57. The Isotopomeric (*Z*)- and (*E*)-2,3-Dimethyl(1,1,1,4,4,4-$^2H_6$)but-2-enes: Mechanistic Probes for Stereospecific Epoxidation

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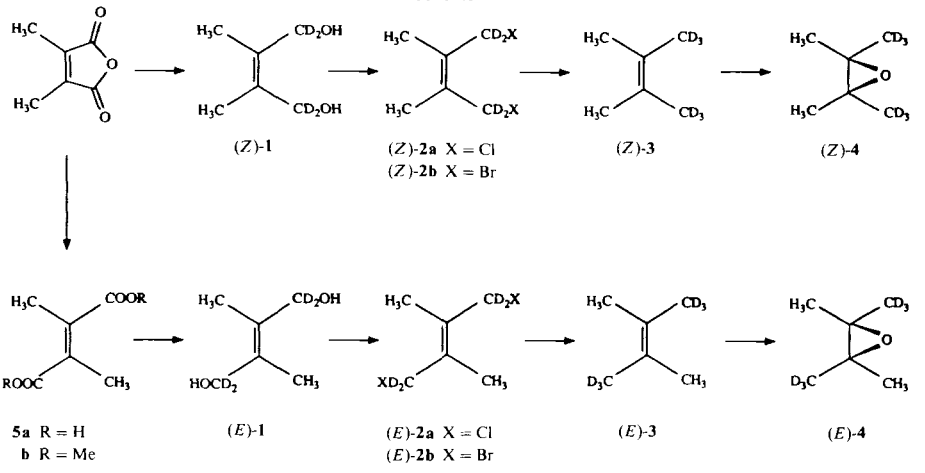
By unambiguous methods, (*Z*)- and (*E*)-2,3-dimethyl(1,1,1,4,4,4-$^2H_6$)but-2-enes (**3**) were synthesized and transformed to the epoxides **4** with 3-chloroperbenzoic acids. Both the isotopomeric olefins and the epoxides are detected separately by ^{1}H-NMR at 400 MHz. Epoxidation of (*Z*)-**3** with [$Rh^ICl(PPh_3)_3$]/cumene hydroperoxide resulted in a 1:1 mixture of (*Z*)- and (*E*)-**4**, while reaction of (*Z*)-**3** with [Fe^{III}(tpp)]Cl/PhIO gave only (*Z*)-**4** (tpp = tetraphenylporphyrin).

Introduction. – The development of enantioselective epoxidation methods is an objective of much current interest. Efficient systems were discovered for allylic alcohols [1] and, more recently, for unfunctionalized mono-, di-, and trisubstituted olefins [2]. In the context of our research on novel catalytic oxidizing systems, we investigated the effect of *tert*-butyl hydroperoxide (*t*-BuOOH)/Rh^I on various organic substrates, such as anthracene, alcohols, and terminal alkenes [3] [4]. In all cases, ketones were obtained as products, but tetramethylethylene (= 2,3-dimethylbut-2-ene) afforded the epoxide. This latter process could, in principle, be developed into an asymmetric catalytic epoxidation if the double bond of the substrate is appropriately substituted. The epoxidation of 2,3-dimethylbut-2-ene by *t*-BuOOH/Rh^I was first reported by *Lyons* and *Turner* [5]. Since the reaction did not exhibit the characteristics expected for a radical chain reaction, a mechanism consisting in epoxidation in the coordination sphere of the metal was proposed [6]. As exemplified by the *Sharpless* [1] and *Jacobsen* [2] epoxidations, such processes may be stereospecific or even enantioselective, while a radical pathway is expected to be nonspecific.

The stereospecificity of epoxidations is more conveniently investigated with disubstituted olefins, but unfortunately, with the exception of stilbene [3], these do not react with *t*-BuOOH/Rh^I. In the case of stilbene, the epoxidation is not stereospecific. Similarly, tri- and tetrasubstituted olefins, except 2,3-dimethylbut-2-ene, were found unreactive with this system, while terminal alkenes were not epoxidized, but reacted to methyl ketones [4].

