow block crystals of **4** and single yellow needle crystals of **5b** were obtained by slow evaporation of EtOH/water solutions (Figure 2). Compound **4** crystallizes in the monoclinic space group $P2_1/n$ (Z = 4) symmetry with a calculated density of 1.879 g·cm^{-3} at 100 K. The bond lengths and bond angles are slightly different from the reported structure.[18] The pyrazole ring is nearly planar (Figure 2a). In the crystal packing of **4**, there are many strong intermolecular along with intramolecular hydrogen bond interactions forming a 3D framework (Figure 2c). Salt, **5b**, crystallizes in the monoclinic space group $P2_1$ (Z = 2) symmetry with a calculated density of 1.809 g·cm^{-3} at 100 K (Figure 2d). Unlike the neutral pyrazole **4**, there are extensive hydrogen bond interactions in **5b** between the hydroxylammonium

Scheme 3. A Plausible Mechanism Pathway for Binary Cleavage of Fused [5,5]-Bicyclic Compound in the Presence of Hydrazine



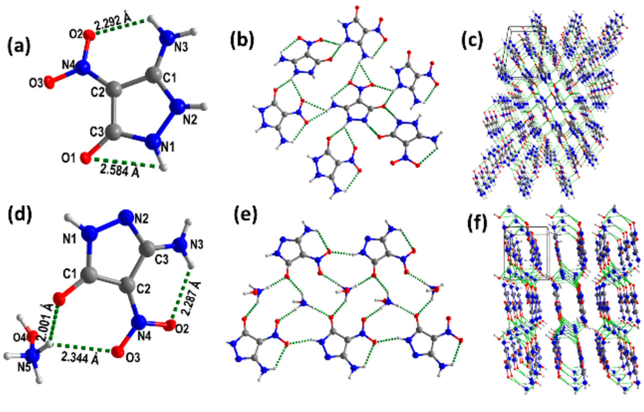


Figure 2. (a–c) Molecular structure (thermal ellipsoid plot (50%)), hydrogen bonding and packing diagram of **4**, and (d–f) **5b**. Dashed lines indicate strong hydrogen bonding.

cation and the nitro and carbonyl groups of the pyrazole anion ring (Figure 2f).

To gain additional insight into the relationship between sensitivity and structure, the Hirshfeld surface plots and 2D fingerprint plots of **4**, and **5b** along with **3**[14] were generated by using Crystal Explorer 17.5 software (Figure 3).[22] The red dots on the Hirshfeld surface represent high close-contact populations and the blue dots represent weak interactions. Red spots on the side faces of the plate denote the close interactions of hydrogen bonds (O⋯H, N⋯H, and H⋯H). All three compounds have exellant hydrogen bond interactions **4** (68.4%), **5b** (69.4%), and **3** (62.9%), respectively.

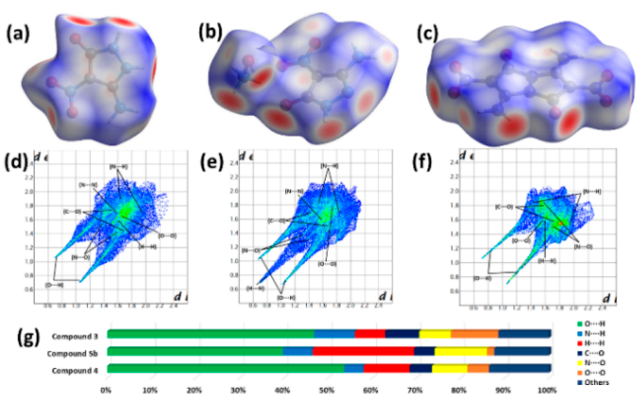


Figure 3. Hirshfeld surface calculations and 2D fingerprint plots in the crystal structures of **4** (a,d), **5b** (b,e), and **3** (c,f); (g) population of close contacts in **4**, **5b**, and **3** in the crystal stacking.

From the 2D fingerprint plots Figure 3d–f, the major interactions are O⋯H (53.6%), H⋯H (10.4%), and N⋯O (8.0%) for **4**; O⋯H (39.7%), H⋯H (22.9%), N⋯O (11.9%), and N⋯H (6.8%) for **5b**; and N⋯H (9.3%), H⋯H (6.8%), and O⋯H (46.8%) for **3**. The higher percentages of O⋯O and N⋯O interactions in the molecular surfaces lead to an increase in sensitivity.[23] Compound **3** has total (O⋯O/N⋯O) interactions of 17.9% which are relatively higher than **4** (12.9%) and **5b** (13.5%), which suggests an increase in sensitivity for **3** compared to **4** and **5b**. These data are in agreement with the experimental impact sensitivity (IS) values, i.e., that both **4** and **5b** are less sensitive than **3** due to high contenet of hydrogen bonding interactions.

