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# Hydrozirconation of Alkynyl Sulfoxides: the Reactions of Zirconated Vinyl Sulfoxide Intermediates

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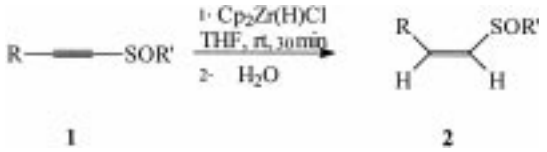
**Abstract**—Alkynyl sulfoxides react with $Cp_2Zr(H)Cl$ in THF at room temperature to give the α-zirconated and β-zirconated vinyl sulfoxides, which react with a wide range of electrophiles to give several types of di- or trisubstituted olefins, such as *Z*-vinyl sulfoxides and α- or β-halo vinyl sulfoxides. © 2000 Elsevier Science Ltd. All rights reserved.

Unsaturated sulfoxides have been widely used as building blocks in organic chemistry,[1–5] and a few routes to such compounds are known.[6–10] For example, oxidation of vinyl thioethers leads to sulfoxides,[6] the Horner–Wittig procedure using carbonyl compounds and sulfinyl methylphosphonate anions leads to a mixture of (*E*)- and (*Z*)-1-alkenyl sulfoxides.[7] (*E*)- and (*Z*)-2-bromovinyl phenyl sulfoxides react with cuprates in a cross-coupling process giving the corresponding 1-alkenyl sulfoxides.[8] Reaction of 1-alkynyl *p*-tolyl sulfoxides with lithium aluminum hydride in THF at −90°C proceeds to give (*E*)-1-alkenyl sulfoxides[9] (*E*)-1-Alkenylmagnesium bromides react with chiral menthyl sulfinate esters to produce chiral (*E*)-1-alkenyl sulfoxides.[10] But the starting materials such as vinyl thioethers, (*Z*)-2-bromovinyl phenyl sulfoxides, and (*Z*)-1-alkenylmagnesium bromides are not easily available.

Acetylenic sulfoxides have been used extensively in organic synthesis as activated acetylene equivalents.[11] Surprisingly, little attention has been paid to their hydrometalation reactions. On the other hand, via the hydrozirconation of alkynes, many bifunctional ethenyl reagents have been synthesized containing elements such as selenium and zirconium,[12] tellurium and zirconium,[13] silicon and zirconium,[14] tin and zirconium,[15] zinc and zirconium,[16] and boron and zirconium.[17] Recently we have reported the synthesis of sulfonylsubstituted alkenylzirconocene compounds via the hydrozirconation of internal acetylenic sulfones.[18] We now report that we have successfully synthesized sulfinylsubstituted alkenylzirconocene compounds via the hydrozirconation of alkynyl sulfoxides, which affords the corresponding *Z*-vinylsulfoxides in high yields by a proton quench (Scheme 1).

Acetylenic sulfoxides **1a**–**f** were synthesized in good yield according to the method of Villar.[11] Hydrozirconation of the acetylenic sulfoxides with 1.1 equiv. of $Cp_2Zr(H)Cl$ in THF for 30 min at room temperature gave a clear yellow solution. *Z*-Vinyl sulfoxides **2a**–**f** were obtained after hydrolysis (Table 1). The configuration was assigned to all compounds (**2**) by the coupling constant ($J$=11.0 Hz) for the vinyl protons in the $^1$H NMR spectra. The signals resulting from the *E*-isomers were not found in any case, indicating that the reactions were stereospecific.




**Scheme 1. 1a**: R=Ph, R′=Ph; **1b**: R=*n*-$C_5H_{11}$, R′=Ph; **1c**: R=*n*-$C_4H_9$, R′=Ph; **1d**: R=Ph, R′=4-Me$C_6H_4$; **1e**: R=*n*-$C_5H_{11}$, R′=4-Me$C_6H_4$; **1f**: R=*n*-$C_4H_9$, R′=4-Me$C_6H_4$.

