Heteroatom Chemistry
Volume 6, Number 6, 1995

Acid-Induced Cyclotrimerization of a Phosphaalkyne with Formal Incorporation of Water [1]

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Received March 1995; revised 19 June 1995

ABSTRACT

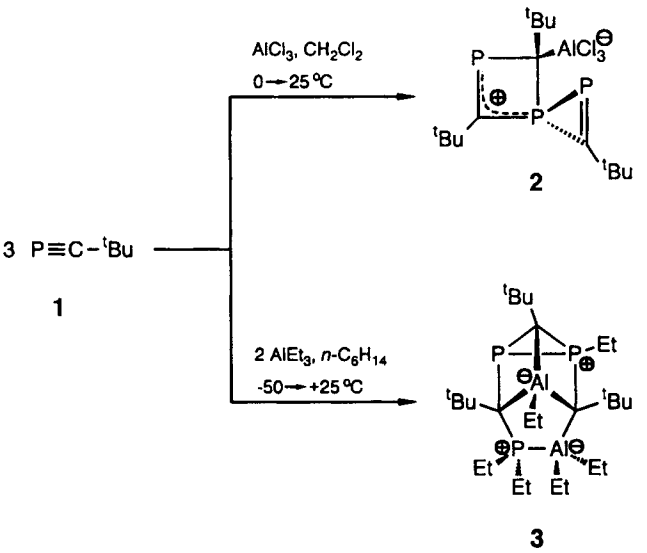
tert-Butylphosphaacetylene **1** *can be cyclotrimerized with incorporation of water to furnish the 1,2,4-triphosphabicyclo[2.1.1]hex-2-ene* **5** *in the presence of trifluoroacetic acid. This novel bicyclic system has been fully characterized by spectral and analytical data. The constitution of* **5** *has been unambiguously demonstrated by X-ray crystallography.* © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

A current research topic in the chemistry of low-coordinated phosphorus comprises the synthesis of cyclooligomers of kinetically stabilized phosphaalkynes [2–4]. The most important monomeric building block for the construction of compounds of these types is the preparatively easily accessible *tert*-butylphosphaacetylene **1**. In addition to the purely thermal cyclotetramerization [5,6], the oligomerization of **1** at transition metal centers has, above all, opened a route to novel carbon-phosphorus polycyclic compounds [6–8].

We have recently shown that **1** can also undergo spirotrimerization with incorporation of the Lewis acid to furnish the stable betaine **2** when treated with aluminum trichloride in a molar ratio of 3:1 (Scheme 1) [9]. On the other hand, reaction with trialkylaluminum derivatives leads to polycyclic products with incorporation of the reagent, as illustrated by compound **3** in Scheme 1 [10].

The previously mentioned reactions thus constitute a certain contrast to carbon chemistry since acetylenes undergo dimerization on treatment with aluminum trichloride to furnish isolable σ complexes of cyclobutadienes (e.g., **4**) [11]. Cyclobutadienyl cations, formed by the cyclodimerization of



SCHEME 1

Dedicated to Professor R. Neidlein on the occasion of his 65th birthday.

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disubstituted acetylenes in the presence of strong protic acids such as, for example, trifluoroacetic acid, have a similar structure (**4**, H in place of $AlCl_3^-$, CF_3COO^- as counterion, Scheme 2) [12,13].

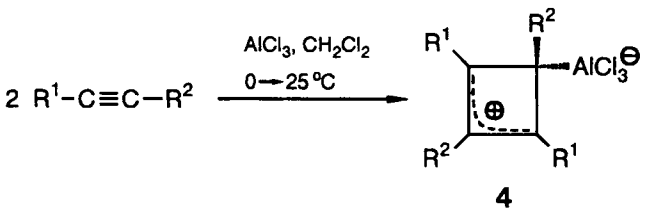
In complete contrast, nothing is yet known about the reactivity of *tert*-butyl-phosphaalkyne **1** toward such acids.

We report here for the first time on the successful acid-induced cyclotrimerization of **1** with incorporation of one equivalent of water to furnish the bicyclic product **5** under the influence of trifluoroacetic acid.

