

# SnCl<sub>2</sub>·2H<sub>2</sub>O Mediated Barbier Type Allylation on Ketones

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## INTRODUCTION

Lewis acid catalyzed Barbier-type allylation of carbonyl mixes is a significant class of carbon–carbon bond shaping response. The item accordingly framed in this response is homoallylic liquor, which can be controlled to get to artificially profitable intermediates, for example, β-hydroxy carbonyl mixes. Additionally, these mixes can be effectively changed over into different structure squares valuable for the blend of regular items. Thus, the advancement of progressively improved engineered techniques for the planning of homoallylic alcohols stays a functioning examination territory.

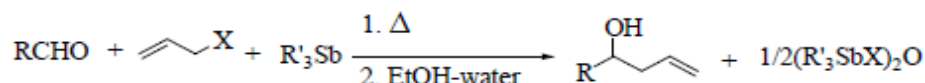
## REVIEW OF LITERATURE

Various strategies have been created for allylation response including different metals, for example, tin, indium, bismuth, manganese, magnesium, antimony, scandium, cobalt, cerium, silver, zinc, and samarium.

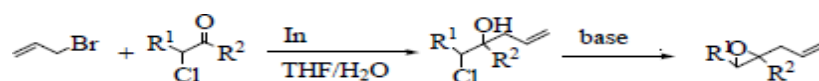
Copper and palladium mixes have pulled in the consideration as impetuses in various C–C bond-shaping responses. As far as anyone is concerned, there are just a not very many reports of SnCl<sub>2</sub>-intervened, one-pot, Barbier-type allylations utilizing an allyl halide, where Pd (II) or Pd (0) mixes were utilized as impetuses. Be that as it may, in the two cases, either a high measure of the impetus or long response time is important to accomplish great yield of homoallyl alcohols. Guo et al<sup>1,2</sup>. detailed a technique for the allylation of carbonyl compound utilizing copper powder. This technique requires two molar counterparts of copper powder to achieve the allylation.

In the late 1980s, Araki and associates<sup>3</sup> detailed the Barbier-type allylation of carbonyl mixes utilizing indium metal in an anhydrous natural dissolvable. Afterward, Li and Chan<sup>4</sup> effectively did the indium-intervened, Barbier-type allylation in watery medium. In 1983, Nokami et al<sup>5</sup>. seen that water had a quickening impact on the allylation of carbonyl mixes with diallyltin dibromide in ether. Chen

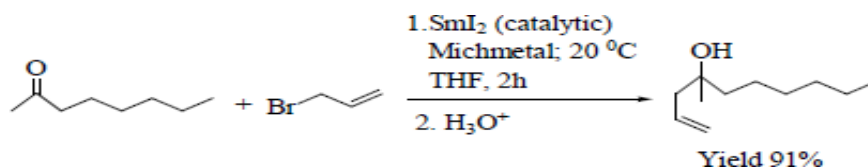
announced Sb-interceded Barbier-type allylation in alcohol-water mixture.



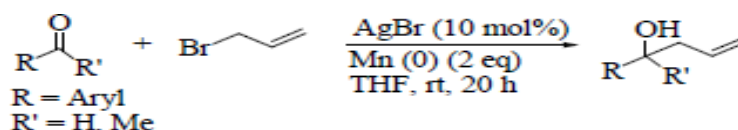
Yadav et al<sup>6</sup> discovered that  $\alpha,\beta$ -Unsaturated ketones smoothly undergo conjugate addition with allyltrimethylsilane in the presence of a catalytic amount of elemental iodine under very mild and convenient conditions to afford the corresponding Michael adducts in high yields with high selectivity. Shin et al<sup>7</sup> revealed indium-intervened allylation of  $\alpha$ -chlorocarbonyl compounds with different allyl bromides in fluid media. The item homoallylic chlorohydrins could be changed into the comparing epoxides within the sight of a base.