Results and Discussion. – We have tested the stereospecificity of the epoxidation with *t*-BuOOH/Rh^I with the isotopomeric (*Z*)- and (*E*)-2,3-dimethyl(1,1,1,4,4,4-$^2H_6$)but-2-enes (**3**). These compounds were previously synthesized by stereochemically unambiguous routes, but no experimental details were reported, and, surprisingly, the isotopomers were not characterized [7]. The significance of the mechanistic conclusions derived from isotope effects of these compounds in photo-oxygenation may, therefore, be questioned. Our synthesis follows the one outlined by *Stephenson* [7] (see *Scheme*). The (*Z*)-isomer of

Scheme



3 was obtained from dimethylmaleic anhydride *via* reduction to the diol (*Z*)-**1** with $LiAlD_4$ in refluxing dimethoxyethane [8]. Reaction of (*Z*)-**1** with PBr_3 [9] or *N*-chlorosuccinimide/Me_2S [10] afforded dibromide (*Z*)-**2b** and dichloride (*Z*)-**2a**, respectively, which were further reduced to (*Z*)-**3** with $LiAlD_4$. For the synthesis of the (*E*)-isomer, dimethylmaleic anhydride was converted to 2,3-dimethylfumaric acid [11] (**5a**) by heating to 190° in the presence of NaOH, and the acid was esterified with diazomethane. Reduction of diester **5b** with AlD_3, which gave better results than $LiAlD_4$, afforded diol (*E*)-**1** which was converted *via* dihalide (*E*)-**2a** or (*E*)-**2b** to (*E*)-**3** as described for (*Z*)-**3**.

Since (*Z*)- and (*E*)-**3** have different symmetry, it was originally planned to characterize then by *Raman* spectroscopy; however, although the *Raman* spectra were not identical, they were too similar to be of use for analytical purposes [12]. Similarly, the MS of (*Z*)- and (*E*)-**3** showed no significant differences. Specifically, fragments corresponding to stereospecific loss of H_2, D_2, and HD or C_2H_6 and its isotopomers could not be found. Finally, it turned out that the isomers (*Z*)- and (*E*)-**3** could be clearly distinguished by ^{1}H-NMR at 400 MHz. *Fig. 1a* shows the spectrum of a *ca.* 3:1 mixture, prepared from independently synthesized (*Z*)- and (*E*)-**3**. The *singlets* of the CH_3 groups (1.64 ppm) are separated by 0.002 ppm, with the (*Z*)-isomer resonating at lower field. This proves that the synthetic sequence is stereospecific, and at the same time adds credibility to be mechanistic studies of *Stephenson* [7].

The alkenes were separately converted to the epoxides (*Z*)- and (*E*)-**4** with 3-chloroperbenzoic acid (*Scheme*). Characterization of the (*E*)- and (*Z*)-epoxides was again possible by ^{1}H-NMR at 400 MHz. A 2:1 mixture (*Z*)/(*E*)-**4** showed two signals for the CH_3 groups, separated by the same distance as those of the olefins (0.002 ppm, *Fig. 1b*). As in the case of **3**, the CH_3 groups of the (*Z*)-isomer resonate at lower field. No signal separation could be observed in the ^{13}C-NMR of the isotopomers of **3** and **4**, however.

The usefulness of (*Z*)- and (*E*)-**3** as mechanistic probes for epoxidations was tested by reaction with iodosylbenzene(PhIO) in the presence of a catalytic amount of (tetraphenylporphinato)iron(III) ([Fe^{III}(tpp)]Cl). This system is of interest as model for cytochrome P450 dependent mono-oxygenases. In particular, it allows for stereospecific epoxidations

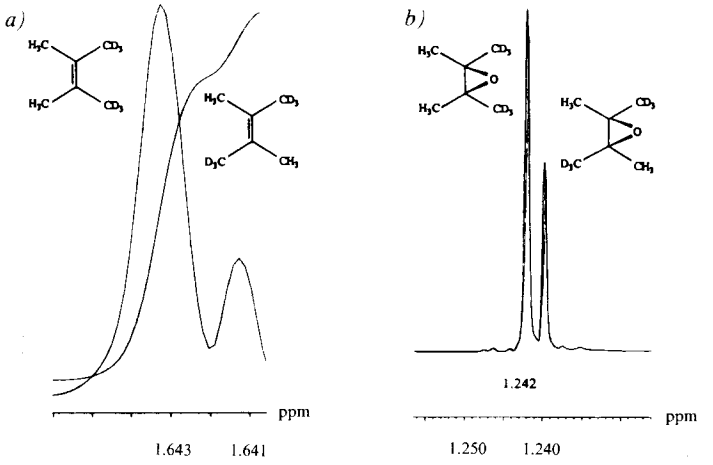


Fig. 1. *^{1}H-NMR* (400 MHz, $CDCl_3$) *of isotopomeric mixtures prepared from pure compounds:* a) *(Z)/(E)*-**3** *3:1 and* b) *(Z)/(E)*-**4** *2:1*