RESULTS AND DISCUSSION

Attempts to bring about reaction of the strong but only weakly nucleophilic trifluoroacetic acid with *tert*-butylphosphaacetylene **1** in a molar ratio of 1:2 in dichloromethane have been unsuccessful; even after stirring for several days at room temperature, no evidence of reaction can be found by spectroscopy. However, in the presence of an excess of the acid, reaction does indeed occur and small amounts of **5** can be detected by $^{31}P\{^1H\}$ NMR spectroscopy. Enrichment of **5** was possible by omitting the solvent and performing the reaction at room temperature with a large excess of trifluoroacetic acid. After separation of polymeric decomposition products by fractional bulb-to-bulb distillation and subsequent twofold column chromatographic purification, analytically pure **5** was obtained (18% yield) in the form of high-melting, practically colorless crystalline needles by recrystallization from diethyl ether (Scheme 3).

Both elemental analysis and high resolution mass spectrometry confirmed the composition of the product **5** obtained as a previously unknown phosphaalkyne trimer with the formal incorporation of one equivalent of water. From a structural point of view, it is an edge-opened 1,2,4-triphosphabenzvalene in which the phosphorus atom P4 is oxidized. The corresponding all-carbon parent compound, bicyclo[2.1.1]hex-2-ene, has been known for more than 25 years [14].



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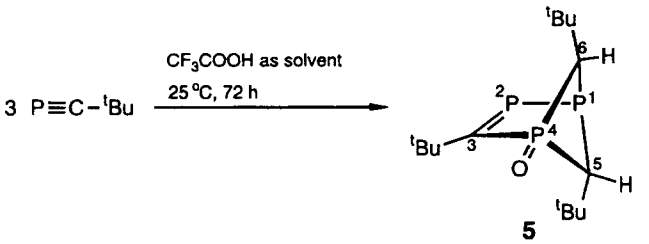
SCHEME 2



5

SCHEME 3

In accord with the proposed structure of **5**, the $^{31}P\{^1H\}$ NMR spectrum reveals three signals with completely different chemical shifts. Thus, the presence of the phosphaalkene unit is confirmed by a low-field signal at $\delta = +282.9$ for P2 [15]. The signal for P4 appears at $\delta = +45.6$ in the region typical for cyclic phosphane oxides [16] while the remaining bridgehead heteroatom P1 experiences a strong deshielding and gives rise to a signal at $\delta = -142.2$.

The ^1H NMR spectrum of **5** contains merely two signals for the three *tert*-butyl groups; the singlet signal at $\delta = 0.94$ can be assigned to the two *tert*-butyl groups in the diphosphetane ring, which must have a *cis* orientation to each other to account for their magnetic equivalence. The signal for the *tert*-butyl group of the phosphaalkene unit appears as a doublet at $\delta = 1.51$ with a $^4J(H,P2)$ coupling of 1.8 Hz. Characteristic for **5** is the signal for the two magnetically equivalent, skeletal protons of the diphosphetane element; they give rise to a double doublet of doublets at $\delta = 2.44$. The signal splittings result solely from couplings with the three phosphorus atoms [$^2J(H,P4) = 10.7$ Hz, $^2J(H,P1) = 8.7$ Hz, and $^3J(H,P2) = 3.6$ Hz], as has been verified by selective heteronuclear decoupling experiments [$^1H\{^{31}P\}$ NMR spectroscopy].

In agreement with the magnetic equivalence of the two CH*t*Bu fragments of the diphosphetane system, the $^{13}C\{^1H\}$ NMR spectrum of **5** contains only six carbon signals. The four signals at highest field are all assigned to the three *tert*-butyl groups. The signals of the carbon atoms in the triphosphabicyclohexene skeleton are of high diagnostic value. As expected, the phosphaalkene carbon atom C3 gives rise to the double doublet signal at lowest field ($\delta = 206.0$) with typical $^1J(C,P)$ coupling constants [15] of 71.8 and 53.0 Hz. The two methine carbon atoms produce a signal at $\delta = 79.0$ that exhibits typical couplings with the three heteroatoms of the skeleton. The additional doubling of this signal with a coupling constant of 127 Hz in the proton-coupled ^{13}C NMR spectrum irrevocably demonstrates the immediate neighborhood of each of these two carbon atoms to a proton.