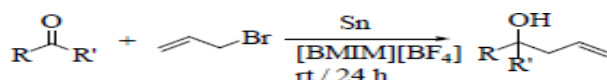
Namy et al<sup>8</sup>. reported the Barbier-type allylation using Samarium diiodide in catalytic amounts together with mischmetal (an alloy of the light lanthanides) as a coreductant.



Jarvo et al<sup>9</sup>. detailed Silver bromide catalyzed Barbier-type allylation of aldehydes and ketones utilizing unactivated manganese powder. In this reaction both aliphatic and sweet-smelling aldehydes and ketones respond. Aryl chlorides and nitriles are likewise endured in this specific reaction.



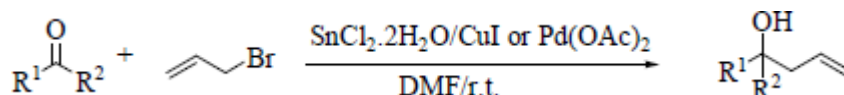
Wang and his associates<sup>10,11</sup> detailed that Barbier-type allylation can be influenced by utilizing tin nano particles in fluid medium. Slaton et al<sup>12</sup> detailed tin interceded Barbier type allylation in ionic fluids. Around the same time, Li and his collaborators revealed a gentle and productive barbier allylation reaction intervened by magnesium powder under dissolvable free conditions.



## PRESENT WORK

### Objective

In spite of the fact that, there are a few reports in the writing for the blend of homoallyl alcohol, in the greater part of the cases just fragrant ketones are reactive, while aliphatic ketones were observed to be idle under comparable reaction condition. By and large, it is important to do the reaction at high temperature and for long time to create great yield of the ideal item. The target of the present examination is to build up a straightforward and productive strategy to integrate homoallyl alcohol utilizing copper and palladium impetus at room temperature. We expect to do a similar report on the Barbier-type allylation reactions of ketones-intervened by  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , utilizing  $\text{CuI}$  and  $\text{Pd}(\text{OAc})_2$  as the impetus to sum up the reaction conditions.



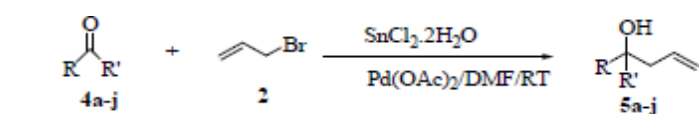
## RESULTS AND DISCUSSION

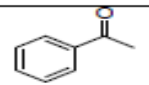
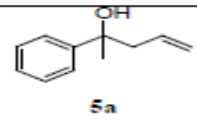
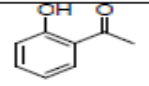
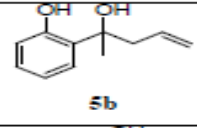
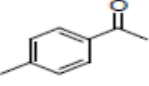
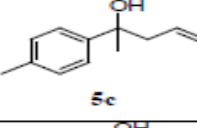
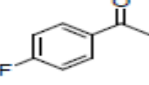
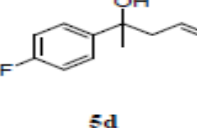
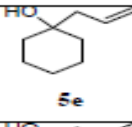
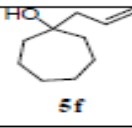
The point of this examination is to assess the synergist effectiveness of  $\text{CuI}$  and  $\text{Pd}(\text{OAc})_2$  for Barbier type allylation of carbonyl compounds. In a run of the mill reaction,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (2 mmol) and  $\text{CuI}$  (10 mol %) were added to a blend of allylbromide (1.1 mmol) and ketone (1 mmol) in DMF (1 mL) at room temperature. The reaction was checked by TLC. The outcomes are displayed in Table 1.

