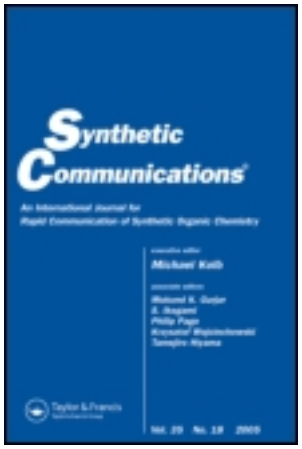

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ZnO as an Effective and Reusable Heterogeneous Catalyst for the Synthesis of Arylaminotetrazoles

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ZnO AS AN EFFECTIVE AND REUSABLE HETEROGENEOUS CATALYST FOR THE SYNTHESIS OF ARYLAMINOTETRAZOLES

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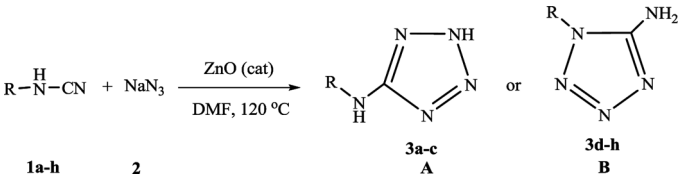
GRAPHICAL ABSTRACT



Abstract *ZnO is an effective heterogeneous catalyst for the reaction between arylcyanamides with sodium azide to synthesize the arylaminotetrazoles in good yields. This method has advantages of good yields, simple methodology, short reaction times, and easy workup. Furthermore, the catalyst can subsequently be reused for several times without any significant loss of activity.*

Keywords 5-Arylamino-1*H*-tetrazole; 1-aryl-5-amino-1*H*-tetrazole; arylcyanamide; heterogeneous catalyst; ZnO

INTRODUCTION

Tetrazoles have been widely used as an isosteric carboxylic acid pharmacophore in medicinal chemistry,[1] as ligands in coordination chemistry,[2–4] and as plant-growth regulators, herbicides, fungicides, explosives, and rocket propellants.[5–7] Hansch has shown that anionic tetrazoles are almost 10 times more lipophilic than the corresponding carboxylates, which is an important factor in designing a drug molecule to pass through the cell membranes.[8] Another important application of tetrazoles is preparation of imidoylazides.[9]

The 5-monosubstitutedamino-1*H*-tetrazoles were previously synthesized by thermal isomerization of 1-substituted-5-amino-1*H*-tetrazoles in boiling ethylene or melt state (180–200 °C).[10,11] Garbrecht and Herbst have shown that cyanamides may be converted to aminotetrazoles using hydrazoic acid, which often results, in a mixture of isomers 5-arylamino-1*H*-tetrazoles and 1-aryl-5-amino-1*H*-tetrazoles.[12]

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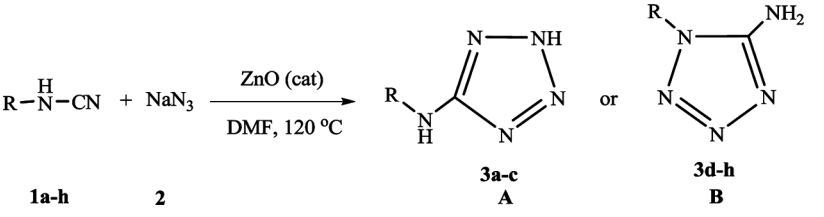
Congreve has reported a two-step synthesis of 1-aryl-5-amino-1*H*-tetrazoles from the corresponding 1-aryltetrazoles.[13] The reaction suffers from some drawbacks such as harsh reaction conditions, low temperatures (−70 °C), and use of large excess of sodium azide and organolithium reagents, which are potentially dangerous. Vorobiov and coworkers published a three-step synthesis of 1-aryl-5-amino-1*H*-tetrazoles, which proceeded in poor yields from the corresponding aromatic amines via isolation of cyanamides intermediate.[14] Unfortunately, this approach is not well developed because of the insufficient stability of these intermediates. In most cases, *N*-arylureas and other by-products were mostly formed, and the cyanamides intermediates were not stable enough to be isolated. Therefore, 1-aryl-5-amino-1*H*-tetrazoles were produced in poor yields.