Finally confirmation of the structure of **5** was provided by a crystal structure analysis. Figure 1 shows a representation of **5** using thermal ellipses [17]. Bond lengths and angles are listed in Table 1 and the atomic coordinates are given in Table 2.

The P2/C3 bond length of 1.650(3) Å is within the typical range for P/C double bonds [18]. The P1/P2 bond length of 2.259(1) Å is longer than the average of the reported values [19] whereas the P4/O1 length of 1.461(2) Å is relatively short [19]. The P/C

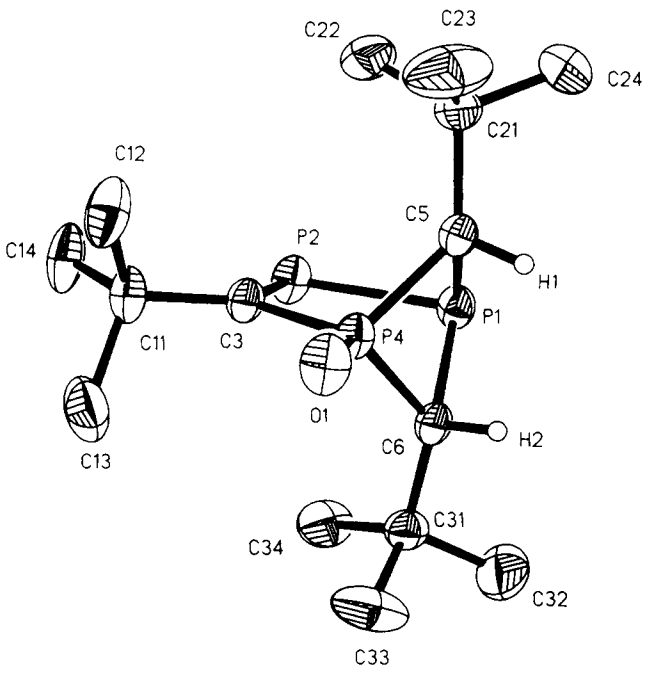


FIGURE 1 X-ray structure of **5**. The hydrogens of the tert-butyl groups are omitted for clarity.

bond lengths within the diphosphetane structural unit differ markedly: thus, the bonds of the carbon atoms C5 and C6 to the $\lambda^5\sigma^4$-phosphorus atom P4 with lengths of 1.817(4) Å are decidedly shorter than those to the $\lambda^3\sigma^3$-phosphorus atom P1 [1.861(3) and 1.874(4) Å]. Even so, the measured values are still within the expected range for P/C single bonds of this type [19]. The crystal structure analysis further reveals that all phosphorus atoms and the oxygen atom, as well as the carbon atoms C3 and C11, all lie in an idealized plane with a maximum deviation of 0.017 Å. The triangular surface (P1,P4,C5) lies at an angle of 114.9° to this plane. The folding angle of the diphosphetane unit [angle between the two triangular planes (P1,P4,C5) and (P1,P4,C6)] is relatively small with 129.7°. From the crystal structure analysis it can further be seen that the two *cis*-orientated and practically eclipsed *tert*-butyl groups occupy *endo* positions within the bicyclic skeleton. The latter presumably effect a steric shielding of the P/C double bond in the molecule that, in turn, would provide an explanation for the high stability of compound **5**.

Questions concerning the mechanism of formation of **5** as well as the origin of the incorporated water cannot yet be conclusively answered; however, a plausible rationale can be given (Scheme 4). In analogy to the aluminum chloride-initiated spirocyclotrimerization **1** → **2** [9], the initial step of the cyclotrimerization should be the *C* protonation of the phosphaalkyne (→ **6**), which is then followed (if necessary after anion addition) by a [2 + 2] as well