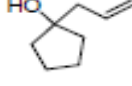
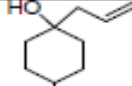
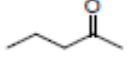
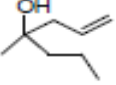
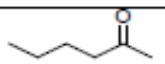
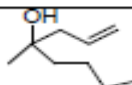
The achievement of the homoallylation of ketones urged us to stretch out the reaction to ketones (Table 1). Introductory reaction with acetophenone utilizing  $\text{CuI}$  as impetus under a similar reaction condition failed to deliver the relating homoallyl alcohol. Be that as it may, the utilization of 3 mol% of  $\text{Pd}(\text{OAc})_2$  could drive the reaction forward to deliver homoallylic alcohols in 85% yield after 3h of reaction. The presence of  $-\text{NO}_2$  and  $-\text{F}$  bunch on the sweet-smelling ring in the ketones brings down the yield as well as it requires long time investment.

The reaction was additionally stretched out to an assortment of ketones and the outcomes are abridged in Table 1.

**Table 1: SnCl<sub>2</sub>. 2H<sub>2</sub>O mediated and Pd(OAc)<sub>2</sub> catalyzed allylation of Ketones<sup>a</sup>**



| Entry | Carbonyl Compound                                                                   | Product <sup>b</sup>                                                                | Catalyst                    | Time (h) | Yield (%) <sup>c</sup> |
|-------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-----------------------------|----------|------------------------|
| 1     |    |    | CuI<br>Pd(OAc) <sub>2</sub> | 12<br>5  | 0<br>85                |
| 2     |    |    | Pd(OAc) <sub>2</sub>        | 6        | 77                     |
| 3     |   |   | Pd(OAc) <sub>2</sub>        | 5        | 81                     |
| 4     |  |  | Pd(OAc) <sub>2</sub>        | 8        | 68                     |
| 5     |  |  | Pd(OAc) <sub>2</sub>        | 7        | 79                     |
| 6     |  |  | Pd(OAc) <sub>2</sub>        | 8        | 72                     |

|    |                                                                                   |                                                                                         |                           |   |    |
|----|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|---------------------------|---|----|
| 7  |  | <br>5g | $\text{Pd}(\text{OAc})_2$ | 5 | 71 |
| 8  |  | <br>5h | $\text{Pd}(\text{OAc})_2$ | 7 | 69 |
| 9  |  | <br>5i | $\text{Pd}(\text{OAc})_2$ | 6 | 75 |
| 10 |  | <br>5j | $\text{Pd}(\text{OAc})_2$ | 6 | 77 |

<sup>a</sup> Reaction conditions: Ketones, 1 mmol; allylbromide, 1.1 mmol;  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , 2mmol; CuI, 10 mol%;  $\text{Pd}(\text{OAc})_2$ , 3 mol%.

b

All products were characterized by IR,

<sup>1</sup>H NMR and

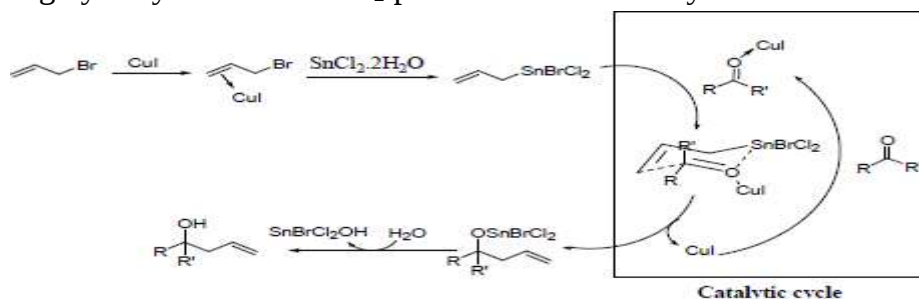
<sup>13</sup>C NMR.

<sup>c</sup> Isolated yield after chromatographic purification.

It very well may be seen from Table 1 that an assortment of ketones experience homoallylation in presence of 3 mol% of Pd(OAc)<sub>2</sub> to create the item in high return. Among the ketones inspected, 4-Fluoro-acetophenone (Table 1, section 4) and 4-Methyl-cyclohexanone (Table 1, passage 8) created somewhat low yield of the item.

