Table II. Comparison of S···S Distances, E-S···S Angle, and Ring Conformation in Derivatives of 1,5-Dithiacyclooctane

compound	S···S, Å	ring conformation	E-S···S, deg	ref
1-acetonyl-1-thionia-5-thiacyclooctane perchlorate	3.121 (5)	boat-chair	178.9 (5)	*a*
1-methyl-1-thionia-5-thiacyclooctane iodide	3.258 (7)	chair-chair	174.0 (1)	*b*
trans-$SnCl_4(1,5\text{-DTCO})_2$	3.271 (3)	boat-chair	171.5 (1)	*c*
catena-$Ni(1,5\text{-DTCO})_2Cl_2$	3.335 (3)	disordered: boat-chair/chair-chair	164.0 (1) 166.1 (1)	*d*
1,5-DTCO·$2I_2$ (two molecules in the asymmetric unit)	I: 3.443 (8)	I: chair-chair	I: 166.3 (5) 171.3 (5)	*e*
	II: 3.227 (8)	II: boat-chair	II: 173.3 (5) 177.2 (5)	
1,5-dithiacyclooctane-3,7-dione ethylenediketal	3.576 (1)	twist-chair		*f*

[a] Johnson, S. M.; Maier, C. A.; Paul, I. C. *J. Chem. Soc. B* **1970**, 1603-1608. [b] Olmstead, M. M., unpublished results. $S_2C_7H_{15}{}^+I^-$ crystallizes in the orthohombic space group $P2_12_12_1$ with $a = 6.736$ (3) Å, $b = 12.287$ (5) Å, $c = 13.046$ (4) Å. $R = 0.030$ for 46 least-squares parameters and 1438 unique observed reflections. Full details of this structure to be published. [c] This work. [d] Hill, N. L.; Hope, H. *Inorg. Chem.* **1974**, *13*, 2079-2082. [e] Nichols, B. G. Ph.D. Dissertation, University of California, Davis, A, 1981. [f] Olmstead, M. M.; Musker, W. K. *Acta Crystallogr., Sect. B* **1981**, *B37*, 261-263.

required to possess a center of symmetry. The coordination about tin is pseudooctahedral, with the four chlorine atoms in a square plane and two monodentate dithioether ligands above and below this plane (Figure 1). An angle of 9.1° is formed between the normal to the $SnCl_4$ plane and the SnS line. The conformation of the eight-membered dithioether ring is boat-chair (Figure 2). There is a transannular contact of 3.271 (3) Å between the two sulfur atoms. The important bond distances and angles are given in Table I. A comparison of the S···S distance to those found in other derivatives of 1,5-dithiacyclooctane is given in Table II.

The photoelectron spectrum of free 1,5-DTCO[7] shows a large splitting of the sulfur-sulfur lone-pair orbitals of 0.43 eV. This observation suggests that the two sulfur lone-pair orbitals must point toward each other to achieve such a large amount of mixing in the gas phase. On the basis of the photoelectron spectrum of 1,5-DTCO and molecular mechanics calculations, the boat-chair conformation has been predicted to be its most stable conformation.[7] Although the crystal structure determination of 1,5-DTCO itself has not been carried out, it can be seen from the compounds listed in Table II that the boat-chair conformation is the most common, and the chair-chair conformation is probably very similar to it in energy. In all of the boat-chair and chair-chair structures, the two sulfur atoms occupy identical 1,5-positions with respect to the ring conformation. In these positions the overlap between sulfur lone-pair orbitals is greater than it would be in the other possible transannular arrangements, in agreement with the large degree of mixing that is indicated by the photoelectron spectrum of 1,5-DTCO itself. It is tempting to conclude that, as positive charge is induced on the sulfur bound to tin, the interaction to the remote sulfur is strengthened. This effect is also thought to be operative in the anchimerically assisted iodine oxidation of thioethers, in which iodine bonds to a thioether sulfur and imparts to it a partial positive charge. The positively charged sulfur atom can then act as an electrophile toward the remote donors OH, NH_2, NHR, or R_2S.[8]

Additional evidence for a long-range intramolecular interaction is found in the angles E-S···S, where E is a substituent on sulfur. As can be seen from the angles tabulated in Table II, the shorter the S···S distance, the closer the E-S···S angle is to 180°. It is possible that theoretical calculations would show that this trend results from the presence of extended σ molecular orbitals over the systems I-I-S···S-I-I, S···S-Sn-S···S, (-Ni-S···S-Ni-S···S-), as well as three-center four-electron bonds in the $R\text{-}S^+\cdots S$ compounds.

