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Research paper

Preparation of Imidazolium 2,4,5-Trinitroimidazolate from Derivatives of Imidazole and Its Oxidation Under Nitration Conditions

Pengbao Lian^{1,2}, Changming Hou², Lizhen Chen²,
Jianxin Xu³, Zishuai Xu³, Jianlong Wang^{2,*}

¹) Shanxi North Xingan Chemical Industry Co., Ltd., China

²) School of Chemical Engineering and Technology, North University of China, Taiyuan 030051, China

³) Gansu Yinguang Cheralical Industry Group Co., Ltd., Baiyin 730900, China

E-mail: 619379961@qq.com

Abstract: In this study, the nitration reactions of imidazole and its nitro derivatives with a mixture of 98% HNO₃ and 98% H₂SO₄ (or 15% SO₃ in H₂SO₄) were reinvestigated. When imidazole or 4(5)-nitroimidazole was nitrated with a mixture of 98% HNO₃ and 98% H₂SO₄ (or 15% SO₃ in H₂SO₄), only 4,5-dinitroimidazole was obtained. Imidazolium 2,4,5-trinitroimidazolate was prepared from 2-nitroimidazole or 2,4(5)-dinitroimidazole with a mixture of 98% HNO₃ and 98% H₂SO₄ (or 15% SO₃ in H₂SO₄); the highest yields were 57.8 and 62.8%, respectively. However, on increasing the reaction temperature, duration, amount of H₂SO₄ or HNO₃, the by-product ethanedioic acid was produced. A possible reaction mechanism for the formation of ethanedioic acid from 2,4,5-trinitroimidazole is suggested. The compounds 4,5-dinitroimidazole, imidazolium 2,4,5-trinitroimidazolate and ethanedioic acid were characterized by infrared spectroscopy, multinuclear ¹H and ¹³C NMR spectroscopy, and elemental analysis. The structures of 4,5-dinitroimidazole and ethanedioic acid were further confirmed by single-crystal X-ray diffraction

Keywords: imidazole, imidazole nitro derivatives, imidazolium 2,4,5-trinitroimidazolate, ethanedioic acid, nitration reaction, reaction mechanism

Supplementary Information (SI)

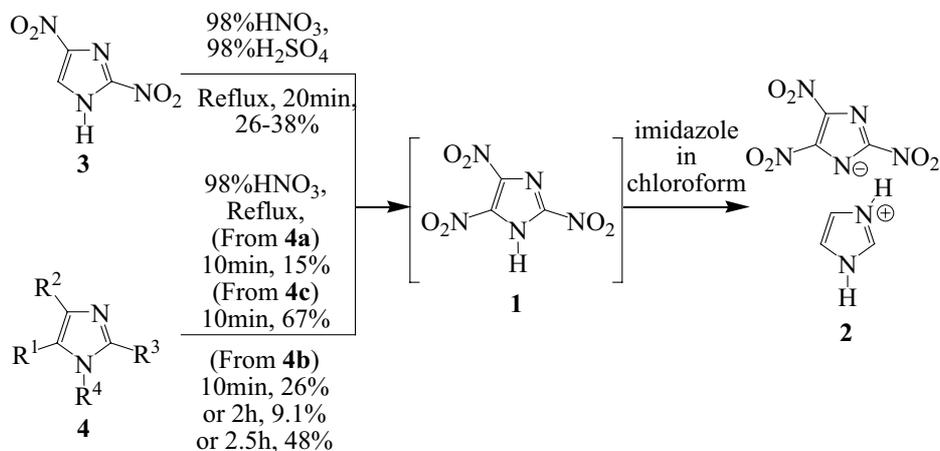
In the SI are presented summaries of the data for the nitration reactions, some crystal data and structure refinement, bond lengths and angles in Tables S1-S7, as well as FTIR, ^1H and ^{13}C NMR spectra in Figures S1-S4.

Supplementary Data (SD)

CCDC-2015172 and -2046010 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre. Data mentioned in this paper are also presented in Table S5 in SI.