of (disubstituted) olefins [13]. With chiral iron porphyrins as catalysts, asymmetric epoxidation was achieved, albeit with only modest induction [14]. PhIO/[Fe^{III}(tpp)]Cl oxidized 2,3-dimethylbut-2-ene to the epoxide in 89% yield [15]. When (*Z*)-**3** was reacted with a slight excess of PhIO [16] in CD_2Cl_2 containing a catalytic amount of [Fe^{III}(tpp)]Cl, *ca.* 80% of the olefin was transformed to the epoxide after 2 h. NMR analysis of the product showed only one signal in the 1.3 ppm range, where the CH_3 groups of the epoxides **4** resonate (*Fig. 2a*). Addition of pure (*Z*)-**4** led to peak enhancement, proving that only (*Z*)-**4** was formed during the reaction. This result is consistent with the previously reported stereospecific [13] and enantioselective [14] epoxidation of disubstituted olefins with PhIO/[Fe^{III}(tpp)]Cl.

The stereospecificity of the Rh^I-catalyzed epoxidation was investigated with cumene hydroperoxide instead of *t*-BuOOH in order to facilitate separation of the reaction products. Thus (*Z*)-**3** was epoxidized with cumene hydroperoxide in presence of [$RhCl(PPh_3)_3$] with an excess of olefin serving as solvent. The resulting epoxides **4** and unreacted (*Z*)-**3** were separated by prep. GLC and the mixtures analyzed by NMR. The epoxide showed two peaks of identical intensities at 1.313 and 1.315 ppm. Addition of pure (*Z*)-**4** to the sample resulted in peak enhancement of the signal at lower field (*Figs. 2b* and *2c*). The recovered olefin, however, showed only a single line. This shows that the Rh^I-catalyzed epoxidation of 2,3-dimethylbut-2-ene is not stereospecific, and that (*Z*)-**3** is not isomerized under the conditions of epoxidation. However, NMR analysis of a small sample of (*Z*)-**3** stored during several month in a sealed tube revealed that total (*E*)/(*Z*)-isomerization had occurred.

In the absence of more detailed mechanistic studies, the implication of the epoxidation experiments is limited. Lack of stereospecificity in the Rh^I-catalyzed epoxidation of 2,3-dimethylbut-2-ene with hydroperoxides does not necessarily imply that the reaction does not occur in the coordination sphere of the metal; it merely proves that the reaction mechanism must involve an intermediate, in which the π-bond is cleaved with loss of