TABLE 1 Bond Distances Å² and Bond Angles (°) for **5**

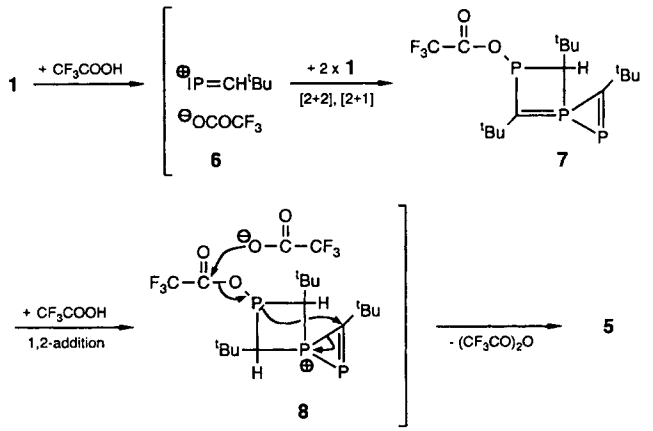
Bond Distance[a]		*Bond Angle*[a]	
P4–O1	1.461(2)	O1–P4–C3	116.8(2)
P4–C3	1.815(3)	O1–P4–C5	123.3(2)
P4–C5	1.817(4)	C3–P4–C5	101.8(2)
P4–C6	1.817(4)	O1–P4–C6	123.0(2)
P4–P1	2.543(1)	C3–P4–C6	102.4(2)
P2–C3	1.650(3)	C5–P4–C6	83.2(2)
P2–P1	2.259(1)	O1–P4–P1	161.61(11)
P1–C6	1.861(3)	C3–P4–P1	81.62(11)
P1–C5	1.874(4)	C5–P4–P1	47.39(11)
C3–C11	1.509(5)	C6–P4–P1	46.98(11)
C6–C31	1.512(5)	C3–P2–P1	94.54(12)
C21–C23	1.503(6)	C6–P1–C5	80.5(2)
C21–C5	1.511(5)	C6–P1–P2	94.78(12)
C21–C24	1.510(7)	C5–P1–P2	94.67(12)
C12–C22	1.512(5)	C6–P1–P4	45.53(11)
C31–C34	1.506(5)	C5–P1–P4	45.51(11)
C31–C32	1.512(6)	P2–P1–P4	72.79(4)
C31–C33	1.516(6)	C11–C3–P2	127.2(2)
C12–C11	1.511(6)	C11–C3–P4	121.8(2)
C13–C11	1.524(6)	P2–C3–P4	111.0(2)
C11–C14	1.523(5)	C31–C6–P4	128.7(3)
C5–H1	0.93(3)	C31–C6–P1	124.3(2)
C6–H2	0.92(3)	P4–C6–P1	87.5(2)
		C23–C21–C5	107.9(4)
		C23–C21–C24	110.7(4)
		C5–C21–C24	107.7(4)
		C23–C21–C22	107.6(4)
		C5–C21–C22	115.1(3)
		H1–C5–C6	80.2(20)
		H2–C6–C5	81.5(18)

[a]Numbers in parentheses are estimated standard deviations.

TABLE 2 Atomic Coordinates and Equivalent Isotropic Displacement Parameters Å² for **5**

Atom	*x*[a]	*y*[a]	*z*[a]	*U(eq)*[a]
P4	0.2203(1)	0.0342(1)	0.6745(1)	0.042(1)
P2	0.1725(1)	0.0297(1)	0.5387(1)	0.052(1)
P1	0.1935(1)	0.2447(1)	0.5940(1)	0.048(1)
O1	0.2414(2)	−0.0465(3)	0.7347(1)	0.060(1)
C3	0.1934(2)	−0.0768(4)	0.6025(1)	0.045(1)
C6	0.2779(2)	0.1767(4)	0.6567(2)	0.044(1)
C21	0.0686(2)	0.1680(5)	0.6422(2)	0.060(1)
C31	0.3527(2)	0.1603(4)	0.6481(2)	0.054(1)
C5	0.1508(2)	0.1800(4)	0.6542(2)	0.047(1)
C12	0.1437(3)	−0.2981(5)	0.6417(2)	0.082(1)
C33	0.4019(2)	0.0701(7)	0.7032(2)	0.102(2)
C34	0.3520(2)	0.0837(6)	0.5877(2)	0.081(1)
C32	0.3839(3)	0.3144(6)	0.6475(3)	0.108(2)
C23	0.0575(3)	0.0973(8)	0.6996(2)	0.119(2)
C22	0.0267(2)	0.0760(6)	0.5850(2)	0.082(1)
C13	0.2702(3)	−0.3037(5)	0.6363(2)	0.090(2)
C11	0.1922(2)	−0.2442(4)	0.6045(2)	0.056(1)
C14	0.1625(3)	−0.3077(5)	0.5375(2)	0.085(2)
C24	0.0370(3)	0.3233(6)	0.6325(3)	0.120(2)
H1	0.1708(18)	0.2487(38)	0.6860(15)	0.046(9)
H2	0.2827(16)	0.2427(33)	0.6892(14)	0.031(8)

