

## [1,3] Oxazine 유도체 합성을 위한 효율적인 One-Pot 합성

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## An Efficient One-Pot Strategies for the Synthesis of [1,3] Oxazine Derivatives

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**요약.** 수용액 속에서 NaHSO<sub>4</sub>, TBAB (phase transfer catalyst), ionic liquid (IL) (1-butyl-3-methyl imidazolium hydrogen sulphate [bmim]HSO<sub>4</sub>)를 사용하여, formalin, β-naphthol, aromatic amines을 반응시켜서 대응하는 2,3-dihydro-2-phenyl-1H-naphtho-[1,2-e] [1,3] oxazine 유도체를 합성할 수 있는 보다 친환경적이고, 수율이 좋고, 크로마토그래피 분리 방법을 사용하지 않는 합성 방법을 개발하였다.

**주제어:** [1,3] Oxazine 유도체, One-pot 전략, Cyclocondensation, Ionic liquid, Grinding

**ABSTRACT.** Sodium hydrogen sulphate (NaHSO<sub>4</sub>), n-tetra butyl ammonium bromide (TBAB) as a phase transfer catalyst (PTC) in water, and 1-butyl-3-methyl imidazolium hydrogen sulphate [bmim]HSO<sub>4</sub> as ionic liquid (IL) has been used as a mild reaction promoter for the cyclocondensation of formalin, β-naphthol and aromatic amines to afford respective 2,3-dihydro-2-phenyl-1H-naphtho-[1,2-e] [1,3] oxazine derivatives. The present protocols are greener, high yielding and involved the non-chromatographic isolation procedure.

**Keywords:** [1,3] Oxazine derivatives, One-pot strategies, Cyclocondensation, Ionic liquid, Grinding

## INTRODUCTION

Heterocyclic compounds occur very widely in nature and are essential to the human life. Among a large variety of heterocyclic compounds, 1,3-oxazine containing moiety possesses wide synthetic utility as a useful intermediate for the variety of functional group interconversions.<sup>1-3</sup> Recently, 1,3-oxazine ring system has been used for the photo induced opening and thermal closing.<sup>4</sup> Furthermore, they can be used as intermediates in the synthesis of *N*-substituted amino alcohols (Betti base) or in enantioselective synthesis of chiral amines.<sup>5</sup>

In recent years, 1,3-oxazine heterocycles have been evaluated for the varied biological properties such as analgesic, anticonvulsant, antitubercular, antibacterial, anticancer activity<sup>6</sup> and shows high activity against a variety of HIV-1 mutant strain.<sup>7</sup> In addition, naphthoxazine derivatives have exhibited therapeutic potential for the treatment of Parkinson's disease.<sup>8</sup> The tautomeric character of 1,3-*O,N*-heterocycles offers a great number of synthetic possibilities.<sup>9</sup> Realizing the importance of 1,3-oxazine derivatives as an

intermediates as well as in the synthesis of various drug sources, reported in a few classical methods using dry methanolic ammonia,<sup>10</sup> ammonium acetate,<sup>11</sup> Cu(OAc)<sub>2</sub>/ZnCl<sub>2</sub>,<sup>12</sup> under basic condition,<sup>13</sup> Au(I) complex,<sup>14</sup> 2-azadienes with alkynes,<sup>15</sup> Bu<sub>4</sub>NF/EtI,<sup>16</sup> and *p*-TsCl, DMAP/CH<sub>2</sub>Cl<sub>2</sub>.<sup>17</sup> But, there have only been a few reports for the synthesis of 2,3-dihydro-2-phenyl-1H-naphtho-[1,2-e] [1,3] oxazine derivatives from formalin, 2-naphthol and aromatic amines.<sup>18</sup> However, most of the reactions require exotic reaction condition, low product yield, longer reaction time and tedious work-up procedure. Therefore in search of better alternatives, we have paid attention to find a convenient and efficient methods on the basis of green approach over reported methods for the synthesis of [1,3] oxazine derivatives.