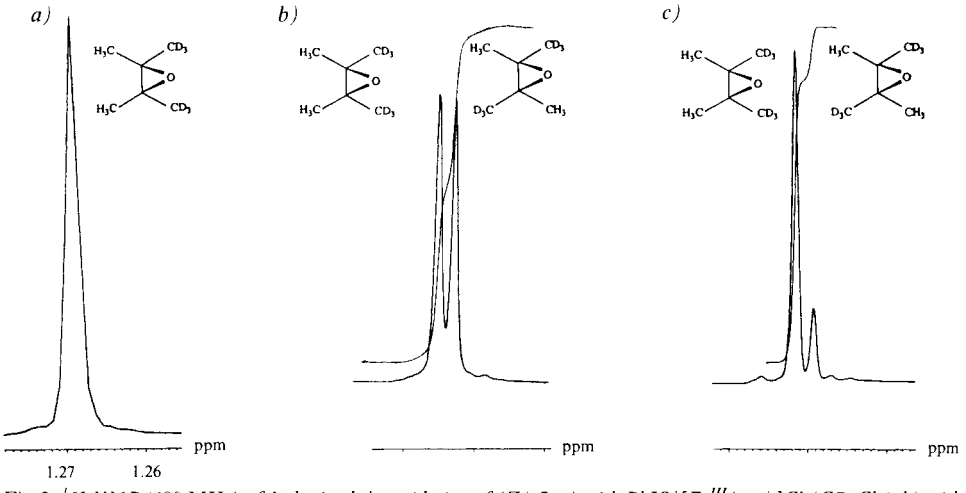


Fig. 2. *^{1}H-NMR* (400 MHz) *of* **4** *obtained* via *oxidation of* (Z)-**3**: a) *with PhIO/[Fe^{III}(tpp)]Cl (CD_2Cl_2)*, b) *with cumene hydroperoxide/[RhCl(PPh_3)$_3$] ($CDCl_3$), and* c) *peak enhancement upon addition of* (Z)-**4** *to the mixture of* b). The spectra of the epoxides are slightly displaced in comparison with those in *Fig. 1b*, owing to variations in the probe and solvent effects.

stereochemistry. Whether this intermediate is a radical or an ionic species, and whether it is bound to the metal or not, cannot be concluded from the present experiment. Irrespective of mechanistic details, it is clear, however, that since the *t*-BuOOH/Rh^I system lacks stereospecificity, it has no potential for asymmetric epoxidation.

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Experimental Part

General. See [17].

(Z)-2,3-Dimethyl(1,1,4,4-$^2H_4$)but-2-ene-1,4-diol ((*Z*)-**1**). Dimethylmaleic anhydride (7.5 g, 59.5 mmol) in dimethyloxyethane (DME, 180 ml) was added dropwise, under N_2, to $LiAlD_4$ (10.0 g, 238 mmol) in DME (300 ml) within 0.5 h. The mixture was refluxed for 2 h. After cooling, AcOEt (8 ml), followed by H_2O (15 ml), 5N NaOH (7 ml), and H_2O (50 ml) were successively added under N_2. Most of the DME was evaporated and the residue diluted with H_2O (150 ml). The soln. was extracted with Et_2O (3 × 50 ml). Drying ($MgSO_4$) and evaporation of the org. layer gave *ca.* 2 g of crude (*Z*)-**1** as viscous oil. The aq. phase was further extracted continuously during 2 d with CH_2Cl_2: 4.2 g of crude diol. Bulb-to-bulb distillation (80°/0.1 Torr) and CC (SiO_2/AcOEt) afforded 3.5 g (49%) of (*Z*)-**1**. ^{1}H-NMR: see [18]. ^{13}C-NMR: 17.3 (CH_3); 62.25 (CD_2OH); 132.49 (C). Physical data of undeuterated (*Z*)-**1**, see [19].

(Z)-1,4-Dichloro-2,3-dimethyl(1,1,4,4-$^2H_4$)but-2-ene ((*Z*)-**2a**). To *N*-chlorosuccinimide (1.122 g, 8.4 mmol) in CH_2Cl_2 (50 ml) was added dropwise at 0° Me_2S (0.53 g, 8.3 mmol). After 15 min, a precipitate was formed. The mixture was cooled to –20°, and (*Z*)-**1** (0.50 g, 4.1 mmol) in CH_2Cl_2 (20 ml) was added dropwise. The mixture was warmed to 0° and allowed to stand for 2 h. Then sat. NaCl soln. (50 ml) and ice (50 g) were added, the org. phase was separated and the aq. phase extracted with Et_2O (2 × 50 ml). The org. layers were washed separately with H_2O and evaporated. The residue was purified by bulb-to-bulb distillation (80–90°/14 Torr): 0.52 g (80%) of (*Z*)-**2a**. ^{1}H-NMR: 1.83 (*s*). ^{13}C-NMR: 17.53 (CH_3); 44.50 (CD_2Cl); 131.75 (C). See also [9].