Ligands having nitrogen or oxygen donors do not have the nominal capacity for accommodating more than eight electrons and therefore will be unable to function as mediators between a remote donor and a metal atom. Thus, only elements of the second row and higher can be expected to fulfill this role.

It has been proposed that in proteins a methionine sulfur can serve as mediator of electron transfer between a metal atom and remote electron pairs.[9] This structural evidence shows that such mediation may be present in the ground state of the molecule.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for support of this research.

Registry No. *trans*-$SnCl_4(1,5\text{-DTCO})_2$, 82917-92-8.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and a listing of structure factor amplitudes for *trans*-$SnCl_4(C_6S_2H_{12})_2$ (13 pages). Ordering information is given on any current masthead page.

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Total Synthesis of Hibiscone C (Gmelofuran)

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Since the classic work by Eaton,[2] Corey,[3] and de Mayo,[4] the photochemical [2 + 2] cycloaddition of α,β-unsaturated carbonyl compounds to olefins has evolved as a significant and powerful synthetic tool for construction of a carbon framework.[5] In recent years the intramolecular version of this reaction has seen increasing popularity in natural product synthesis.[6] Surprisingly, however, a search of the literature revealed *no examples* of the intramolecular [2 + 2] photocycloaddition of enones to acetylenic moieties. In this communication we disclose the *first examples* of such a process as well as exploitation of this methodology as cornerstone for the *first* total synthesis of hibiscone C (gmelofuran), **1** (eq 1), a structurally novel furanosesquiterpenoid isolated from the

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(1) Camille and Henry Dreyfus Teacher-Scholar, 1978-1983; National Institute of Health (National Cancer Institute) Career Development Awardee, 1980-1985.

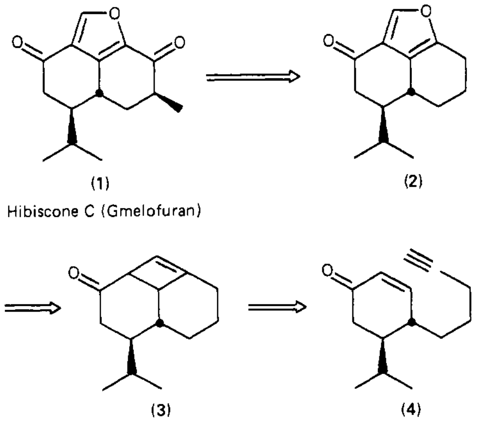
(2) Eaton, P. E. *J. Am. Chem. Soc.* **1962**, *84*, 2454. Also see: Eaton, P. E. *Tetrahedron Lett.* **1964**, 3695.

(3) Corey, E. J.; Mitra, R. B.; Uda, H. *J. Am. Chem. Soc.* **1964**, *86*, 485. Corey, E. J.; Nozoe, S. *Ibid.* **1964**, *86*, 1652.

(4) de Mayo, P.; Takeshita, H.; Sattar, A. B. M. A. *Proc. Chem. Soc.* **1962**, 119. de Mayo, P.; Takeshita, H. *Can. J. Chem.* **1963**, *41*, 440.

(5) For a recent review of the synthetic aspects of [2 + 2] photoaddition reaction of α,β enone, see: Baldwin, S. W., Padwa, A., Eds. "Organic Photochemistry"; Marcel Dekker, 1981; Vol. 5, 123.

(6) Oppolzer, W. *Acc. Chem. Res.*, in press.