[a]Numbers in parentheses are estimated standard deviations.



SCHEME 4

as a [2 + 1] cycloaddition step to give 7, as described for the formation of 2 [9].

C protonation of 7 by a second equivalent of trifluoroacetic acid is then responsible for the intermediate formation of 8 as starting point for the last step of the sequence: [1,3] rearrangement commencing at the diphosphirane increment and take-up of a trifluoroacetyl group by the trifluoroacetate anion to give trifluoroacetic anhydride then complete the sequence (→ 5). The water incorporated in the product thus most probably originates from the trifluoroacetic acid and is not the result of insufficient care during the preparative work [20]. In the latter case, a saturation of the reactive intermediates would have to be expected before cyclotrimerization of 1 could take place.

CONCLUSIONS

Trifluoroacetic acid is able to effect the cyclotrimerization of the phosphaalkyne 1 (albeit with incorporation of water into the product). A delineation of the scope of application of protic acid-induced cyclotrimerization reactions for the construction of polycyclic carbon-phosphorus compounds remains to be undertaken.

EXPERIMENTAL

All procedures were performed in glass apparatus previously baked out in an argon atmosphere. The anhydrous solvents were distilled and stored under argon prior to use. Trifluoroacetic acid was purified by distillation. The bulb-to-bulb distillations were carried out in a Büchi GKR 50 apparatus; the temperatures stated are oven temperatures. The melting point was determined with a Mettler FP 61 apparatus (heating rate 2°C/min) and is uncorrected. The IR spectrum was taken on a Perkin-Elmer 881 infrared spectrometer and the mass spectra were measured on a Finnigan MAT 90 at an ionization potential of 70 eV. The microanalyses were performed with a Perkin-Elmer Analyser 240. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AMX 400 spectrometer (operating at 400.13, 100.64, and 161.98 MHz, respectively) using TMS as internal standard (^{1}H and ^{13}C) or 85% orthophosphoric acid as external standard (^{31}P).

3,5,6-Tri-tert-butyl-1,2,4-triphosphabicyclo[2.1.1]hex-2-ene 4 Oxide (5)

A solution of 0.80 g (8.0 mmol) of 1 [21] in 4 mL trifluoroacetic acid was stirred for 72 hours in a Schlenk pressure tube. After evaporation of the excess acid at 30°C / $5 \cdot 10^{-3}$ hPa, the yellow, oily residue was distilled in a bulb-to-bulb distillation apparatus. The fraction collected at 150–180°C / $5 \cdot 10^{-3}$ hPa, a pale yellow, partly crystalline, partly oily, residue, was chromatographed on silica gel with diethyl ether. A second column chromatography under the same conditions and subsequent recrystallization from diethyl ether furnished 0.15 g (18%) of analytically pure 5 as nearly colorless needles; mp 184°C.