1 Introduction

2,4,5-Trinitroimidazole (Scheme 1, **(1)**) is an important precursor for preparing its energetic ion salts and 1-methyl-2,4,5-trinitroimidazole [1-10]. However, **(1)** is considered unstable at room temperature [3]. Consequently **(1)** is often stored in the form of its potassium salt, ammonium salt or imidazolium salt [1-10]. Imidazolium 2,4,5-trinitroimidazolate (**(2)**) is a representative of the 2,4,5-trinitroimidazole-based energetic salts [1, 2, 8-10]. The crystal density, impact sensitivity, friction sensitivity, detonation velocity and detonation pressure of **(2)** were reported as 1.65 g/cm^3 , 43 cm (drop hammer weight 2 kg), 46%, $7057\text{ m}\cdot\text{s}^{-1}$ and 19.70 GPa, respectively [8]. At present, two approaches for the preparation of **(2)** have been reported in the literature (Scheme 1) [1, 2, 8-10]. In the first approach, 2,4(5)-dinitroimidazole (**(3)**) was nitrated with a mixture of 98% HNO_3 and 98% H_2SO_4 to obtain **(1)**, which was then neutralized with imidazole in chloroform to give **(2)** [1]. In the second method, nitration of 1,2,4,5-tetra-iodoimidazole (**(4a)**), 2,4,5-tri-iodoimidazole (**(4b)**) or 2,4(5)-dinitro-5(4)-iodoimidazole (**(4c)**) with 98% HNO_3 gave **(1)**, which was reacted with imidazole in chloroform to obtain **(2)** [2, 8-10].



Scheme 1. Methods for the synthesis of **2** reported in the literature

The first method had many disadvantages, such as an expensive and not easy to prepare raw material (**3**), a large amount of waste acid, and the yield of (**2**) was less than 38%. Although the second method had less waste acid, more expensive iodine-containing reagents were used, and did not meet the requirements of atom economy. In conclusion, there are many aspects that need to be improved in the preparation of (**2**).

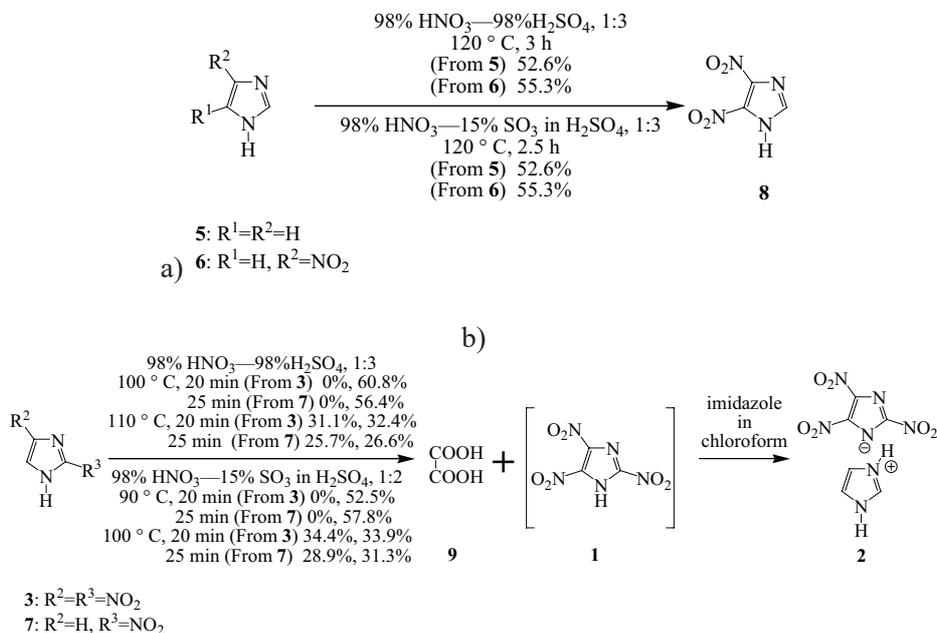
In the present paper, the nitration reactions of imidazole (**5**), 4(5)-nitroimidazole (**6**), and (**3**) with a mixture of HNO₃ and H₂SO₄ were reinvestigated. It is also reported for the first time that (**2**) may be prepared from 2-nitroimidazole (**7**). Fourier transform infrared (FTIR) spectroscopy, ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and single-crystal X-ray diffraction (XRD) were used to characterize the structures of the various compounds.