*Keywords*: sulfoxides; alkynes; alkenes; zirconium; compounds.

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**Table 1.** Synthesis of *Z*-vinylsulfoxides **2a–f**

| Entry | R | R′ | Yield[a] (%) |
|---|---|---|---|
| **2a** | Ph | Ph | 78 |
| **2b** | $n$-$C_5H_{11}$ | Ph | 73 |
| **2c** | $n$-$C_4H_9$ | Ph | 80 |
| **2d** | Ph | 4-$MeC_6H_4$ | 74 |
| **2e** | $n$-$C_5H_{11}$ | 4-$MeC_6H_4$ | 70 |
| **2f** | $n$-$C_4H_9$ | 4-$MeC_6H_4$ | 77 |

[a] Isolated yield.

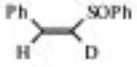
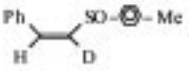
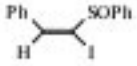
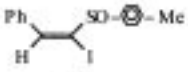
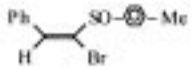
Sulfinylsubstituted alkenylzirconocene compounds were found to react with various electrophiles (Table 2). The total inversion of regioselectivity was observed when a phenyl group is linked to the triple bond as in the (arylsulfinyl)phenylacetylene **1a** and **1d**. In this case, the α-zirconated sulfinylalkenes **3** were the intermediates formed and after treatment with $D_2O$, $I_2$ or NBS, the compounds **4** were isolated as sole products in 57%–73% (Scheme 2).

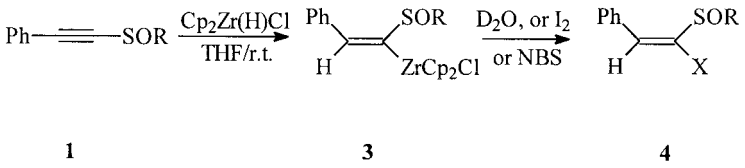
On the other hand, the hydrozirconation of 1-arylsulfinyl-2-alkylethynes **1b,1c,1e** and **1f** results in the formation of mixtures of the regioisomers α-zirconated **9** and β-zirconated vinylsulfoxides **10** that by reaction with $D_2O$, $I_2$ or NBS, afforded a mixture of **11** and **12** as depicted in Scheme 3.

The complete regioselectivity to the hydrozirconation of compounds **1a**, **1d** (R=Ph) could be explained on the basis of simple steric and conventional electronic effects (phenyl is a large group, the beta carbon of sulfoxide is the most electrophilic). However, the mixtures of regioisomers (**9**, **10**) was formed when R was the smaller group (R=*n*-alkyl).

In conclusion, the hydrozirconation strategy provides a direct route to (*Z*)-1-alkenyl sulfoxides from acetylenic sulfoxides. The method has some attractive advantages such as readily available starting materials, high yields, mild

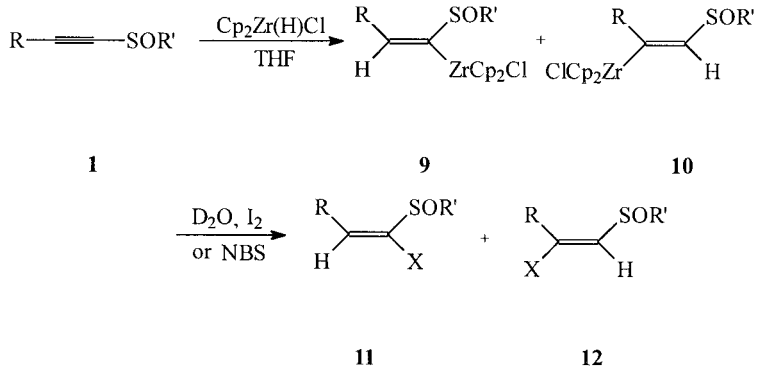
**Table 2.** Vinyl sulfoxides obtained from alkynyl sulfoxides