IR (KBr) ν = 2977 (s), 2960 (vs), 2897 (s), 2862 (s), 1470 (s), 1393 (m), 1364 (s), 1343 (m), 1302 (w), 1243 (s), 1218 (vs), 1194 (vs), 1177 (vs), 1101 (m), 1063 (m), 1029 (m), 1016 (m), 931 (m), 809 (m), 796 (m), 734 (m), 702 (m) cm^{-1}; $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ = −142.2 (d, $^{1}J(P,P)$ = 167.9 Hz, P1), +45.6 (d, $^{2}J(P,P)$ = 30.5 Hz, P4), +282.9 (dd, $^{1}J(P,P)$ = 167.9 Hz, $^{2}J(P,P)$ = 30.5 Hz, P2); ^{1}H NMR (C_6D_6) δ = 0.94 (s, 18H, C5/C6–C(CH_3)$_3$), 1.51 (d, $^{4}J(H,P2)$ = 1.8 Hz, 9H, C3–C(CH_3)$_3$), 2.44 (ddd, $^{2}J(H,P4)$ = 10.7 Hz, $^{2}J(H,P1)$ = 8.7 Hz and $^{3}J(H,P2)$ = 3.6 Hz, 2H, C*H*tBu); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ = 30.4 (dd, $^{3}J(C,P)$ = 11.7 Hz, $^{3}J(C,P)$ = 3.6 Hz, C3–C(CH_3)$_3$), 33.4 (d, $^{3}J(C,P)$ = 7.2 Hz, C5/C6–C(CH_3)$_3$), 34.1 (dd, $^{2}J(C,P)$ = 4.5 Hz, $^{2}J(C,P)$ = 2.7 Hz, C5/C6–C(CH_3)$_3$), 43.2 (ddd, $^{2}J(C,P)$ = 12.4 Hz, $^{2}J(C,P)$ = 7.6 Hz, $^{3}J(C,P)$ = 2.2 Hz, C3–C(CH_3)$_3$), 79.0 (ddd, $^{1}J(C,P)$ = 45.8 Hz, $^{1}J(C,P)$ = 34.1 Hz, $^{2}J(C,P)$ = 3.6 Hz, C5/C6), 206.0 (dd, $^{1}J(C,P)$ = 71.8 Hz, $^{1}J(C,P)$ = 53.0 Hz, C3); EI MS *m/z* (%) = 318 (100, M^+), 303 (60, $M^+ - CH_3$), 261 (90), 247 (25), 217 (51), 192 (30), 175 (16), 131 (73), 117 (11), 85 (16), 69 (12), 57 (39), 41 (26); HR MS *m/z* calcd. for $C_{15}H_{29}OP_3$, 318.1431; found, 318.1427; anal. calcd.: C, 56.60; H, 9.18; found: C, 57.0; H, 9.0.

Crystal Structure Analysis of 5 *[22]*

Crystal Data. $C_{15}H_{29}OP_3$, M = 318.29 g · mol^{-1}, crystal dimensions 0.3 × 0.25 × 0.3 mm, a = 19.124(4), b = 9.004(2), c = 22.263(4) Å, β = 108.98(3)°, space group C2/c (Int. Tab. No. 15), V = 3625.1(13) Å^3, Z = 8, d_{calc} = 1.166 g · cm^{-3}, μ = 3.21 cm^{-1}.

Data Collection. Data were collected using an automatic four-circle diffractometer (Siemens P4,

Mo-Kα radiation, graphite monochromator). Exact lattice constants were determined from the least-squares refinement of the 2 Θ values of 30 reflections.

Structure Solution and Refinement. Structure solution and refinement were performed by direct methods (SHELXS-86 [23]) and by full-matrix least-squares on F^2 (SHELXL-93 [24]), respectively. Graphical presentation of the molecule was achieved with SHELXTL-Plus [17]. A total of 4002 reflections were measured in the range $1.93° \leq \Theta \leq 24.99°$, of which 3200 with $I \geq 2\sigma_{(I)}$ were considered in the refinement. The number of parameters was 180. The positions of the H atoms of the three *tert*-butyl groups were calculated geometrically with group-wise common temperature factors. The structure refinement converged at R1 = 0.0517 and wR2 = 0.1234; the difference Fourier synthesis on the basis of the final structural model showed a maximum of 0.300 e · Å^{-3} and a minimum of −0.241 e · Å^{-3}, and the goodness-of-fit was 1.045.

ACKNOWLEDGMENTS

We are grateful to the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Phosphor als Bindeglied verschiedener chemischer Disziplinen") and the Fonds der Chemischen Industrie for generous financial support of our work. T. W. Mackewitz is indebted to the Fonds der Chemischen Industrie for a postgraduate grant.

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[20] This statement is further confirmed by the following fact: When trifluoroacetic acid is replaced by tetrafluoroboric acid in diethyl ether or fluorosulfuric acid in dichloromethane, no cyclotrimerization of **1** could be detected.

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