These syntheses require the use of highly toxic and explosive hydrazoic acid, so it is desirable to develop a more efficient and convenient method for the regiospecific synthesis of arylaminotetrazoles. On the other hand, in most cases only the 1-aryl-5-amino-1*H*-tetrazoles were obtained. We needed to develop a method without application of homogeneous system as well as hydrazoic acid or in situ generation of hydrazoic acid because of the presence of azide sources as well as the synthesis of regiospecific products.

In recent years, application and design of environmentally friendly solid catalysts have been increased to reduce the amount of toxic wastes. The use of metal oxide catalysts have received the considerable attention in organic synthesis because of their environmental compatibility, ease of handling, nontoxic nature, reusability, and development of solventless reactions, which have environmental advantages[15–18] of all the heterogeneous solid catalysts, application of zinc oxide has widely increased because it is commercially available, inexpensive, moisture stable, reusable, and environmentally benign, and it has been used in several reactions such as Beckmann rearrangements,[15] Friedel–Crafts acylation,[16] and synthesis of cyclic ureas.[18]

Recently, we described a sufficiently simple and convenient synthesis of arylaminotetrazoles from the corresponding arylcyanamides using $ZnCl_2$ in water.[19] $ZnBr_2$ is homogeneous and cannot be separated from the reaction mixture, whereas zinc oxide is heterogeneous and can easily be recovered and reused.

In continuation of our recent work on the synthesis of heterocycles[20] and application of heterogeneous reagents for development of the useful synthetic methodologies,[21–26] we herein describe a new, simple, and effective procedure for the synthesis of arylaminotetrazoles (**3a–h**) via the reaction of arylcyanamides (**1a–h**) and sodium azide (**2**) in the presence of zinc oxide as a heterogeneous catalyst (Scheme 1).



Scheme 1. Synthesis of different arylaminotetrazoles.

EXPERIMENTAL

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Products were characterized by spectroscopic data [infrared (IR), fourier transform (FT)–IR, ^{1}H NMR, and ^{13}C NMR spectra], elemental analyses (CHN), and melting points. The NMR spectra were recorded in dinethylsulfoxide (DMSO) and acetone. ^{1}H NMR spectra were recorded on Bruker Avance DRX 300- and 500-MHz instruments. The chemical shifts (δ) are reported in parts per million (ppm) relative to the tetrametleysilene (TMS) as internal standard. *J* values are hertz given in (Hz). ^{13}C NMR spectra were recorded at 125 and 75 Hz. IR (KBr) and FT-IR (KBr) spectra were recorded on Shimadzu 470 and Perkin-Elmer 781 spectrophotometers, respectively. Melting points were taken in open capillary tubes with a Buchi 510 melting-point apparatus and were uncorrected. The elemental analysis was performed using Heraeus CHN-O-Rapid analyzer. Thin-layer chromatography (TLC) was performed on silica gel polygram SIL G/UV 254 plates.

The arylcyanamides (**1a–h)** were prepared according to the literature.[27]

Typical Procedure for Preparation of Arylaminotetrazoles 3

ZnO (0.1 g) was added to a mixture of cyanamides (**1a–h**) (2 mmol), NaN_3 (**2**) (0.2 g, 3 mmol) in distilled dimethylformamide (6 mL) and stirred at 120 °C for the appropriate time (Table 1). After completion of the reaction (as monitored by TLC), the ZnO was centrifuged and the centrifugate was treated with ethyl acetate (35 mL) and 5 N HCl (20 mL) and stirred vigorously. The resultant organic layer was separated, and the aqueous layer was again extracted with ethyl acetate (25 mL). The combined organic layers were washed with water, the solvent was removed, and the crude solid arylaminotetrazole was recrystallized (aqueous ethanol). The physical data (mp, IR, NMR) of known compounds were found to be identical with those reported in the literature.[19]