2 Materials

All of the reagents were analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and were used without further purification. Compounds (**3**) [11], (**6**) [12], and (**7**) [13] were prepared according to published procedures.

3 Nitration Reaction

The nitration of (**5**) and its nitro derivatives with a mixture of HNO₃ and H₂SO₄ is shown in Scheme 2. HNO₃ (98%, 2.6 mL) was added dropwise to H₂SO₄ (98%, 7.8 mL) while maintaining the temperature below 15 °C. After the addition was complete, the mixture was stirred for an additional 15 min. In the course of the reaction, a small amount of nitrogen oxides will be formed in the system. Imidazole (**5**) (1.36 g, 0.02 mol) was then slowly added with care. The addition rate was maintained such that the internal reaction temperature remained below 15 °C. After completion of the addition, the mixture was gradually warmed to 120 °C, stirred for 3 h, cooled to room temperature, and then poured over crushed ice (50 g) The mixture was extracted with diethyl ether (5×30 mL), the extracts were combined and dried over Na₂SO₄, and then concentrated under reduced pressure.



Scheme 2. The nitration reaction of (**5**) and its nitro derivatives with a mixture of HNO₃ and H₂SO₄: a) imidazole (**5**), and 4(5)-nitroimidazole (**6**); b) 2,4(5)-dinitroimidazole (**3**), and 2-nitroimidazole (**7**)

4 Test Methods

The FTIR spectra were recorded from 400 to 3600 cm^{-1} at a resolution of 2 cm^{-1} on a Bruker Model Vertex 80 FTS spectrometer. A total of 32 scans were averaged into one spectrum using IR solution software Opus 6.5 (Bruker). Background spectra were recorded and subtracted during each analysis. The uniformity of three samples was verified at different locations.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer with deuteriated acetone or DMSO solvents at 400 and 100.58 MHz, respectively.

Elemental analyses were performed on an Elementar Vario EL elemental analyzer. The sample, of approximately 1 mg, was pyrolyzed with chromium oxide catalyst in an atmosphere of helium gas with 3% oxygen. Carbon, hydrogen and nitrogen were converted into carbon dioxide, water, and nitrogen oxides, respectively. The nitrogen oxides were then converted to nitrogen by metallic copper reduction in a reduction furnace at 650 $^{\circ}\text{C}$. Excess oxygen was absorbed by copper, and the nitrogen, carbon dioxide and water of the gas mixture were separated by a gas chromatographic column and detected by thermal conductivity. All analyses were performed in triplicate.

The XRD patterns were recorded on a Bruker D8 VENTURE PHOTON100 CMOS diffractometer equipped with a graphite-monochromator and MoK α radiation ($\lambda = 0.071073$ nm). The structures were solved by direct methods (SHELXL-2015 software) [14, 15] and refined by the fullmatrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (OLEX2 software) [16]. The hydrogen atoms were added according to theoretical models.

5 Results and Discussion

5.1 Experiment

In our initial experiment, (2) was synthesized by nitration of (3) with a mixture of 98% HNO_3 and 98% H_2SO_4 , according to the procedure of Cho *et al.* [3], however the yield of (2) was only 31% ([3] reported 60%), and a large amount of ethanedioic acid (9) was obtained. A possible reason for the oxidation of the imidazole ring may be the same as in the previously observed nitration of 2-methylimidazole [17, 18], imidazolone [19] and 2,4,5-tri-iodoimidazole [9, 20] to obtain parabanic acid, and nitration of 1-methyl-2,4,5-trinitroimidazole [21, 22] and methylation of (3) [23] to 1-methylimidazolidine-2,4,5-trione.