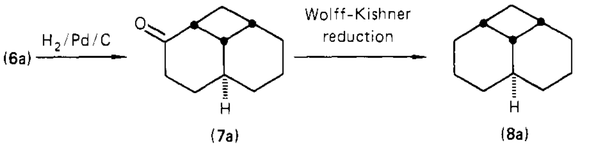


(1)

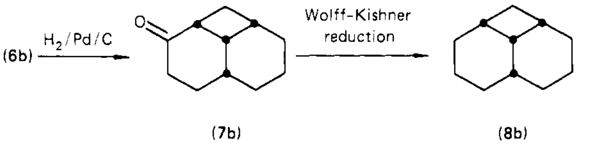
heart wood of *Hibiscus elatus* (Blue Mahoe), the national tree of Jamaica.[7]

From the retrosynthetic perspective, tricyclic ketone **3** appeared to be an ideal advanced synthetic intermediate in that the cyclobutene ring could serve as a latent furan. That is, oxidative cleavage of the olefinic linkage followed by dehydration would afford the requisite furan (**2**). Subsequent introduction of a carbonyl group at C(7) and an axial methyl at C(6) would then complete the synthesis. Such a scenario, of course, depends critically on the viability of the proposed intramolecular [2 + 2] photocycloaddition. To ensure the feasibility of this process, we completed the model study illustrated in Scheme I.

Enone **5**, substrate for the proposed model study, was readily available via the method of Stork.[9] Alkylation of the kinetic enolate of 3-ethoxy-2-cyclohexenone[10] (1.1 equiv, LDA/THF, −78 °C) with 1-iodo-4-pentyne[11] (1.5 equiv, HMPA/THF, −40 → 25 °C) followed by reduction ($LiAlH_4/Et_2O$, 25 °C) and hydrolysis (2 N HCl) gave **5**[12a] in 60% overall yield after purification by column chromatography (silica, ethyl acetate/hexane, 1:10). Subsequent irradiation[13] for 16 h produced a 2:1 mixture of **6a**[12] and **6b**[12] in a combined yield of 55%. After separation by MPLC [silica, hexane/ethyl acetate (20:1)], definition of the skeletal framework was secured via conversion of **6a** and **6b**, respectively, to hydrocarbons **8a**[12a] and **8b**[12a] [i.e., hydrogenation (Pd) followed by Wolff–Kishner reduction; eq 2 and 3].[14] In each case the fully decoupled ^{13}C NMR spectra revealed seven lines, consistent with

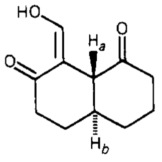


(2)

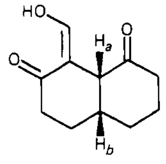


(3)

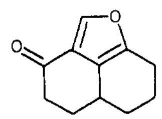
the highly symmetrical tricyclo[5.3.1.$0^{3,11}$] undecane skeleton.[15] Stereochemical assignments, on the other hand, rest on the following observations. Individual ozonolysis of **6a** and **6b** followed by reduction [(a) O_3/CH_2Cl_2, −78 °C; (b) Me_2S, −78 → 25 °C] afforded **9a**[12a] (mp 76–77 °C) and **9b**,[12a] respectively. Analysis



(9a)



(9b)



(10)

of the high-field ^1H NMR spectra of **9a** revealed J_{ab} to be 9.4 Hz, while this value in **9b** was 5.6 Hz. Such coupling constants[16] are consistent, respectively, with the assigned trans and cis ring fusion of **9a** and **9b** and in turn allow stereochemical assignment of **6a** and **6b**. Finally, and of considerable significance for the proposed synthesis of hibiscone C, brief acid treatment of **9a** or **9b** (*p*-TsOH/benzene, 80 °C) afforded a mixture of **9a** and **9b** along with furan **10**,[12a] while prolonged acid treatment with water removal (Dean–Stark) led to **10** in 64% yield, the latter at the expense of **9a** and **9b**.