The physicochemical properties for all new compounds and standard energetic properties for comparison are reported in Table 2. The thermal stabilities (onset temperature) were measured by differential scanning calorimetry (DSC) at a heating rate of 5 °C min^{-1}. Neutral pyrazole **4** and its salts **5a–c** have high decomposition temperatures (>290 °C), while the other salts have relatively high thermostabilities. The triaminoguanidinium salt, **7c**, has a lower decomposition temperature of 190 °C. Densities were measured using a gas pycnometer at 25 °C and were found to be moderately high within the range 1.71–1.84 $g \cdot cm^{-3}$. Compound **4** has a higher density of 1.84 $g \cdot cm^{-3}$, and other compounds, **5b**, **5c**, and **7e**, have good densities, which approach RDX (1.80 $g \cdot cm^{-3}$). The heats of formation (ΔH_f) for neutral compound **4** and its salts were determined using the Gaussian 03 suite of programs (Supporting Information).[24] Compounds **4**, **5b**, **5c**, and **7a** exhibit negative heats of formation, while the other compounds have high positive heats of formation.

Using the calculated heats of formation and experimental densities, the detonation properties of all the new materials were calculated with the Explo5 (version 6.01) code program.[25] The detonation velocities (vD) range between 8105 and 8731 m s^{-1}, and the detonation pressures (P) are between 24.21 to 32.25 GPa. All compounds exhibited better detonation properties than TNT (2,4,6-trinitrotoluene) as well

Table 2. Energetic Properties and Detonation Parameters of 3, 4, 5a−c, and 7a−e Compared with HNS, TNT, NTO, and RDX

Compd	T_d[a](°C)	P[b][g cm^{-3}]	ΔH_f[c][kJ mol^{-1}/kJ g^{-1}]	vD[d][m s^{-1}]	P[e][GPa]	IS[f] [J]	FS[g][N]
3[h]	329	1.88	−707.1/−2.76	7720	24.33	8.2	>360
4	291	1.84	−18.0/−0.12	8424	29.05	>40	>360
5a	297	1.77	13.7/0.07	8731	28.62	>40	>360
5b	296	1.77	−86.1/−0.48	8553	28.59	>40	>360
5c	293	1.74	−140.6/−0.87	8163	24.35	>40	>360
7a	210	1.71	−54.9/−0.25	8105	23.13	>40	>360
7b	198	1.72	54.6/0.23	8401	25.01	>40	>360
7c	190	1.72	164.3/0.66	8611	26.64	>40	>360
7d	221	1.75	263.1/1.08	8391	25.91	>40	>360
7e	226	1.77	403.4/1.35	8394	26.06	>40	>360
HNS[h]	320	1.74	172.9/0.38	7220	21.98	5	240
TNT[i]	295	1.65	−59.4/−0.30	6881	19.50	15	353
NTO[j]	286	1.91	−25.7/−0.19	8544	30.90	22	>353
RDX[i]	204	1.80	92.6/0.41	8795	34.90	7.5	120

[a] Decomposition temperature (onset). [b] Density−gas pycnometer at 25 °C. [c] Calculated molar enthalpy of formation. [d] Calculated detonation velocity (Explo5 v6.01). [e] Calculated detonation pressure (Explo5 v6.01). [f] Impact sensitivity. [g] Friction sensitivity. [h] Hexanitrostilbene, ref 14. [i] Reference 3. [j] Reference 27.

as the starting precursor **3**, and **5a** (vD: 8731 m s^{-1}, P: 28.62 GPa) has excellent detonation properties approaching RDX (vD: 8795 m s^{-1}, P: 34.9 GPa). Impact and friction sensitivity values were measured by using BAM fallhammer and friction tester techniques, and all new compounds were found to be insensitive (IS > 40 J, FS > 360 N) to impact and friction.[26]

In summary, we have studied the binary cleavage of the fused [5,5]-bicyclic compound **3**, with various amine-based nucleophiles. Under all reaction conditions, the fused bicyclic ring gave highly thermostable, high performing, and insensitive pyrazole, **4**, in good yields. To our knowledge, this is the first example of the structural binary cleavage of **3**, by a nonmetal catalyzed reaction. Here it occurs in the presence of hydrazine. Compound **4** has higher detonation properties than **3** comparable to NTO (nitrotriazolone). Various salts of **4** were synthesized and well characterized. Structures of pyrazole, **4**, and hydroxylammonium salt **5b** were confirmed by single crystal X-ray analysis. The Hirshfeld surface and 2D fingerprint plot analysis of **3**, **4**, and **5b** crystals were examined to investigate the relationship between their structures and sensitivities. Both **4** and **5b** are more highly hydrogen bonded than **3** via intermolecular bonding which result in high thermostability and low mechanical sensitivity. This simple and versatile methodology opens a new avenue for the future exploration of formation of high performing materials from inefficient energetic materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c03534.

> Details of experimental procedures, characterizations, theoretical calculations, X-ray crystal diffraction data and crystal structures for compounds **4** (CCDC 2088875) and **5d** (CCDC 2088876), and copies of NMR spectra (PDF)

Accession Codes

CCDC 2088875−2088876 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The Rigaku Synergy S Diffractometer was purchased with support from the National Science Foundation MRI program under Grant No. 1919565.

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