Table 1. Summary of the data for the nitration of imidazole (**5**)^{*} with a mixture of 98% HNO₃ and 98% H₂SO₄ to give 4,5-dinitroimidazole (**8**) with a purity of not less than 98.0%

Entry	Temperature [°C]	Time [h]	HNO ₃ [mL]	H ₂ SO ₄ [mL]	Product [g]	Yield isolated [%]
1	110	3	2.6	7.8	1.46	46.1
2	120				1.66	52.6
3	130				1.64	51.9
4	120	2	2.1	6.3	1.31	41.4
5		4			1.65	52.2
6		3	2.1	6.3	1.35	42.8
7		3	3.5	10.5	1.60	50.5
8		3	2.6	5.2	1.32	41.8
9		3			10.4	1.55

* The amount of starting material was the same in all cases, 20 mmol

Table 2. Summary of the data for the nitration, oxidation and hydrolyzation of 2,4(5)-dinitroimidazole (**3**)^{*} with a mixture of 98% HNO₃ and 98% H₂SO₄

Entry	Temperature [°C]	Time [min]	HNO ₃ [mL]	H ₂ SO ₄ [mL]	(2)**		(9)**	
					Product [g]	Yield of isolated product [%]	Product [g]	Yield of isolated product [%]
1	90	20	2.1	6.3	2.48	45.8	0	0
2	100				3.30	60.8	0	0
3	110				1.76	32.4	0.56	31.1
4	100	15	1.7	5.1	2.76	50.9	0	0
5		25			2.85	52.5	0.12	6.7
6		20	1.7	5.1	2.31	42.6	0	0
7		20	2.6	7.8	2.78	51.2	0.13	7.1
8		20	2.1	4.2	2.67	49.3	0	0
9		20	2.1	8.4	2.99	55.1	0.07	3.9
		20	2.1					

* The amount of starting material was the same in all cases, 20 mmol.;

** The purity of compounds (**2**) and (**9**) were not less than 98.0%

Compounds (**5**) and (**6**) were subjected to nitration under a variety of nitration conditions (Scheme 2a and Table 1 (above), and Tables S1 and S2 in SI). The reactions of (**5**) and (**6**) with a mixture of 98% HNO₃ and 98% H₂SO₄ (volume

ratio, 1:3) at 120 °C for 3 h resulted in the formation of (**8**) with isolated yields of 52.6% and 55.3%, respectively (Table 1, entry 2; Table S1, entry 2). An increase in the reaction temperature or duration did not improve the yield of (**8**) (Table 1, entries 3 and 5; Table S1, entries 3 and 5), however the yield of (**8**) was reduced when the reaction temperature or duration were decreased (Table 1, entries 1 and 4; Table S1, entries 1 and 4). When the amount of H₂SO₄ (HNO₃–H₂SO₄, 1:2 or 1:4) or HNO₃ was increased or decreased, the yield of (**8**) was reduced (Table 1, entries 6-9; Table S1, entries 6-9). The reactions of (**5**) and (**6**) with a mixture of 98% HNO₃ and 15% SO₃ in H₂SO₄ gave similar results (Table S2), the highest yields of (**8**) being 62.7% and 66.0%, respectively (Table S2, entries 2 and 11). Clearly, **2** cannot be obtained from (**5**) or (**6**), which only gave (**8**).

When the nitration reactions of (**3**) and (**7**) were carried out with a mixture of 98% H₂SO₄ and 98% HNO₃ (volume ratio, 1:3) at 100 °C for 20 (or 25) min, a pure sample of (**2**) was obtained, in 60.8% and 56.4% yield, respectively (Scheme 2b; Table 2, entry 2; Table S3, entry 2). Increasing the reaction temperature, duration, amounts of HNO₃ or H₂SO₄, reduced the yield of compound (**2**), while by-product (**9**) was obtained (Table 2, entries 3, 5, 7 and 9; Table S3, entries 3, 5, 7 and 9). Similar results were obtained in the nitration of (**3**) and (**7**) with a mixture of 98% HNO₃ and 15% SO₃ in H₂SO₄, the highest yields of (**2**) being 62.5% and 57.8%, respectively (Table S4, entries 2 and 11).

5.2 FTIR spectra

FTIR spectra (KBr pellet) for (**2**), (**8**) and (**9**) are shown in Figure S1 in SI. The following results were obtained for:

- (**2**) [cm⁻¹]: 3146 (–NH), 2984 (=C–H), 2853 (–NH⁺), 1587 (C=C), 1541 (–NO₂), 1470 (C=C), 1387 (C=N), 1331 (–NO₂).
- (**8**) [cm⁻¹]: 3435 (–NH), 3142 (=C–H), 1553 (–NO₂), 1512 (C=C), 1433 (C=C), 1383 (C=N), 1340 (–NO₂).
- (**9**) [cm⁻¹]: 3433 (–OH), 1690 (C–OH), 1441 (C–OH), 1254 (C–OH).