With the photochemical cyclization of **4** now assured, we turned to the synthesis of hibiscone C (**1**). By employment of procedures identical with those used for the preparation of **10**, 5-isopropyl-3-ethoxy-2-cyclohexenone[17] was converted to **4** in 60% yield. Photolysis then gave a 1.5:1 mixture of **11a**[12] (mp 63–64 °C) and **11b**[12] (60%; see Chart I). Stereochemical assignments here were tentatively made via comparison of the high-field ^1H NMR spectra to those of **6a** and **6b**. Subsequent ozonolysis followed by reduction led to **12**,[12] again as a mixture of epimers. Finally, cyclization–dehydration afforded the desired advanced intermediate **2**[12] in 50% yield.

At this point all that remained to complete a synthesis of hibiscone C was oxygenation at C(7) and axial methylation of C(6). In pursuit of this goal, **2** was exposed to *N*-bromosuccimide (1.1 equiv, CCl_4/THF, *hν*, 25 °C)[18] followed by aqueous workup to afford **13a**[12a] in modest (ca. 40%) albeit useful yield. Collins oxidation[19] then gave **13b**.[12a] This dione (**13b**) was also available from **2** via direct allylic oxidation ($CrO_3 \cdot 2py/CH_2Cl_2$, 25 °C);[20] the yield, however, was only 20%. Finally, ketalization of **13b** [ethylene glycol/*p*-TsOH/benzene/$-H_2O$] afforded monoketal **14**[12a] in 45% yield after chromatography [silica, hexane/ethyl acetate (1:1)], the remainder of the product mixture consisted of starting material along with the diketal and undesired monoketal.[21a] Hydrolysis of the latter two (10% aqueous HCl/THF,

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(7) Gmelofuran (**1**), isolated from the roots of *Gmelina Aborea* in 1978, was shown by Thomson et al.[8] to be identical with hibiscone C; see: Joshi, K. C.; Singh, P.; Pardasani, R. T.; Pelter, A.; Ward, R. S.; Reinhardt, R. *Tetrahedron Lett.* **1978**, 4719.

(8) Hibiscone C (Gmelofuran) was isolated in 1980 from the heartwood of *Hibiscus elatus* (Blue Mahoe), the national tree of Jamaica; see: Thomson, R. H.; Ali, S.; King, T. J.; Ferreira, M. A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 249.

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(12) (a) All new compounds gave 250-MHz ^1H NMR, IR, and high-resolution mass spectra in accord with the structures given. (b) This compound also gave satisfactory C, H combustion analysis. **6a**: IR (CCl_4) 3050 (w), 2940 (s), 1710 (s), 900 (m) cm^{-1}; 250-MHz ^1H NMR ($CDCl_3$) δ 1.04–1.30 (m, 2 H), 1.48–1.7 (m, 2 H), 1.88–2.1 (m, 4 H), 2.16–2.46 (m, 3 H), 2.58–2.72 (m, 1 H), 3.52 (t, *J* = 3.4 Hz, 1 H), 5.58 (s, 1 H). **6b**: IR (CCl_4) 3050 (w), 2940 (s), 1710 (s), 900 (m) cm^{-1}; 250-MHz ^1H NMR ($CDCl_3$) δ 1.4–1.8 (m, 4 H), 2.0–2.3 (m, 6 H), 2.6 (d, *J* = 14 Hz, 1 H), 3.0 (br s, 1 H), 3.35 (m, 1 H), 5.54 (s, 1 H). **9a**: IR ($CHCl_3$) 3100–2800 (s), 1710 (s) 1625–1575 (s), 1300 (m), 750 (w) cm^{-1}; 250-MHz ^1H NMR ($CDCl_3$) δ 1.52–2.6 (m, 11 H), 3.26 (d, *J* = 9.36 Hz, 1 H), 8.84 (d, *J* = 2.3 Hz, 1 H), (enolic proton not observed). **9b**: IR ($CHCl_3$) 3100–2800 (s), 1710 (s), 1625–1575 (s), 1300 (m), 750 (w) cm^{-1}; 250-MHz ^1H NMR ($CDCl_3$) δ 1.1–2.56 (m, 11 H), 3.37 (d, *J* = 5.8 Hz, 1 H), 8.6 (d, *J* = 2.3 Hz, 1 H), (enolic proton not observed). **2**: IR (CCl_4) 2960 (s), 2850 (m), 1690 (s), 1120 (m) cm^{-1}; 250-MHz ^1H NMR ($CDCl_3$) δ 0.94 (d, *J* = 7 Hz, 3 H), 1.06 (d, *J* = 7 Hz, 3 H), 1.66–2.0 (m, 3 H), 2.04–2.36 (m, 4 H), 7.82 (s, 1 H).