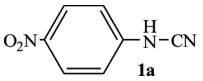
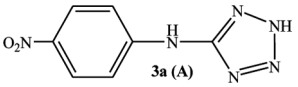
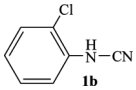
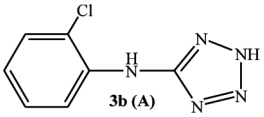
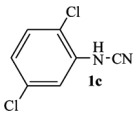
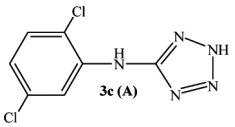
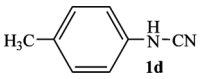
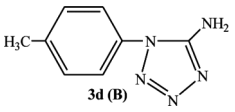
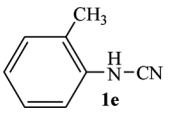
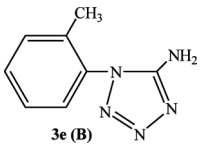
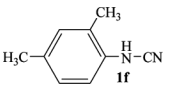
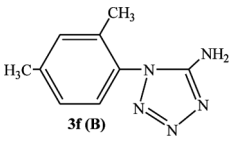
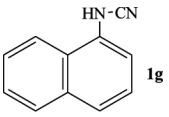
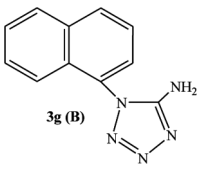
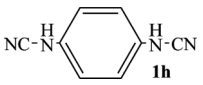
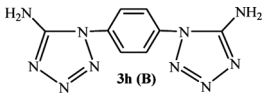
1-(4-(5-Amino-1*H*-tetrazole-1-yl)phenyl)-5-amino-1*H*-tetrazole (3h, Table 1, entry 8)

Mp. 264–266 °C; IR (KBr): 3357, 3139, 1652, 1588, 1519, 1426, 1293, 1141, 1070, 843 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.03 (2H, s), 7.83 (4H, s); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 126.3, 134.6, 155.9; Anal. calcd. for $C_8H_8N_{10}$: C, 39.35; H, 3.30; N, 57.35; Found: C, 39.46; H, 3.42; N, 57.23.

RESULTS AND DISCUSSION

Arylcyanamides (**1a–h**) were treated with sodium azide (**2**) in dimethylformamide (DMF) in the presence of ZnO to give the desired arylaminotetrazoles (**3a–h**) in moderate to good yields (Scheme 1). Reactions were performed at 120 °C and stirred for the appropriate time. To investigate both the electrical and steric effects, the arylcyanamides carrying either electron-releasing or electron-withdrawing substituents studied having different groups in *ortho*, *meta*, or *para* positions. As shown in

Table 1. Synthesis of arylaminotetrazoles (**3a–h**) in the presence of ZnO by reaction of sodium azide (**2**) and arylcyanamides (**1**) at 120 °C

Entry	Substrate (**1**)	Product	Time (min)	Yield[a] %
1	 **1a**	 **3a (A)**	120	77
2	 **1b**	 **3b (A)**	115	80, 78[b]
3	 **1c**	 **3c (A)**	110	75
4	 **1d**	 **3d (B)**	55	73
5	 **1e**	 **3e (B)**	55	74
6	 **1f**	 **3f (B)**	50	77
7	 **1g**	 **3g (B)**	75	75
8	 **1h**	 **3h (B)**	50	75

[a]Yield refers to the pure isolated products.
[b]Yield after the third cycle.

Table 1, among the various cyanamides, those having the electron-releasing groups on the aromatic rings (entries 4–6) complete at 120 °C after 50–55 min, whereas the electron-withdrawing species (entries 1–3) require longer reaction times.