| Entry | E-X | Product | 11:12 | Yield(%)[a] |
|---|---|---|---|---|
| 1 | $D_2O$ |  **4a** | | 73 |
| 2 | $D_2O$ |  **4b** | | 66 |
| 3 | $D_2O$ |  **11a** **12a** | 40:60 | 70 |
| 4 | $D_2O$ |  **11b** **12b** | 44:56 | 64 |
| 5 | $I_2$ |  **4c** | | 68 |
| 6 | $I_2$ |  **4d** | | 69 |
| 7 | $I_2$ |  **11c** **12c** | 43:57 | 62 |
| 8 | NBS |  **4e** | | 57 |
| 9 | NBS |  **11d** **12d** | 43:57 | 58 |
| 10 | NBS |  **11e** **12e** | 41:59 | 60 |



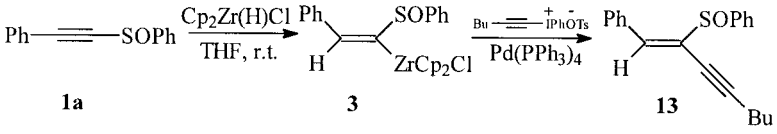

1 3 4

**Scheme 2.** R=Ph, 4-MeC$_6$H$_4$; X=D, I, Br.




1 9 10 11 12

**Scheme 3. 11a**, **12a**: R=*n*-C$_4$H$_9$, R′=Ph, X=D; **11b**, **12b**: R=*n*-C$_5$H$_{11}$, R′=4-MeC$_6$H$_4$, X=D; **11c**, **12c**: R=*n*-C$_5$H$_{11}$, R′=4-MeC$_6$H$_4$, X=I; **11d**, **12d**: R=*n*-C$_5$H$_{11}$, R′=4-MeC$_6$H$_4$, X=Br; **11e**, **12e**: R=*n*-C$_4$H$_9$, R′=4-MeC$_6$H$_4$, X=Br.




1a 3 13

**Scheme 4.**

reaction conditions and straightforward access to exclusive (*Z*)-configured products. Furthermore, the hydrozirconation strategy provides a direct route to trisubstituted alkenes from acetylenic sulfoxides. For example, treatment of alkynyl sulfoxide **1a** with $Cp_2Zr(H)Cl$, followed by treatment with alkynylphenyliodonium tosylates in the presence of $Pd(PPh_3)_4$, affords compound **13** in 54% (Scheme 4).

## Experimental

### General remarks

$^1$H NMR spectra were recorded on a Bruker AM-300 spectrometer with TMS as internal standard in $CDCl_3$. Chemical shifts were reported in parts per million ($\delta$, ppm). Mass spectra were determined using a Finigan 8230 mass spectrometer. IR spectra were obtained in neat capillary cell on a Shimadzu IR-408 instrument. The reaction were carried out in pre-dried glassware (150°C, 4 h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use. Acetylenic sulfoxides and alkynylphenyliodonium tosylates were prepared according to the literature methods respectively.[11,19]

### General procedure for the synthesis of *Z*-vinylsulfoxides 2a–f, 4a–b, 11a–b and 12a–b

To a freshly prepared suspension of $Cp_2Zr(H)Cl$ (1.5 mmol) in THF (6 ml) at rt was added a solution of acetylenic sulfoxides **1** (1.36 mmol) in THF (0.5 ml) under nitrogen, the reaction mixture was stirred for about 30 min until the precipitate completely disappeared. To the resulting clear green solution was then added 0.2 ml water (or 0.2 ml $D_2O$), the mixture was stirred for 1 h at ambient temperature. The solvent was removed by rotary evaporator under reduced pressure to give a crude oil, which was purified by preparative TLC (silica gel, hexane/AcOEt=10:1) to give **2a–f**, **4a–b**, **11a–b** and **12a–b**, respectively.