(Z)-1,4-Dibromo-2,3-dimethyl(1,1,4,4-$^2H_4$)but-2-ene ((*Z*)-**2b**). To (*Z*)-**1** (3.20 g, 25 mmol) and pyridine (3.2 ml) in Et_2O (150 ml) was added during 30 min PBr_3 (14.8 g, 54 mmol) at 0°. After stirring overnight at r.t., the mixture was poured on ice-water and extracted with Et_2O. The aq. phase was further extracted 3 times with CH_2Cl_2. The org. layers were washed with sat. $NaHCO_3$ soln. to neutrality and evaporated. Bulb-to-bulb distillation (100°/0.1 Torr) gave 2.90 g (44%) of (*Z*)-**2b**. ^{1}H-NMR: 1.827 (*s*). ^{13}C-NMR: 19.04 (CH_3); 32.93 (CD_2Br); 132.19 (C). Other data see [19].

(Z)-2,3-Dimethyl(1,1,1,4,4,4-$^2H_6$)but-2-ene ((*Z*)-**3**). A soln. of (*Z*)-**2a** (1.0 g, 6.6 mmol) in dry triglyme (5.0 ml) was added in 15 min under N_2 by syringe to $LiAlD_4$ (290 mg, 7 mmol) in triglyme (12 ml) at −30°. The mixture was stirred at −25° for 1 h, then warmed to r.t., and stirred for 2 additional h. The reaction flask was then connected to 3 successive cold traps (the first cooled with dry-ice, the others with liq. N_2) and evacuated to 50 Torr. Pure (*Z*)-**3** distilled out of the reaction flask, after heating the latter to 50°, and collected in the cold traps: 0.40 g (70%) of (*Z*)-**3**. ^{1}H-NMR ($CDCl_3$): 1.643 (*s*). ^{13}C-NMR ($CDCl_3$): 19.40 (CD_3); 19.80 (CH_3); 123.27 (C). MS: 90 (71, $M^{+\cdot}$), 75 (86), 72 (100).

The same procedure, applied to (*Z*)-**2b**, produced (*Z*)-**3** in 33% yield.

(Z)-2,3-Epoxy-2,3-dimethyl(1,1,1,4,4,4-$^2H_6$)butane ((*Z*)-**4**). To (*Z*)-**3** (190 mg (2.1 mmol) in triglyme (1.5 ml) was added by syringe anh. 3-chloroperbenzoic acid (0.6 g, 3.4 mmol) in triglyme (2 ml) at 10–15° in 30 min. After 4 h at r.t., the flask was connected to 3 successive traps as described for (*Z*)-**3**. Epoxide (*Z*)-**4** (98% pure) distilled at 60–80°/14 Torr and was identified by comparison of the GLC retention time with that of an authentic sample of undeuterated material. ^{1}H-NMR ($CDCl_3$): 1.242 (*s*). ^{13}C-NMR: 20.15 (CD_3); 20.89 (CH_3); 61.81 (C). MS: 106 (5, M^+), 91 (10), 88 (12), 77 (5), 63 (71), 62 (100), 61 (57).

Dimethylfumaric Acid (**5a**) [11]. Dimethylmaleic anhydride (10.0 g, mmol) was heated in an autoclave with NaOH (6.5 g) and H_2O (35 ml) to 190° during 50 h. After cooling, the aq. phase was acidified with conc. HCl soln. under cooling, whereupon **5a** separated, Unreacted dimethylmaleic anhydride was removed by sublimation (80°/12 Torr) and the residue purified by recrystallization from H_2O: 3.0 g (26%) of **5a**. M.p. 242° ([11]: 244°). ^{1}H-NMR ((D_6)DMSO): 1.90 (*s*, 6H); 12.8 (*s*, 2H).

Dimethyl Dimethylfumarate (**5b**). Overnight, **5a** (2.0 g, 13.2 mmol) in Et_2O (100 ml) was reacted with diazomethane [20]. Evaporation and sublimation yielded 2.0 g (84%) of **5b**. M.p. 35° ([21]: 41–42°). ^{1}H-NMR (60 MHz, $CDCl_3$): 2.0 (*s*, 6H); 3.70 (*s*, 6H). ^{13}C-NMR ($CDCl_3$): 17.32 (CH_3–C); 51.82 (CH_3O); 133.41 (C=C); 169.29 (C=O).