The best tools used to combine economic aspects with the environmental ones is the multicomponent reaction strategy; this process consists of only one synthetic step which is carried out without isolating of any intermediate, this reduces time and saving money, energy and raw materials.<sup>19</sup> Now a day's chemist has attracted much attention toward the green and clean approach whilst using non-toxic reagents, solvents

and catalysts.<sup>20</sup> Therefore, we would like to perform some of the safer processes such as, use of ionic liquid, use of phase transfer catalyst in water and grinding for the preferred reaction.

One of the alternatives for organic solvents under investigation in organic transformations is an ionic liquid.<sup>21</sup> The use of ionic liquids as a solvent as well as catalyst is surprisingly effective because of non-inflammability, high temperature tolerance, high solubility, non-volatile nature, negligible vapour pressure, recovery and reusability. In continuation of our work on IL in search of benign methods for the synthesis of various organic compounds,<sup>22</sup> herein, we would like to report for first time, the selective and rapid synthesis of 1,3-oxazine derivatives in the presence of [bmim]HSO<sub>4</sub> acidic ionic liquid. On the other side of this method, one ideal alternative under examination as a greener solvent for organic reaction is water.<sup>23</sup> The use of water as a solvent/reaction media is often surprisingly effective because of low cost, easy availability in abundant quantity, non-inflammability, non-toxic, ecofriendly, and easy product isolation when product is solid. The introduction of PTC to the reaction in water has developed synthetic methodology and made progress in approaching green chemistry. As far as we know, PTC is widely used in chemical reaction since it offers high yield with reduced cycle time, reduced or non added solvent, mild reaction condition, enhanced environmental performance and sometime better selectivity.<sup>24</sup>

Furthermore, the solid state reaction by grinding has many advantages such as reduced pollution, low costs, simplicity in process, handling and there is no need for the use of harmful organic solvents. These factors are beneficial to industry as well as to environment. Therefore solid state reactions or solvent free reactions are one of the most important synthesis techniques in green chemistry. Various solvent free reactions were found to occur by hand grinding in mortar and pestle.<sup>25</sup>

## EXPERIMENTAL

### General procedures for compounds 4(a-n)

**Method A.** A mixture of formalin (2 mmol), aromatic amine (1 mmol), 2-naphthol (1 mmol) in [bmim]HSO<sub>4</sub> (5 mol %) at 60 °C was stirred for specified time period as shown in Table 4. The progress of reaction was monitored on TLC. Upon completion of reaction, the reaction mixture was extracted with ethyl acetate (2 × 20 mL) leaving behind [bmim]HSO<sub>4</sub>, organic layer was washed by brine (2 × 10 mL) solution and dried over anhydrous sodium sulphate. The organic layer was evaporated under reduced pressure in Rota

evaporator. The solid obtained was crystallized from ethanol to get pure product.

**Method B.** A mixture of formalin (2 mmol), aromatic amine (1 mmol), 2-naphthol and PTC (0.5 mmol) was stirred in water (10 mL) at room temperature upto the completion of reaction as monitored by TLC for appropriate time period. After completion of the reaction, further procedure was performed as per method A.

**Method C.** A mixture of formalin (2 mmol), aromatic amine (1 mmol), 2-naphthol and NaHSO<sub>4</sub> (3 mmol) was ground by pestle and mortar at room temperature for specified period of time as mentioned in Table 4. After completion of reaction, as monitored by TLC, the reaction mixture was poured on cold water. The solid thus obtained was filtered, dried and crystallized in ethanol to get pure product.

### Spectroscopic data of the products

**2,3-Dihydro-2-*m*-tolyl-1*H*-naphtho-[1,2-*e*][1,3] oxazine (4c):** IR (KBr,  $\nu_{\max}/\text{cm}^{-1}$ ) 1029 (sym. C-O-C), 1231 (asym. C-O-C); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$  ppm) 2.20 (q, 3H, Ar-CH<sub>3</sub>), 4.90 (s, 2H, Ar-CH<sub>2</sub>-N-), 5.60 (s, 2H, -O-CH<sub>2</sub>-N-), 6.70-7.80 (m, 10H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz,  $\delta$  ppm) 20.2, 50.1, 79.1, 113.2, 116.1, 117.4, 119.2, 120.5, 124.7, 125.8, 126.1, 126.8, 127.9, 129.7, 130.4, 147.2, 148.1, 149.2, 150.4; MS: *m/z* 276.2 (m+1); Elemental analysis: C<sub>19</sub>H<sub>17</sub>NO Calcd.: C: 82.88%; H: 6.22%; N: 5.09%; Found: C: 82.71%, H: 6.29%, N: 5.06%.