**2a.**[6] Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.05–7.55 (m, 10H, C$_6$*H*$_5$), 6.95 (d, *J*=10.5 Hz, 1H, =C*H*), 6.22 (d, *J*=10.5 Hz, 1H, =C*H*). IR $\nu$ (cm$^{-1}$): 3090, 1600, 1490, 1040. Anal. Calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30%. Found: C, 73.87; H, 5.37%.

**2b.**[10] Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.30–7.60 (m, 5H, C$_6$*H*$_5$), 5.95–6.20 (m, 2H, =C*H*), 2.20–2.40 (m, 2H, =CHC*H*$_2$), 1.15–1.65 (m, 6H, C*H*$_2$), 0.90 (t, *J*=6.5 Hz, 3H, C*H*$_3$). IR $\nu$ (cm$^{-1}$): 3090, 3020, 2970, 2870, 1590, 1490, 1025. Anal. Calcd for $C_{13}H_{18}OS$: C, 70.23; H, 8.16%. Found: C, 70.56; H, 8.12%.

**2c.**[8] Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.40–7.65 (m, 5H, C$_6$*H*$_5$), 6.10–6.27 (m, 2H, =C*H*), 2.30–2.50 (m, 2H, =CHC*H*$_2$), 1.12–1.62 (m, 4H, C*H*$_2$), 0.87 (t, *J*=6.5 Hz, 3H, C*H*$_3$). IR $\nu$ (cm$^{-1}$): 3090, 3020, 2970, 2870, 1590, 1485, 1090, 1025. Anal. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74%. Found: C, 69.54; H, 7.79%.

**2d.**[20] Yellow solid, Mp: 60–61°C (lit.[17], mp 60–61°C). $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.20–7.55 (m, 9H, C$_6$*H*$_5$, C$_6$*H*$_4$),

7.02 (d, $J$=10.5 Hz, 1H, =C*H*), 6.30 (d, $J$=10.5 Hz, 1H, =C*H*), 2.26 (s, 3H, C$H_3$). IR $\nu$ ($cm^{-1}$): 3100, 1610, 1495, 1450, 1040, 1015. Anal. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82%. Found: C, 74.57; H, 5.79%.

**2e.**[9] Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.10 (d, $J$=8 Hz, 2H), 7.65 (d, $J$=8 Hz, 2H), 6.35 (m, 1H, =C*H*), 6.05 (d, $J$=10.5, 1H, =C*H*), 2.40 (s, 3H, C$H_3$), 1.95–2.35 (m, 2H, =CHC$H_2$), 1.05–1.80 (m, 6H, C$H_2$), 0.92 (br, t, $J$=6 Hz, 3H, $CH_3$). IR $\nu$ ($cm^{-1}$): 2980, 1625, 1600, 1495, 1090, 1020. Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.52%. Found: C, 71.51; H, 8.48%.

**2f.**[9] Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.10 (d, $J$=8 Hz, 2H), 7.70 (d, $J$=8 Hz, 2H), 5.90–6.30 (m, 2H, =C*H*), 2.40 (s, 3H, C$H_3$), 1.90–2.30 (m, 2H, =CHC$H_2$), 1.10–1.70 (m, 4H, C$H_2$), 0.90 (br t, $J$=6 Hz, 3H, C$H_3$). IR $\nu$ ($cm^{-1}$): 2980, 1620, 1598, 1495, 1090, 1040, 1020. Anal. Calcd for $C_{13}H_{18}OS$: C, 70.23; H, 8.16%. Found: C, 69.94; H, 8.10%.

**4a.** Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.05–7.60 (m, 10H, $C_6H_5$), 6.98 (s, 1H, =C*H*). IR $\nu$ ($cm^{-1}$): 3080, 1595, 1485, 1085, 1045, 1020. MS: $m/z$ 229 ($M^+$).