## PROBABLE MECHANISM

A plausible unthinking pathway to clarify the homoallylation procedure is exhibited in Scheme 2. At first, the reaction continues by means of an allylbromodichlorotin intermediate<sup>9b</sup> formed by oxidative addition of allylbromide to SnCl<sub>2</sub>·2H<sub>2</sub>O. In the following stage, the reaction continues by starting coordination of the impetus with the carbonyl compound which encourages O–Sn bond formation. Resulting hydrolysis of OSnBrCl<sub>2</sub> produced the homoallylic alcohol.



## Probable mechanistic pathway Experimental Section

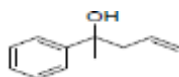
### General procedure for synthesis of homoallyl alcohol

To a solution of ketone (1 mmol) and allylbromide (1.1 mmol) in DMF (1 ml), SnCl<sub>2</sub>·2H<sub>2</sub>O (2 mmol) and catalyst, (CuI, 10 mol% or Pd(OAc)<sub>2</sub>, 3 mol%) were added successively at room temperature. After stirring the reaction for about appropriate time (TLC) at room temperature, water (10 mL) was added and the mixture was extracted with diethylether (3x10 mL). The organic phase was dried over sodium sulphate, filtered and evaporated. The crude product was purified by column chromatography over silica gel (230-400 mesh) using ethylacetate-petroleum ether (5:95) as eluent ether (5:95) as eluent.

### Experimental data

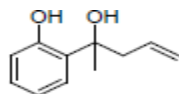
All the chemicals used were of analytical grade.  $^1\text{H}$  NMR and  $^{13}\text{C}$  spectra were recorded in Bruker 300 MHz instrument. Chemical shifts are shown in  $\delta$  units relative to the tetramethylsilane (TMS) signal as an internal reference in  $\text{CDCl}_3$ . Coupling constants ( $J$ ) are reported in Hz. IR spectra are recorded in Perkin-Elmer Spectrum RXI FT-RI spectrometer. Mass spectra were recorded on Perkin Elmer Claurus 600 C mass spectrometer. Silica gel (230-400 Mesh) was used for column chromatography.

## 1. 1-phenyl-1-methylbut-3-en-1-ol



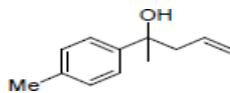
|                                                |                                                                                                                                                                       |
|------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| IR (KBr, $\text{cm}^{-1}$ )                    | : 3440, 3069, 2977, 1641, 1444, 1371, 1068.                                                                                                                           |
| $^1\text{H}$ NMR (300 MHz, $\text{CDCl}_3$ )   | : $\delta$ 7.47-7.23 (m, 5H), 5.72-5.62 (m, 1H), 5.18-5.12 (m, 2H), 2.71 (dd, $J_1 = 13.6$ Hz, $J_2 = 6.42$ Hz, 1H), 2.55-2.48 (m, 1H), 1.57 (s, 3H, $\text{CH}_3$ ). |
| $^{13}\text{C}$ NMR (75 MHz, $\text{CDCl}_3$ ) | : $\delta$ 147.5, 133.5, 128.0, 126.6, 125.0, 119.3, 73.5, 48.3, 29.7.                                                                                                |
| ESIMS (m/z)                                    | : 163 $[\text{M}+\text{H}]^+$ .                                                                                                                                       |

## 2. 1-(o-Hydroxyphenyl)-1-methylbut-3-en-1-ol



|                                                |                                                                                                                                                       |
|------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|
| IR (KBr, $\text{cm}^{-1}$ )                    | : 3439, 3072, 2975, 1645, 1441, 1377, 1071.                                                                                                           |
| $^1\text{H}$ NMR (300 MHz, $\text{CDCl}_3$ )   | : $\delta$ 9.26 (s, 1H), 7.19-6.81 (m, 4H), 5.83-5.75 (m, 1H), 5.22-5.17 (m, 2H), 2.84-2.77 (m, 1H), 2.59-2.52 (m, 1H), 1.63 (s, 3H, $\text{CH}_3$ ). |
| $^{13}\text{C}$ NMR (75 MHz, $\text{CDCl}_3$ ) | : $\delta$ 155.7, 132.9, 129.3, 128.8, 125.9, 120.3, 119.5, 117.5, 76.6, 46.5, 28.3.                                                                  |
| ESIMS (m/z)                                    | : 179 $[\text{M}+\text{H}]^+$ .                                                                                                                       |