**2,3-Dihydro-2-(3-methoxyphenyl)-1*H*-naphtho[1,2-*e*][1,3] oxazine (4j):** IR (KBr,  $\nu_{\max}/\text{cm}^{-1}$ ) 1029 (sym. C-O-C), 1211 (asym. C-O-C); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$  ppm) 3.54 (s, 3H, -OCH<sub>3</sub>), 4.70 (s, 2H, Ar-CH<sub>2</sub>-N-), 5.50 (s, 2H, -O-CH<sub>2</sub>-N-), 6.11-7.53 (m, 10H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz,  $\delta$  ppm) 49.1, 53.4, 79.2, 112.1, 114.5, 115.8, 117.3, 118.2, 120.9, 124.5, 125.6, 125.9, 126.5, 127.5, 130.3, 133.2, 146.7, 148.9, 151.1; MS: *m/z* 292.2 (m+1); Elemental analysis: C<sub>19</sub>H<sub>17</sub>NO<sub>2</sub> Calcd.: C: 78.33%; H: 5.88%; N: 4.81%; Found: C: 78.21%, H: 5.78%, N: 4.90%.

**2,3-Dihydro-2-(4-methoxyphenyl)-1*H*-naphtho[1,2-*e*][1,3] oxazine (4k):** IR (KBr,  $\nu_{\max}/\text{cm}^{-1}$ ) 1019 (sym. C-O-C), 1228 (asym. C-O-C); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$  ppm) 3.62 (s, 3H, -OCH<sub>3</sub>), 4.87 (s, 2H, Ar-CH<sub>2</sub>-N-), 5.40 (s, 2H, -O-CH<sub>2</sub>-N-), 6.77-7.82 (m, 10H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz,  $\delta$  ppm) 48.2, 52.2, 80.1, 111.2, 113.2, 115.6, 117.4, 119.5, 121.1, 124.2, 125.7, 125.9, 126.8, 127.2, 130.1, 132.3, 146.8, 148.6, 150.1; MS: *m/z* 292.2 (m+1); Elemental analysis: C<sub>19</sub>H<sub>17</sub>NO<sub>2</sub> Calcd.: C: 78.33%; H: 5.88%; N: 4.81%; Found: C: 78.45%, H: 5.90%, N: 4.72%.

**2-(2-ethoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3] oxazine (4l):** IR (KBr,  $\nu_{\max}/\text{cm}^{-1}$ ) 1021 (sym. C-O-C), 1234

(asym. C-O-C);  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz,  $\delta$  ppm) 1.29 (t, 3H,  $J = 14$  Hz, -O-CH $_2$ -CH $_3$ ), 3.96 (q, 2H,  $J = 14$  Hz, -O-CH $_2$ -CH $_3$ ), 4.61 (s, 2H, Ar-CH $_2$ -N-), 5.40 (s, 2H, -O-CH $_2$ -N-), 6.17-7.44 (m, 10H, Ar-H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 75 MHz,  $\delta$  ppm) 13.9, 48.8, 64.7, 81.5, 111.8, 114.7, 115.8, 117.5, 118.5, 121.2, 122.2, 124.5, 125.4, 125.7, 126.2, 127.4, 128.8, 133.2, 146.1, 149.3; MS:  $m/z$  306.2 (m+1); Elemental analysis: C $_{20}$ H $_{19}$ NO $_2$  Calcd.: C: 78.66%; H: 6.27%; N: 4.59%; Found: C: 78.48%, H: 6.37%, N: 4.67%.