**4b.**[21] Yellow solid, Mp: 64–66°C. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.50 (d, $J$=8 Hz, 2H), 7.60 (d, $J$=8 Hz, 2H), 7.30–7.40 (m, 5H, $C_6H_5$), 7.10 (s, 1H, =C*H*), 2.25 (s, 3H, $CH_3$). IR $\nu$ ($cm^{-1}$): 3070, 1610, 1495, 1445, 1040, 1018. MS: $m/z$ 243 ($M^+$).

**11a and 12a.** Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.20–7.70 (m, 5H, $C_6H_5$), 6.30 (t, $J$=6 Hz, 0.4H, =C*H*), 6.18 (s, 0.6H, =C*H*), 2.20–2.45 (m, 2H, =CHC$H_2$), 1.10–1.60 (m, 4H, C$H_2$), 0.85 (t, $J$=6.5 Hz, 3H, C$H_3$). IR $\nu$ ($Cm^{-1}$): 3090, 3010, 2980, 2950, 2880, 1593, 1085, 1020. MS: $m/z$ 209 ($M^+$).

**11b and 12b.**: Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.10–7.40 (m, 4H, $C_6H_4$), 6.30 (t, $J$=6 Hz, 0.43H, =C*H*), 6.10 (s, 0.57H, =C*H*), 2.35 (s, 3H, C$H_3$), 2.00–2.30 (m, 2H, =CHC$H_2$), 1.05–1.70 (m, 6H, C$H_2$), 0.85 (br, t, $J$=6 Hz, 3H, $CH_3$). IR $\nu$ ($cm^{-1}$): 3080, 2930, 1645, 1500, 1090, 1020. MS: $m/z$ 237 ($M^+$).

## General procedure for the synthesis of 4c–e, 11c–e and 12c–e

To a freshly prepared suspension of $Cp_2Zr(H)Cl$ (1.5 mmol) in THF (6 ml) at rt was added a solution of acetylenic sulfoxides **1** (1.36 mmol) in THF (0.5 ml) under nitrogen, the reaction mixture was stirred for about 30 min until the precipitate completely disappeared. To the resulting clear green solution was then added 1.30 mmol of $I_2$ (or NBS), the mixture was stirred for 1 h at ambient temperature. The reaction mixture was then poured into 20 ml of saturated aqueous $NaHCO_3$ and extracted with 10% EtOAc/hexanes (15 ml, 2×). The combined organic layers were washed with saturated aqueous NaCl, dried over $Na_2SO_4$, and filtered through a pad of Celite atop silica gel. Solvent was removed by rotary evaporator under reduced pressure to give a crude oil, which was purified by preparative TLC (silica gel, hexane/AcOEt=10:1) to give **4c–e**, **11c–e** and **12c–e**.

**4c.** Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.30–7.50 (m, 10H, $C_6H_5$), 7.10 (s, 1H, =C*H*). IR $\nu$ ($cm^{-1}$): 3080, 1595, 1485, 1085, 1045, 1020. MS: $m/z$ 354 ($M^+$). Anal. Calcd for $C_{14}H_{11}IOS$: C, 47.47; H, 3.13%. Found: C, 47.87; H, 3.09%.

**4d.** Yellow solid, Mp: 78–80°C. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.50 (d, $J$=8 Hz, 2H), 7.57 (d, $J$=8 Hz, 2H), 7.30–7.40 (m, 5H, $C_6H_5$), 7.33 (s, 1H, =C*H*), 2.20 (s, 3H, $CH_3$). IR $\nu$ ($cm^{-1}$): 3060, 1600, 1495, 1450, 1078, 1020. MS: $m/z$ 368 ($M^+$, 2.50), 202 (100). Anal. Calcd for $C_{15}H_{13}IOS$: C, 48.93; H, 3.56%. Found: C, 49.16; H, 3.69%.

**4e.** Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.18–7.65 (m, 9H, $C_6H_5$, $C_6H_4$), 7.06 (s, 1H, =C*H*), 2.28 (s, 3H, C$H_3$). IR $\nu$ ($cm^{-1}$): 3065, 1605, 1497, 1450, 1080, 1020. MS: $m/z$ 321 (M+1). Anal. Calcd for $C_{15}H_{13}BrOS$: C, 56.08; H, 4.08%. Found: C, 56.43; H, 4.13%.