(E)-2,3-Dimethyl(1,1,4,4-$^2H_4$)but-2-ene-1,4-diol ((*E*)-**1**). A soln. of AlD_3, prepared from $LiAlD_4$ (1.8 g) and freshly sublimed $AlCl_3$ (2.1 g) in Et_2O at −30°, was added in small portions to **5b** (2.80 g, 16.2 mmol) in Et_2O at 0°. The mixture was kept at 0° during 2 h, then at r.t. overnight. After cooling to 0°, it was decomposed with H_2O (50 ml). The aq. layer was extracted continuously with CH_2Cl_2 overnight twice. After evaporation of the org. phases, (*E*)-**1** was purified by sublimation (60°/0.1 Torr). A small amount was recrystallized from AcOEt: 850 mg (48%). M.p. 72°. ^{1}H-NMR (60 MHz, CD_3CN); 1.85 (*s*, 6H); 2.68 (*s*, 2H). ^{13}C-NMR (CD_3CN): 15.82 (CH_3); 62.88 (CD_2); 132.0 (C). MS: 120 (10, $M^{+\cdot}$), 102 (27), 87 (100), 73 (55), 72 (80), 59 (83).

(E)-1,4-Dichloro-2,3-dimethyl(1,1,4,4-$^2H_4$)but-2-ene ((*E*)-**2a**). Prepared in 58% yield from (*E*)-**1** (2.13 g, 33.6 mmol) as described for (*Z*)-**2a**. ^{1}H-NMR: 1.88 (*s*). ^{13}C-NMR: 16.63 (CH_3); 45.51 (CD_2); 131.23 (C).

(E)-1,4-Dibromo-2,3-dimethyl(1,1,4,4-$^2H_4$)but-2-ene ((*E*)-**2b**). Prepared as described for (*Z*)-**2b** in 34% yield. ^{1}H-NMR ($CDCl_3$): 1.85 (*s*). For an alternative preparation and data of undeuterated (*E*)-**2b**, see [22].

(E)-2,3-Dimethyl(1,1,1,1,4,4,4,4-$^2H_6$)but-2-ene ((*E*)-**3**). The reduction of (*E*)-**2a** as described for (*Z*)-**3** afforded (*E*)-**3** in 49% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.641 (*s*). ^{13}C-NMR: MS: 90 (73, $M^{+\cdot}$), 75 (89), 72 (100).

(E)-2,3-Epoxy-2,3-dimethyl(1,1,1,1,4,4,4,4-$^2H_6$)butane ((*E*)-**4**). Epoxidation of (*E*)-**3** as described for (*Z*)-**4** afforded (*E*)-**4** in 67% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.240 (*s*). ^{13}C-NMR ($CDCl_3$): 20.15 (CD_3); 20.89 (CH_3); 61.81 (C). MS: 106 (5, $M^{+\cdot}$), 91 (10), 88 (12), 84 (8), 77 (13), 63 (72), 62 (100), 61 (58).

Epoxidation of (Z)-3 with PhIO/[Fe^{III}(tpp)]Cl. To (*Z*)-**3** (100 mg) and [Fe^{III}(tpp)]Cl (20 mg) in CD_2Cl_2 (0.5 ml) was added PhIO [23] (300 mg) in small portions under cooling with H_2O. After 2 h (GLC: *ca.* 80% conversion), the volatiles were distilled *in vacuo* and collected in cold traps. The fraction containing most of the epoxide was directly subjected to ^{1}H-NMR (CD_2Cl_2): single peak at 1.269 ppm, which was enhanced when pure (*Z*)-**4** was added.

Epoxidation of (Z)-3 with [RhCl(PPh$_3$)$_3$]/Cumene Hydroperoxide. To (*Z*)-**3** (0.20 ml) and [RhCl(PPh_3)$_3$] in triglyme (0.6 ml) was added dropwise cumene hydroperoxide (720 mg, 2 equiv.) in triglyme (0.2 ml) at 0°. The mixture was stirred at r.t. for 3 h. After cooling, PPh_3 (500 mg) was added to decompose remaining hydroperoxides. After 2 h, the volatiles were distilled out of the flask *in vacuo* and collected in cold traps. GLC: only *ca.* 10% of epoxides. The unreacted olefin and the epoxides were separated by prep. GLC (*Carbowax* column). ^{1}H-NMR ($CDCl_3$): single peak for (*Z*)-**3** at 1.639 ppm; 2 *s* of equal intensities for the epoxides at 1.313 and 1.315 ppm; addition of pure (*Z*)-**4** resulted in enhancement of the peak at 1.315.

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