**2-(4-ethoxyphenyl)-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazine (4m):** IR (KBr,  $\nu_{\text{max}}/\text{cm}^{-1}$ ) 1028 (sym. C-O-C), 1224 (asym. C-O-C);  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz,  $\delta$  ppm) 1.20 (t, 3H,  $J = 14$  Hz, -O-CH $_2$ -CH $_3$ ), 3.90 (q, 2H,  $J = 14$  Hz, -O-CH $_2$ -CH $_3$ ), 4.90 (s, 2H, Ar-CH $_2$ -N-), 5.40 (s, 2H, -O-CH $_2$ -N-), 6.80-7.80 (m, 10H, Ar-H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 75 MHz,  $\delta$  ppm) 14.6, 48.4, 65.1, 80.6, 112.6, 114.8, 115.9, 117.5, 119.7, 120.1, 123.4, 124.8, 125.4, 125.7, 126.5, 127.7, 129.8, 130.0, 147.2, 148.8; MS:  $m/z$  306.2 (m+1); Elemental analysis: C $_{20}$ H $_{19}$ NO $_2$  Calcd.: C: 78.66%; H: 6.27%; N: 4.59%; Found: C: 78.71%, H: 6.28%, N: 4.24%.

**2-(4-fluorophenyl)-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazine (4n):** IR (KBr,  $\nu_{\text{max}}/\text{cm}^{-1}$ ) 1026 (sym. C-O-C), 1245 (asym. C-O-C);  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz,  $\delta$  ppm) 1.20 (t, 3H,  $J = 14$  Hz, -O-CH $_2$ -CH $_3$ ), 4.90 (s, 2H, Ar-CH $_2$ -N-), 5.60 (s, 2H, -O-CH $_2$ -N-), 6.80-7.80 (m, 10H, Ar-H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 75 MHz,  $\delta$  ppm) 49.2, 78.5, 112.2, 114.2, 115.7, 116.1, 117.2, 118.2, 122.4, 123.1, 125.1, 125.6, 125.9, 127.5, 128.4, 130.4, 150.2, 151.8; MS:  $m/z$  280.2 (m+1); Elemental analysis: C $_{18}$ H $_{14}$ FNO Calcd.: C: 77.40%; H: 5.05%; N: 5.01%; Found: C: 77.87%, H: 5.14%, N: 5.15%.

## RESULTS AND DISCUSSION

In continuation of our research to synthesize 1,3-oxazine derivatives<sup>11</sup> and for developing benign methodologies for various organic compounds<sup>22,26</sup> encourage us to propose an effective strategy by applying greener approach. For this synthesis, we have condensed the 2-naphthol, formalin and aniline as a representative substrates to synthesis respective 1,3-oxazine.

Our initial investigation focused on the use of ionic liquid as a solvent as well as catalyst for the synthesis of 1,3-oxazine by the condensation of said reactants. In search of an efficient IL and the best experimental condition the preferred reaction in the presence of IL at 60 °C has been considered. A variety of ILs was employed for this synthesis. After successful screening of different ionic liquids such as, 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF $_4$ , 1-butyl-3-methylimidazolium hexafluorophosphate [bmim]

**Table 1.** Screening of IL for the synthesis of [1,3] oxazines

Entry	IL	Time (h)	Yield (%) <sup>a</sup>
1	[bmim]BF $_4$	2	65
2	[bmim]PF $_6$	2	40
3	[bmim]Cl	3	45
4	[bnmim]Cl	2	60
5	[emim]Br	2.5	40
6	[bmim]HSO $_4$	0.5	90

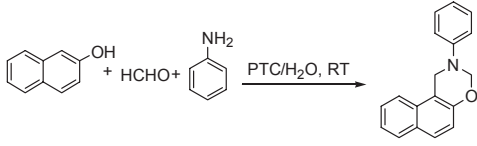
<sup>a</sup>Isolated yield

PF $_6$ , 1-butyl-3-dimethylimidazolium chloride [bmim]Cl, 1-benzyl-3-methylimidazolium chloride [bnmim]Cl, 1-ethyl-3-methylimidazolium bromide [emim]Br, and 1-butyl-3-methylimidazolium hydrogen sulphate [bmim]HSO $_4$  for the said reactants (Table 1).