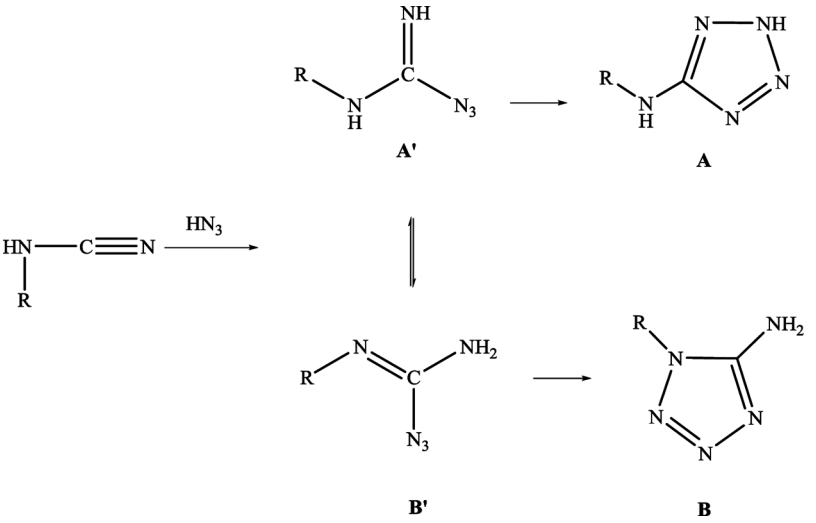
In the first set of experiments, the catalytic potential of some catalysts were investigated for the reaction between 2-chlorophenylcyanamide and sodium azide at 120 °C (Table 2). We observed that the regiospecificity of the cycloaddition reaction of azide ion with the cyanamides is strongly affected by the type of catalysts (compare entries 1–6 with 7–11 in Table 2). According to the obtained results, PPh_3, $FeCl_3$-SiO_2, SiO_2-$HClO_4$, Al_2O_3-SO_3H, LiCl, and glacial HOAc catalysts gave the mixture of isomers (**A** + **B**), while with ZnO only the sole isomer (**A**) was produced. The best result was obtained with 0.1 g of ZnO at 120 °C, which gave 5-(2-chlorophenyl)-amino-1*H*-tetrazole (**3b,** entry 2, Table 1) in good yield. This observation is in contrast with the reports that were presented for the synthesis of arylaminotetrazoles using hydrazoic acid, which often produced a mixture of isomers (Scheme 2).[12]

In the research carried out earlier, the nature of the substituent did not have any effect.[1,10,11,12,28–32] Substituents with different electrical natures such as -methyl or -nitrophenyl groups will form the same compound, presumably through the formation of a guanyl azide as an intermediate. Surprisingly, ring closure of the substituted guanyl azide in all of these methods yields 1-alkyl- or 1-aryl-5-aminotetrazole as a major product (as much as 95% in certain cases), whereas in the our method tetrazoles (**3**) are strongly afflicted by the type of substituents in arylcyanamides (**1**) and the obtained isomers **A** or **B** (Table 1). Generally, when the substituent on the aryl ring of arylcyanamides is electron releasing, formation of 1-aryl-5-amino-1*H*-tetrazoles (**B**) is favored via the guanidine azide intermediate **B'** (entries 4–8, Table 1), and as the electronegativity of substituent is increased, the product is shifted toward the formation of 5-arylamino-1*H*-tetrazole (**A**) via the guanidine azide intermediate **A'** (entries 1–3, Table 1). This observation is similar to the substituent effect on aryl ring of the mechanism that was presented by Henry and coworkers for thermal isomerization.[11]

Table 2. Comparison of different amounts of ZnO catalyst with PPh_3, $FeCl_3$-SiO_2, SiO_2-$HClO_4$, Al_2O_3-SO_3H, glacial acetic acid, and LiCl in the synthesis of 5-(2-chlorophenyl)amino-1*H*-tetrazole (**3b**) at 120 °C

Entry	Catalyst	Solvent	Time (min)	Yield[a] %	Product (**A** or **B**)
1	PPh_3	DMF	120	64	**A** + **B**
2	$FeCl_3$-SiO_2	DMF	120	75	**A** + **B**
3	SiO_2-$HClO_4$	—[b]	30	87	**A** + **B**
4	Al_2O_3-SO_3H	—[b]	30	85	**A** + **B**
5	LiCl	DMF	100	65	**A** + **B**
6	Glacial HOAc	Glacial HOAc[c]	24 h[d]	86	**A** + **B**
7	ZnO (0.05 g)	DMF	115	70	**A**
8	ZnO (0.07 g)	DMF	115	74	**A**
9	ZnO (0.10 g)	DMF	115	80	**A**
10	ZnO (0.10 g)	DMSO	115	80	**A**
11	ZnO (0.14 g)	DMF	115	81	**A**

[a]Isolated yield.
[b]Under solvent-free and thermal conditions at 80 °C.
[c]Glacial acetic acid as a solvent and a proton donor source.
[d]Room temperature.