**11c and 12c.** Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.25–7.65 (m, 4H, $C_6H_4$), 7.06 (t, $J$=6.5 Hz, 0.43H, =C*H*), 6.60 (s, 0.57H, =C*H*), 2.30 (s, 3H, C$H_3$), 2.10–2.35 (m, 2H, =CHC$H_2$), 1.05–1.75 (m, 6H, C$H_2$), 0.90 (br, t, $J$=6 Hz, 3H, $CH_3$). IR $\nu$ ($cm^{-1}$): 2970, 1620, 1600, 1090, 1020. MS: $m/z$ 345 (M-17, 2.0), 218 (100). Anal. Calcd for $C_{14}H_{19}IOS$: C, 46.42; H, 5.29%. Found: C, 46.71; H, 5.23%.

**11d and 12d.** Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.30–7.66 (m, 4H, $C_6H_4$), 7.10 (t, $J$=6.8 Hz, 0.43H, =C*H*), 6.55 (s, 0.57H, =C*H*), 2.38 (s, 3H, C$H_3$), 2.30–2.45 (m, 2H, =CHC$H_2$), 1.00–1.65 (m, 6H, C$H_2$), 0.86 (br t, $J$=6 Hz, 3H, $CH_3$). IR $\nu$ ($cm^{-1}$): 2980, 1620, 1600, 1090, 1020. MS: $m/z$ 315 (M+1). Anal. Calcd for $C_{14}H_{19}BrOS$: C, 53.34; H, 6.07%. Found: C, 53.72; H, 6.11%.

**11e and 12e.** Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.30–7.60 (m, 4H, $C_6H_4$), 6.95 (t, $J$=6 Hz, 0.4H, =C*H*), 6.50 (s, 0.4H, =C*H*), 2.26 (s, 3H, C$H_3$), 2.30–2.45 (m, 2H, =CHC$H_2$), 1.00–1.65 (m, 4H, C$H_2$), 0.90 (br t, $J$=6 Hz, 3H, $CH_3$). IR $\nu$ ($cm^{-1}$): 2980, 1620, 1600, 1090, 1020. MS: $m/z$ 301 (M+1). Anal. Calcd for $C_{13}H_{17}BrOS$: C, 51.83; H, 5.69%. Found: C, 51.76; H, 5.61%.

## General procedure for the synthesis of 13

To a freshly prepared suspension of $Cp_2Zr(H)Cl$ (1.5 mmol) in THF (6 ml) at rt was injected a solution of acetylenic sulfoxides **1a** (1.36 mmol) in THF (0.5 ml) under nitrogen, the reaction mixture was stirred for about 30 min until the precipitate completely disappeared. To the resulting clear green solution was then added $Pd(PPh_3)_4$ (0.07 mmol) and alkynyliodonium tosylates (1.36 mmol), the mixture was stirred for 2 h at ambient temperature. The product was washed with saturated aq. $NH_4Cl$ (8 ml) then extracted into diethyl ether, dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC (silica gel, hexane/AcOEt=10:1) to give **13**.

**13.** Yellow oil. $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.02–7.16 (m, 10H, $C_6H_5$), 6.90 (s, 1H, =C*H*), 2.15–2.40 (m, 2H, =CC$H_2$), 1.05–1.70 (m, 4H, C$H_2$), 0.91 (br t, $J$=6 Hz, 3H, $CH_3$). IR $\nu$ ($cm^{-1}$): 3060, 3005, 2970, 2940, 2895, 2870, 2160, 1570, 1500, 1090, 1015. MS: $m/z$ 308 ($M^+$).

Anal. Calcd for $C_{20}H_{20}OS$: C, 77.88; H, 6.53%. Found: C, 77.57; H, 6.59%.

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