(13) Irradiations were carried out in hexane (ca. 4 mg/mL of enone employing the standard Hanovia 450-W medium-pressure Hg arc fitted with a uranium glass filter to prevent secondary photochemical decomposition of the derived β,γ-unsaturated ketones).

(14) Huang-Minlon, *J. Am. Chem. Soc.* **1946**, *68*, 2487.

(15) The high-field (62.9 MHz) ^{13}C NMR spectra of **8a** and **8b** were as follows: (8a) δ ($CDCl_3$) 22.1 nt), 25.5 (t), 27.3 (t), 29.5 (d), 31.6 (d), 35.3 (t), 38.6 (d); (8b) δ ($CDCl_3$) 19.8 (t), 26.9 (t), 28.9 (t), 29.2 (d), 31.2 (d), 33.2 (d), 35.4 (t).

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(18) For a discussion of allylic oxidations of furans, see: Dean, F. M. *Adv. Heterocycl. Chem.* **1982**, *30*, 167.

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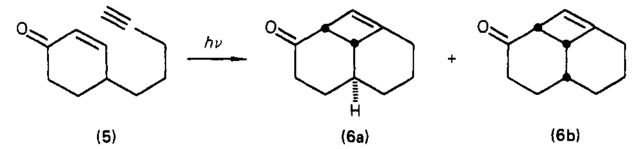
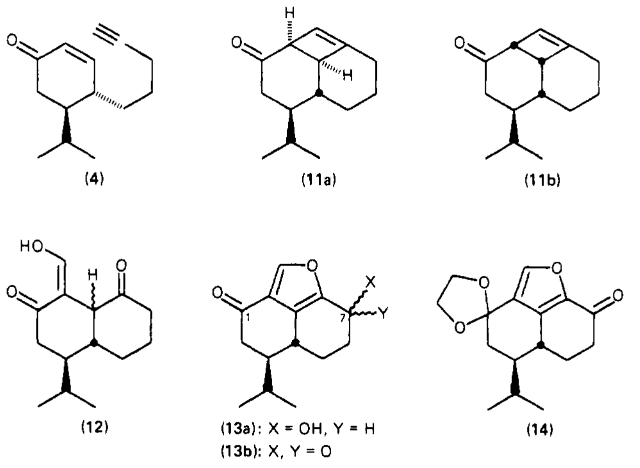
(20) Fullerton, D. S.; Chen, C.-M. *Synth. Commun.* **1976**, *6*, 217.

Scheme I



(5) (6a) (6b)

Chart I



(4) (11a) (11b)

(12) (13a): X = OH, Y = H
(13b): X, Y = O (14)

25 °C, 1 h) regenerated **13b**, which could be recycled.[21b]

From the outset our strategy for hibiscone C called for introduction of an axial C(6)-methyl substituent as the penultimate step. Our confidence that in fact the axial configuration would obtain derived from examination of molecular models of the enolate of **14**. In particular, axial approach of an electrophile to the α or undesired face of this enolate results in considerable tortional strain of the furan–C(7)-carbonyl π system during product development. In contrast, axial approach to the desired β face permits maintenance of a high degree of overlap throughout the bond forming process.

In practice, deprotonation of **14** [$\mathrm{LiN(Me_3Si)_2}$/THF, −50 °C] followed by addition of excess methyl iodide and acidic hydrolysis (10% HCl/THF, 25 °C, 1 h) afforded racemic hibiscone C in 64% yield, accompanied by less than 7% of the equatorial methyl epimer. That indeed hibiscone C was in hand derived from careful spectral (e.g., NMR, IR, MS, and UV) and TLC comparisons to authentic material kindly provided by Professor Thomson.[22]

In summation, the first total synthesis of hibiscone C has been achieved. Central to the successful strategy was the intramolecular [2 + 2] photocycloaddition of an enone (i.e., **4**) to an acetylenic bond. Studies to explore and extend the utility of this process are under active investigation in our laboratory and will be reported in due course.