Scheme 2. Effect of different substituents in the synthesis of arylaminotetrazoles.

In all cases, the products were characterized by ^{1}H NMR, ^{13}C NMR, IR, FT-IR, elemental analyses (CHN), and melting points. The disappearance of one strong and sharp absorption band (CN stretching band) and the appearance of a NH stretching band in the IR spectra provided clear evidence for the formation of arylaminotetrazoles. ^{13}C NMR spectra displayed signals at $\delta = 154$–157.5 ppm, indicative of C5 in the tetrazole ring (depending on the nature of the substituents in the amino functionality) (Fig. 1).[19,33–35]

On the basis of ^{1}H NMR spectra, we have considered two possible structures, **A** and **B**. A comparison of ^{1}H NMR spectra revealed that 5-arylamino-1*H*-tetrazoles isomers (**A**) contain two NH bonds [NH of the amine attached to the aryl group (NH^{A}) and NH of the tetrazole ring (NH^{T})] and 1-aryl-5-amino-1*H*-tetrazoles isomers (**B**) contain a NH_2 bond. The free N–H bond of tetrazoles (NH^{T}) makes them acidic molecules, and not surprisingly it has been shown that both the aliphatic and aromatic heterocycles have pKa values that are similar to the corresponding carboxylic acids, due to the ability of the moiety to stabilize a negative charge by electron delocalization.[36–38] In general, tetrazolic acids exhibit physical characteristics similar those of to carboxylic acids. Thus, the signal of the NH proton of the tetrazole ring (NH^{T}) shifted downfield (see Fig. 2 and ^{1}H NMR data of **3a–h**). Indeed, ^{1}H NMR spectra showed signals at $\delta = 9$–10 ppm, indicative of NH^{A} in 5-arylamino-1*H*-tetrazoles isomers (**A**) (Fig. 2), whereas ^{1}H NMR spectra of 1-aryl-5-amino-1*H*-tetrazoles isomers (**B**) showed one peak at $\delta = 6$–7 ppm, indicative of the NH_2 group (Fig. 3).

Not many organic solvents are suitable for the cycloaddition reactions, which usually need high temperatures (sometimes as high as 130 °C), and so DMF is a most commonly used solvent for this purpose.[1,6,39]

ZnO can easily be handled and removed from the reaction mixture by simple filtration in the workup stages. The recovered catalyst was consecutively reused three

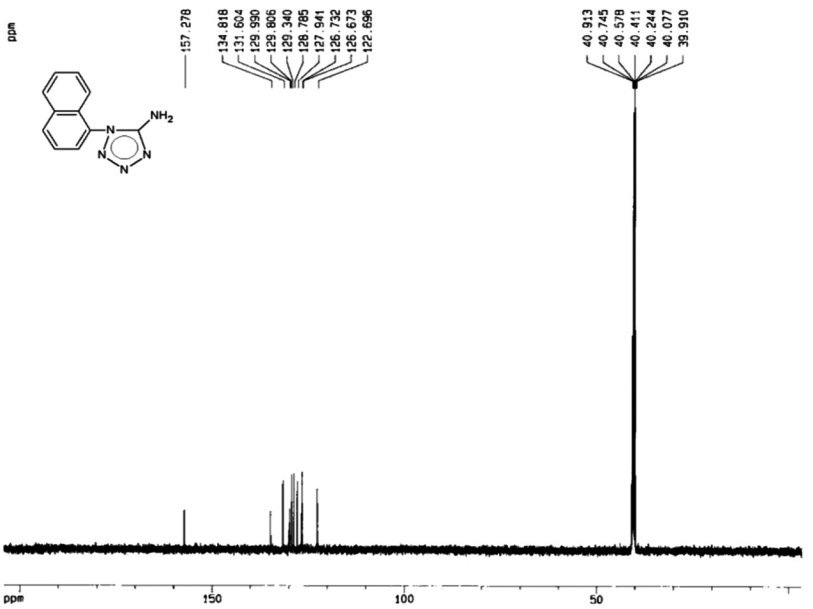


Figure 1. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) 1-(1-naphthyl)-5-amino-1*H*-tetrazole (**3g**).

times with a minimum variation of the yields of the products (Table 1, entry 2). After completion of the reaction, the catalyst was filtered, thoroughly washed with ethanol, dried and used for the subsequent runs.