After these successful screening it has been found that acidic IL [bmim]HSO $_4$  5 mol % was the best promoter for this reaction which gives 90% product yield within 30 min at 60 °C (Table 1, entry 6). Encouraged by this result, we extended this condition for derivatization with substituted anilines furnishing the respective 1,3-oxazine derivatives. These results are listed in Table 4. Also we have investigated the reusability of this IL [bmim]HSO $_4$  for **4a** (Table 4, entry 1) and observed that it was successfully recovered and reused for three cycles affording 90, 89, 89% yield with no significant loss of activity. The simple experimental and product isolation procedure combined with ease of recovery and reusability of IL is expected to the development of green strategy for the synthesis of 2,3-dihydro-2-phenyl-1H-naphtho[1,2-e][1,3]oxazine.

Our next attempt was to perform the reaction in water under magnetic stirring at room temperature. We observed that even after 3 - 5 hr the starting materials were remained in heterogeneous form, they exist as a non-miscible mixture like oil and water. Therefore, it has been undertaken, the use of PTCs for this transformations (Table 2).

Consequently, we tested various PTCs such as tridecyl trimethyl ammonium bromide (TDTMAB), cetyl pyridinium chloride (CPC), tetraethyl ammonium bromide (TEAB), sodium dodecyl sulphate (SDS) and tetra butyl ammonium bromide (TBAB) to perform the preferred reaction. Accordingly, TDTMAB was applied for this reaction; the result

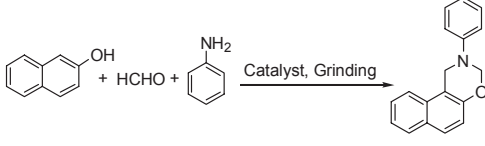
**Table 2.** Selection of PTC for the synthesis of [1,3] oxazines.


Entry	PTC	Time (h)	Yield (%) <sup>a</sup>
1	TDTMAB	12	60
2	CPC	15	45
3	TEAB	11	70
4	SDS	17	40
5	<b>TBAB</b>	<b>5</b>	<b>92</b>

<sup>a</sup>Isolated yield

showed that the reaction requires longer time duration and gave low yield 60% (Table 2, entry 1).

Further attempts were made by using other PTCs like CPC, TEAB in water but we did not get appreciable % yield within shorter reaction time (Table 2, entry 2, 3). Providentially, the target compound could be obtained by using TBAB due to the fact, which facilitates the migration of the reactants in heterogeneous system from one phase into another phase effectively. Hence by using TBAB the reaction was completed successfully within 5 hr that affords respective yield 92% (Table 2, entry 5). Even though, we have screened for

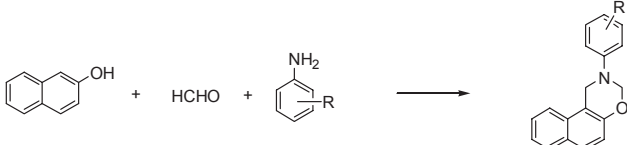
**Table 3.** Screening of suitable catalyst for synthesis of [1,3] oxazines.


Entry	Catalyst	Time (min)	Yield (%) <sup>a</sup>
1	EPZ-10	35	45
2	EPZG	40	30
3	SnCl <sub>2</sub> ·H <sub>2</sub> O	30	65
4	FeCl <sub>3</sub>	30	60
5	<b>NaHSO<sub>4</sub></b>	<b>7</b>	<b>89</b>

<sup>a</sup>Isolated yield

the non-ammonium ion PTC like, SDS having amphiphilic properties, but we found that the time required was comparatively very high 17 hr regarding product yield 40% (Table 2, entry 4). In due course to prepare more derivatives with aromatic amines having different substituents at various positions were reacted smoothly giving excellent product yield when subjected with TBAB in water at room temperature as shown in Table 4.