Acknowledgment. It is a pleasure to acknowledge the support of this investigation by the National Institutes of Health (National Cancer Institute) through Grant No. 22807. In addition, we thank S. T. Bella of the Rockefeller University for the microanalyses and Drs. G. Furst and T. Terwilliger of the University of Pennsylvania Spectroscopic Facilities for aid in obtaining the high-field NMR and MS spectral data, respectively.

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(21) (a) That in fact the major product was the desired monoketal **14** was deduced from the NMR spectral data. In particular, ketalization of the C(1)-carbonyl of **2** results in a 0.46-ppm upfield shift of the furan hydrogen (δ 7.82 to 7.36). A similar effect upon ketalization of **13b** to give **14** would lead to a predicted value of δ 7.64 for the same hydrogen. In the event the observed value was δ 7.56. In the case of the C(7)-monoketal the resonance for the furan hydrogen would not be expected to undergo a significant shift from the δ 7.82 value. (b) In our initial approach to **14**, we attempted to oxidize the C(7) position of the ketal of **2** via both the NBS/hydrolysis and the $\mathrm{CrO_3\cdot 2py}$ sequences. These procedures resulted in the loss of the ketal functionality.

(22) We thank Professor R. H. Thomson of the University of Aberdeen for providing us with a generous sample of hibiscone C as well as copies of the spectral data (i.e., ^{1}H and IR).

Electron-Transfer Mechanism for a Hydride-Transfer Reaction: Evidence for Selective α-Hydride Abstraction from a Transition-Metal Alkyl

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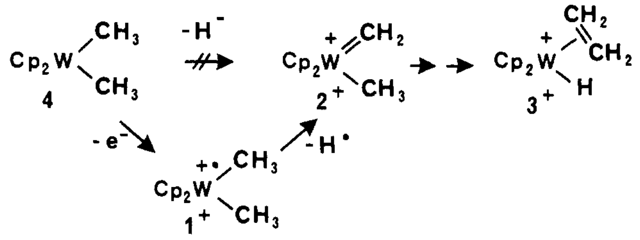
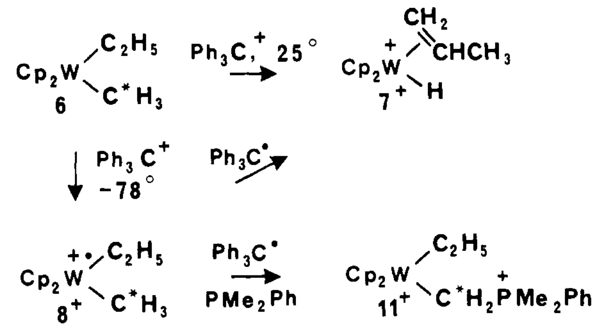
Received December 7, 1981

It has been demonstrated that transfers of alkyl anions and hydride ions from main-group organometallics and from both simple and complex hydrides to organic substrates can occur by mechanisms involving initial electron-transfer steps,[1] and there is growing interest in the general importance of electron-transfer mechanisms in reactions of organometallics.[2] We report the first examples in which hydride transfers from transition-metal alkyls to hydride acceptors occur by a two-step electron-transfer/radical-transfer mechanism and evidence suggesting that this pathway is associated with an α regioselectivity that contrasts dramatically with the normal β regioselectivity for hydride transfers from transition-metal alkyls.

Scheme I. Formation of $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{C_2H_4})\mathrm{H}]^+$ from $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_3})_2]$ (Cp = η-$\mathrm{C_5H_5}$)



Scheme II. Reactions of $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_3})(\mathrm{C_2H_5})]$ (Cp = η-$\mathrm{C_5H_5}$, *H = H or D)



[†] Fellow of the Alfred P. Sloan Foundation, 1982–1984.

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