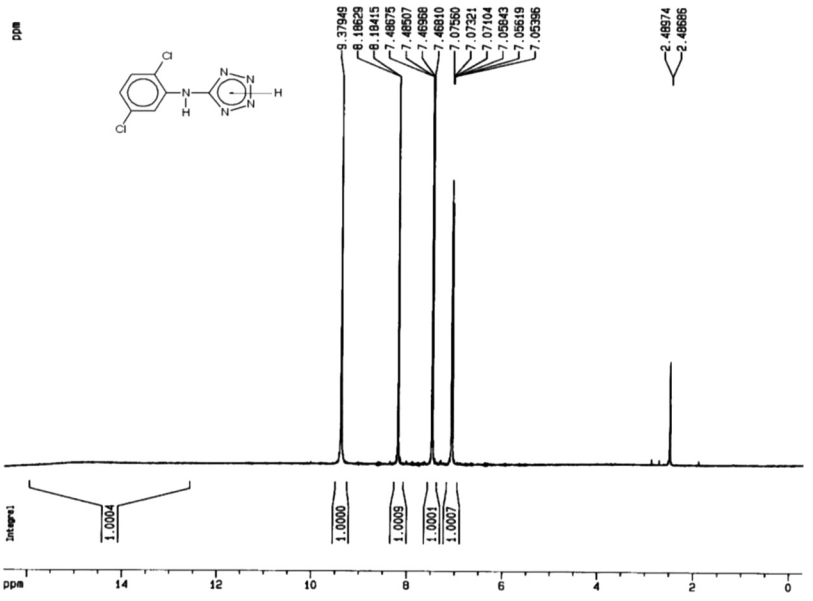


Figure 2. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) 5-(2,5-dicholorophenyl)-amino-1*H*-tetrazole (**3c**).

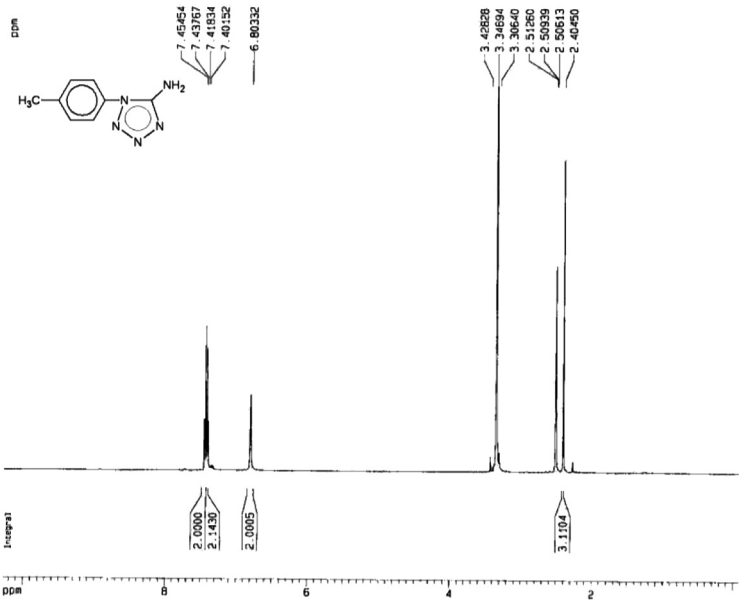


Figure 3. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) 1-(4-methylphenyl)-5-amino-1*H*-tetrazole (**3d**).

CONCLUSION

In conclusion, we have developed a novel and highly efficient method for the synthesis of arylaminotetrazoles by treatment of cyanamides with sodium azide in the presence of ZnO as an effective heterogeneous catalyst. The significant advantages of this methodology are good yields, short reaction times, a simple workup procedure, and easy preparation and handling of the heterogeneous catalyst. This methodology may find widespread uses in organic synthesis for the preparation of aminotetrazoles.

ACKNOWLEDGMENT

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