Finally, attempts were made using grinding approach which is less hazardous to human health and environment. In order to select an appropriate catalyst for the synthesis of

**Table 4.** Synthesis of 1,3-oxazine derivatives 4(a-n).


Entry	R	IL/60 °C (Method A)		PTC/H <sub>2</sub> O (Method B)		Grinding (Method C)		M. P. (°C)
		Time (min)	Yield (%) <sup>a</sup>	Time (h)	Yield (%) <sup>a</sup>	Time (min)	Yield (%) <sup>a</sup>	
<b>4a</b>	H	30	90	5	92	7	89	49-51 <sup>b</sup>
<b>4b</b>	2-Me	35	92	4.5	92	7	90	56-58 <sup>b</sup>
<b>4c</b>	3-Me	32	90	5	87	7	85	70-72
<b>4d</b>	4-Me	30	89	5	90	8	87	88-90 <sup>b</sup>
<b>4e</b>	2-NO <sub>2</sub>	30	90	6	91	7	89	110-112 <sup>b</sup>
<b>4f</b>	3-NO <sub>2</sub>	32	91	5	90	7	90	129-131 <sup>b</sup>
<b>4g</b>	4-NO <sub>2</sub>	29	89	5	89	7	87	165-167 <sup>b</sup>
<b>4h</b>	4-Br	29	92	4.5	90	6	90	115-117 <sup>b</sup>
<b>4i</b>	2,4,6-tri Br	40	87	6	85	8	89	96-98 <sup>b</sup>
<b>4j</b>	3-OMe	30	93	4	93	7	91	66-68
<b>4k</b>	4-OMe	35	91	4.5	88	6	87	78-80
<b>4l</b>	2-OEt	29	89	5	90	8	89	100-102
<b>4m</b>	4-OEt	30	90	5	91	7	90	69-71
<b>4n</b>	4-F	29	91	4.5	92	6	96	135-137

<sup>a</sup>Isolated yield. <sup>b</sup>Reported in reference No. 18, other compounds are characterized with the help of Spectroscopic analysis (IR, <sup>1</sup>H NMR, MS and Elemental analysis).

1,3-oxazine by simply grinding method in mortar and pestle that provides an adequate energy for reaction (Table 3). We have screened an acidic clays such as, EPZ-10 and EPZG for the preferred reaction, it was observed that the reaction mass became semi-solid and remained for a long time; the reaction time was very high and product yield was very low (Table 3, entries 1, 2).

In addition, starting materials were subjected with Lewis acids such as, SnCl<sub>2</sub> and FeCl<sub>3</sub> as compared to acidic clays; these gives more yield (Table 3, entries 3, 4). Moreover, when we used acidic salt NaHSO<sub>4</sub> amazingly we observed that, within five min the reaction mixture became semi-solid; we continued grinding process up to complete conversion of reactants into product as showed by TLC. The reaction time required was very less 7 min and product yield was very high 89% as shown in (Table 3, entry 5).

With optimized reaction conditions in hand, we explored the scope and generality of the methodologies with the aromatic amines having electron donating as well as electron withdrawing substituents at different positions reacted smoothly providing excellent yields within shorter reaction time as shown in Table 4.

## CONCLUSION

In conclusion, we have described simple, efficient and one-pot multicomponent synthesis of some new 2,3-dihydro-2-phenyl-1*H*-naphtho-[1,2-*e*][1,3] oxazine derivatives from cyclocondensation of formalin, aromatic amines and 2-naphthol under conventional heating in acidic ionic liquid [bmim] HSO<sub>4</sub>, at room temperature stirring in water in the presence of TBAB as a phase transfer catalyst and hand grinding with NaHSO<sub>4</sub>. The synthetic utility of the methodologies demonstrated in this work, whilst contributing the part of green and clean chemistry to sustain the human health and environment unaffected. The remarkable advantages offered by the methods presented are use of safer catalysts, use of ecofriendly solvents, mild reaction conditions, simplicity of the reaction procedure and high yielding strategies.

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