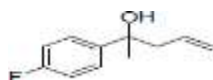
## 3. 1-(p-Methylphenyl)-1-methylbut-3-en-1-ol



|                             |                                             |
|-----------------------------|---------------------------------------------|
| IR (KBr, $\text{cm}^{-1}$ ) | : 3441, 3064, 2977, 1641, 1444, 1373, 1062. |
|-----------------------------|---------------------------------------------|

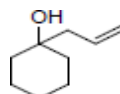
|                                                  |                                                                                                                                                                                                                                                                                                                                                 |
|--------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <sup>1</sup> H NMR (300 MHz, CDCl <sub>3</sub> ) | : δ 7.37 (d, <i>J</i> = 7.93 Hz, 2H), 7.19 (d, <i>J</i> = 7.55 Hz, 2H), 5.71-5.62 (m, 1H), 5.19-5.13 (m, 2H), 2.71 (dd, <i>J</i> <sub>1</sub> = 13.6 Hz, <i>J</i> <sub>2</sub> = 6.42 Hz, 1H), 2.52 (dd, <i>J</i> <sub>1</sub> = 13.6 Hz, <i>J</i> <sub>2</sub> = 8.31 Hz, 1H), 2.38 (s, 3H, CH <sub>3</sub> ), 1.56 (s, 3H, CH <sub>3</sub> ). |
| <sup>13</sup> C NMR (75 MHz, CDCl <sub>3</sub> ) | : δ 144.7, 136.2, 133.9, 128.9, 124.8, 119.4, 73.6, 48.5, 29.9, 21.0.                                                                                                                                                                                                                                                                           |
| ESIMS (m/z)                                      | : 177 [M+H] <sup>+</sup> .                                                                                                                                                                                                                                                                                                                      |

## 4. 1-(p-Fluorophenyl)-1-methylbut-3-en-ol



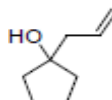
|                                                  |                                                                                                                                                                                                                               |
|--------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| IR (KBr, cm <sup>-1</sup> )                      | : 3445, 3062, 2971, 1639, 1440, 1372, 1062.                                                                                                                                                                                   |
| <sup>1</sup> H NMR (300 MHz, CDCl <sub>3</sub> ) | : δ 7.43-7.38 (m, 2H, ArH), 7.12-6.99 (m, 2H, ArH), 5.66-5.57 (m, 1H), 5.16-5.11 (m, 2H), 2.66 (dd, <i>J</i> <sub>1</sub> = 13.6 Hz, <i>J</i> <sub>2</sub> = 6.42 Hz, 1H), 2.52-2.45 (m, 1H), 1.54 (s, 3H, CH <sub>3</sub> ). |
| <sup>13</sup> C NMR (75 MHz, CDCl <sub>3</sub> ) | : δ 163.2, 159.9, 143.3, 133.3, 126.4, 119.7, 114.6, 73.3, 48.4, 29.9.                                                                                                                                                        |
| ESIMS (m/z)                                      | : 181 [M+H] <sup>+</sup> .                                                                                                                                                                                                    |

## 5. 1-Cyclohexylbut-3-en-1-ol



|                                                  |                                                                                  |
|--------------------------------------------------|----------------------------------------------------------------------------------|
| IR (KBr, cm <sup>-1</sup> )                      | : 3362, 3067, 2926, 2856, 1828, 1640, 1452, 1376.                                |
| <sup>1</sup> H NMR (300 MHz, CDCl <sub>3</sub> ) | : δ 5.95-5.81 (m, 1H), 5.16-5.13 (m, 2H), 2.23-2.20 (m, 2H), 1.70-1.38 (m, 10H). |
| <sup>13</sup> C NMR (75 MHz, CDCl <sub>3</sub> ) | : δ 138.8, 133.7, 122.7, 118.7, 70.9, 46.6, 37.3, 29.7, 25.5, 22.1.              |
| ESIMS (m/z)                                      | : 141 [M+H] <sup>+</sup> .                                                       |