5.3 ¹H and ¹³C NMR spectra

¹H NMR and ¹³C NMR spectra for (**2**), (**8**) and (**9**) are shown in Figures S2-S4 in SI, respectively. The following results were obtained for:

- (**2**):
 - (i) ¹H NMR (acetone-*d*₆) [ppm]: 9.05 (s, 1H, –C(2)–H), 7.74 (s, 2H, –C(4,5)–H),
 - (ii) ¹³C NMR (DMSO-*d*₆) [ppm]: 146.5, 139.4, 138.0, 134.5, 119.4.
- (**8**):
 - (i) ¹H NMR (acetone-*d*₆) [ppm]: 11.25 (br, 1H, –N–H), 8.08 (s, 1H, –C–H),

- (ii) ^{13}C NMR (acetone- d_6) [ppm]: 134.7, 120.5.
- (9):
 - (i) ^1H NMR (DMSO- d_6) [ppm]: 7.64 (s, 2H, –O–H),
 - (ii) ^{13}C NMR (DMSO- d_6) [ppm]: 162.0.

5.4 Elemental analysis

Compound (2) [%]:

- calc. for $\text{C}_6\text{H}_5\text{N}_7\text{O}_6$: C 26.58, H 1.86, N 36.16,
- found: C 26.43; H 1.89; N 36.32.

Compound (8) [%]:

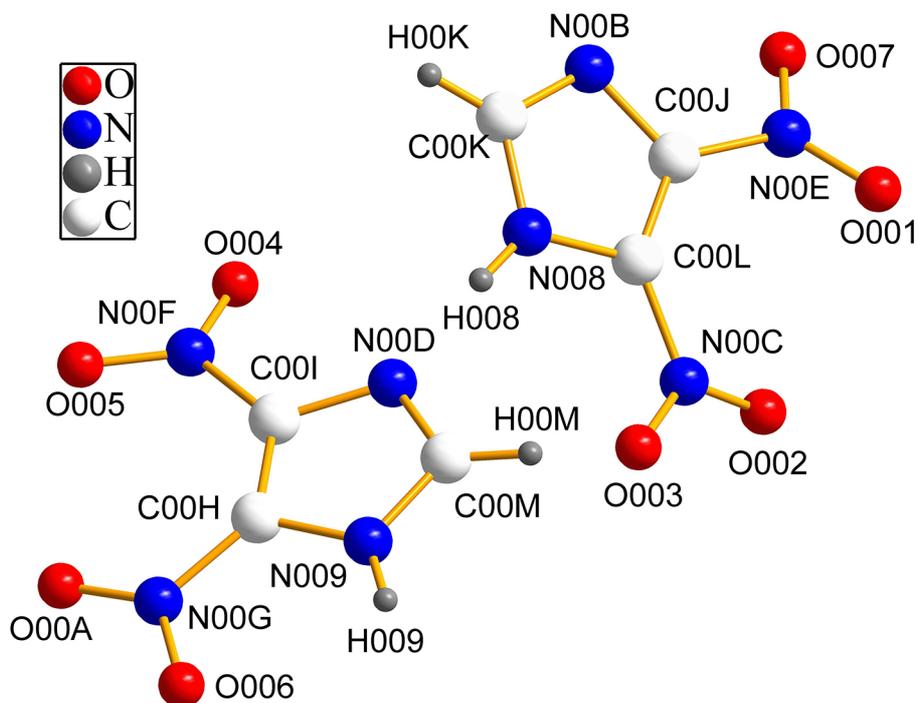
- calc. for $\text{C}_3\text{H}_2\text{N}_4\text{O}_4$: C 22.79, H 1.28, N 35.44,
- found: C 22.92, H 1.24, N 35.32.

Compound (9) [%]:

- calc. for $\text{C}_2\text{H}_2\text{O}_4$: C 26.68, H 2.24,
- found: C 26.52, H 2.20.