## 6. 1-Cyclopentylbut-3-en-1-ol



IR (KBr,  $\text{cm}^{-1}$ ) : 3360, 3072, 2919, 2845, 1826, 1640, 1457, 1376.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  5.94-5.85 (m, 1H), 5.16-5.12 (m, 2H), 2.35-2.32 (m, 2H), 1.80-1.61 (m, 8H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) :  $\delta$  134.6, 118.6, 81.3, 45.8, 38.4, 23.8.

ESIMS (m/z) : 127  $[\text{M}+\text{H}]^+$ .

## 7. 1-Cycloheptylbut-3-en-1-ol



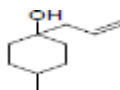
IR (KBr,  $\text{cm}^{-1}$ ) : 3550, 3068, 2936, 1621, 1505, 1185, 1056.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  5.94-5.80 (m, 1H), 5.13-5.05 (m, 2H), 2.21-2.19 (m, 2H), 1.65-1.54 (m, 12H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) :  $\delta$  134.0, 118.5, 74.8, 47.7, 41.4, 30.3, 22.2.

ESIMS (m/z) : 155  $[\text{M}+\text{H}]^+$ .

## 8. 1-(4-MethylCyclohexyl)but-3-en-1-ol



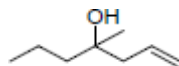
IR (KBr,  $\text{cm}^{-1}$ ) : 3381, 3065, 2942, 1621, 1510, 1432, 1181, 1056.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  5.14-5.07 (m, 2H), 2.37-2.34 (m, 2H), 1.38-1.25 (m, 12H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) :  $\delta$  133.7, 118.6, 70.2, 48.4, 40.8, 34.7, 32.2, 31.1, 30.2, 22.3.

ESIMS (m/z) : 155  $[\text{M}+\text{H}]^+$ .

## 9. 4-Methyl-hept-1-en-4-ol



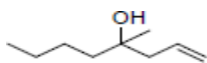
IR (KBr,  $\text{cm}^{-1}$ ) : 3542, 3067, 2932, 1508, 1183, 1056.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  5.87-5.78 (m, 1H), 5.10-5.04 (m, 2H), 2.18 (d,  $J = 7.18$  Hz, 2H), 1.41-0.91 (m, 10H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) :  $\delta$  134.2, 118.4, 72.2, 46.3, 44.1, 26.6, 17.2, 17.0, 14.6.

ESIMS (m/z) : 129  $[\text{M}+\text{H}]^+$ .

## 10. 4-Methyl-oct-1-en-4-ol



|                                                |                                                                                                                                                                                       |
|------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| IR (KBr, $\text{cm}^{-1}$ )                    | : 3542, 3072, 2940, 1620, 1510, 1431.                                                                                                                                                 |
| $^1\text{H}$ NMR (300 MHz, $\text{CDCl}_3$ )   | : $\delta$ 5.84-5.73 (m, 1H), 5.03-4.97 (m, 2H), 2.33 (t, $J = 7.18$ Hz, 2H), 2.13 (d, $J = 7.18$ Hz, 2H), 2.04 (s, 1H, OH), 1.51-1.43 (m, 4H), 1.41-1.21 (m, 3H), 1.06-0.95 (m, 3H). |
| $^{13}\text{C}$ NMR (75 MHz, $\text{CDCl}_3$ ) | : $\delta$ 134.2, 118.1, 72.1, 46.2, 43.4, 41.4, 26.5, 25.9, 23.2, 22.2.                                                                                                              |
| ESIMS ( $m/z$ )                                | : 143 $[\text{M}+\text{H}]^+$ .                                                                                                                                                       |

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