5.5 Single-crystal XRD patterns

The single crystal X-ray diffraction analysis of compounds (8) and (9)•2H₂O confirmed that they belong to a monoclinic system with the P2₁/n and P2₁/c space group (Figure 1 and Table S5 in SI), respectively. The single crystal data of (8) and (9)•2H₂O were identical to those reported by Bracuti [24] and Martin *et al.* [25], respectively. The crystallographic data for (8) and (9)•2H₂O have been deposited with CCDC numbers of 2046010 and 2015172, respectively (see SD and Table S5 in SI).



(a)

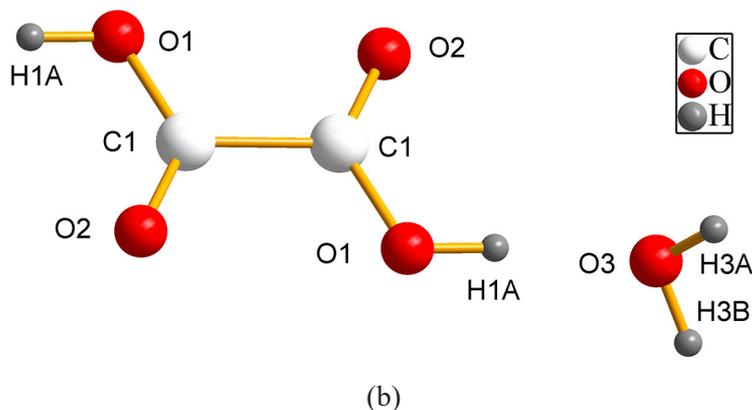


Figure 1. Crystal structures of compounds (8) (a) and (9)•2H₂O (b)

5.6 Possible reaction mechanism

Analyzing the results of these experiments, we suggest that (9) was produced from parabanic acid, and parabanic acid was obtained from (1), rather than (5), (6), and (8). A possible mechanism for the production of (9) from (1) is as follows (Scheme 3) [9, 17-23]:

- Firstly, the nitro group at the C-2 position forms a carbonyl group, – nitro group is rearranged intramolecularly to a nitrite group, and then nitrogen monoxide is eliminated to form a carbonyl group, and the stability of the ring is destroyed.
- Secondly, under a mixture of nitric acid and sulfuric acid, a *gem*-dinitro compound is formed, and a carbonyl group is formed by elimination of dinitrogen trioxide.
- Thirdly, the nitro group at the C-4 position forms a carbonyl group in the same way as the nitro group at the C-2 position. Finally, the N(1)-C(5) and N(3)-C(4) bonds of parabanic acid undergo hydrolysis and cleavage to generate ethanedioic acid and urea, and the urea is then further hydrolyzed into ammonia and carbon dioxide.

From the above reactions of direct nitration of imidazole and its nitro derivatives with a mixture of HNO₃ and H₂SO₄, it can be seen that the success of the preparation of (2) depends on several factors:

- there must be a nitro group at the C-2 position of the imidazole ring, otherwise (2) was not obtained and only gave (8),
- the nitration conditions (*e.g.* ratio of HNO₃ to H₂SO₄, reaction temperature and time, *etc.*) should be selected appropriately, otherwise, the produced (2) will be rapidly oxidized and hydrolyzed to form (9).

6 Conclusions

- ◆ In summary, we have studied the nitration reactions of imidazole and its nitro derivatives with a mixture of 98% HNO₄ and 98% H₂SO₄ (or 15% SO₃ in H₂SO₄). Only 4,5-dinitroimidazole is formed, when there is no nitro group at the C-2 position of the imidazole ring. When the imidazole ring has a nitro group at the C-2 position, the highest yield of imidazolium 2,4,5-trinitroimidazolate is 62.5%. However, if the nitration conditions are too strong, a portion of the 2,4,5-trinitroimidazole will be converted to ethanedioic acid. The products of these reactions indicate that the nitro group at the C-2 position of the imidazole ring has a significant impact on the formation of imidazolium 2,4,5-trinitroimidazolate. At the same time, the stability to oxidation of the imidazole ring declines, and it will then be further hydrolyzed into small molecules.
- ◆ The product distribution was strongly dependent on the volume ratio of HNO₃ to H₂SO₄, the reaction temperature and duration.
- ◆ A possible reaction mechanism for the production of ethanedioic acid from 2,4,5-trinitroimidazole is proposed.

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