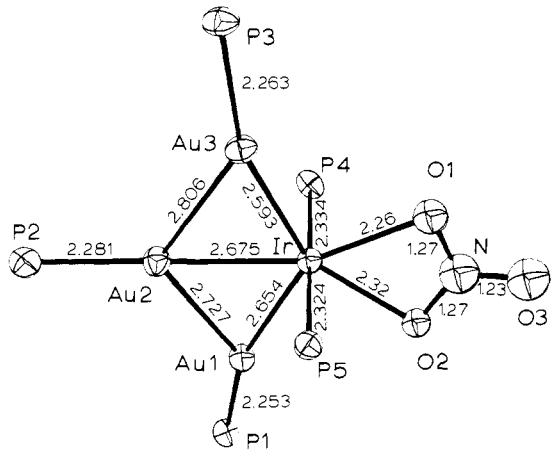

Figure 2. ORTEP drawing of the core of cation **4**. Selected angles (deg) where the numbers refer to respective Au atoms are: 1-2-3, 115.24 (3); 2-1-Ir, 59.60 (3); 2-3-Ir, 59.24 (3); 1-Ir-3, 125.90 (3); 2-1-P1, 138.0 (1); 2-3-P3, 140.1 (1); Ir-1-P1, 161.8 (1); Ir-3-P3, 160.5 (1); 1-2-P2, 122.2 (1); 3-2-P2, 122.6 (1); P4-Ir-P5, 176.6 (2); O1-Ir-O2, 57.4 (4). Phenyl carbon atoms have been omitted for clarity.

(**5**). The structure of **5** is confirmed by ^{31}P and ^{1}H NMR.[13] Complex **3** is originally isolated as the nitrate because $Au(NO_3)PPh_3$ undergoes ligand exchange with **5** to yield $[Au(PPh_3)_2]^+$ and **3**.

The ^{1}H NMR spectrum of complex **4** shows no resonances in the hydride region and the $^{31}P\{^{1}H\}$ NMR spectrum consists of three resonances with relative intensities of 1:2:2 [(CH_2Cl_2) δ 42.0, P2, (t, J = 9.5 Hz) intensity = 1; 13.7 (mult) intensity = 2; -4.43 (t, J = 7.5 Hz) intensity = 2]. The assignment of the resonances at 13.7 and -4.43 ppm is, at present, unknown. This spectrum is consistent with the structure shown in Figure 2. NMR monitoring of the reaction mixture shows the presence of several additional species. Efforts are under way to crystallize these other compounds especially because a new polyhydride species is evident.[14]

In order to verify the structures of these compounds and to add to our understanding of the structural features of mixed-metal gold clusters, we determined the single-crystal X-ray structures of **3** and **4**.[15] The molecular structures of the cations are shown in Figures 1 and 2 along with selected bond lengths and angles. The structure of **3** consists of an approximate $AuIr_3$ tetrahedron. The internal M-M-M angles are all very near 60° (max, min = 64.1°, 57.8°). The M-M bond distances (av Ir-Ir = 2.842 (1) Å, av Ir-Au = 2.705 (1) Å) are significantly different, however. The Ir-Au distances are short while the Ir-Ir distances are longer than those in the similar μ_3-H compound $[Ir_3(\mu_3\text{-}H)(\mu\text{-}H)_3(H)_3(dppp)_3]^{2+}$ [dppp = $Ph_2P(CH_2)_3PPh_2$].[9] The Ir-P bond lengths reflect the positioning of the hydride ligands (see drawing of **3**). Thus the Ir-P bonds that are trans to μ-H ligands are lengthened [av Ir-P = 2.287 (4) Å] relative to the ones that are trans to the Au atom [av Ir-P = 2.245 n(4) Å]. This latter distance is identical with that found in the μ_3-H dppp analogue [av Ir-P = 2.243 (2) Å][9] and illustrates the electronic similarity between μ_3-H and μ_3-Au. In support of this the geometry of the $Ir_3H_6(dppe)_3$ grouping in **3** is very similar to that of the analogous μ_3-H complex $[Ir_3(\mu_3\text{-}H)(\mu\text{-}H)_3(H)_3(dppp)_3]^{2+}$.[9]

The structure of **4** consists of a nearly planar Au_3Ir grouping with deviations from the least-squares plane of +0.011 Å for Au2 and Ir and -0.013 Å for Au1 and Au3. In addition, P2 and the entire NO_3 group lie approximately within this plane, while P1 and P3 are displaced -0.19 and -0.13 Å, respectively, from this plane. The Ir-P4 and Ir-P5 vectors are orthogonal to this plane. The three gold atoms are bonded to the Ir atom with unusually short bond distances (av Au-Ir = 2.641 (1) Å) and Au1 and Au3 are bonded to Au2 in a bent arrangement [Au1-Au2-Au3 115.24 (3)°]. The Au-Au separations [av 2.767 (1) Å] are typical of other gold cluster complexes.[16]

A more detailed account of the synthetic and crystallographic details will appear at a later date.

Acknowledgment is made to the National Science Foundation (NSF Grant CHE 81-08490 to L.H.P.) and to NATO for a travel grant to J.J.S. and L.H.P. The Johnson-Matthey Co. is acknowledge for a generous loan of $IrCl_3$. A.L.C. is the recipient of an NSF Graduate Fellowship.

Supplementary Material Available: Tables of positional and thermal parameters for the cations **3** and **4** (6 pages). Ordering information is given on any current masthead page.

(13) $^{31}P\{^{1}H\}$ NMR of **5** ($CDCl_3$) δ 81.7 (q, J = 38 Hz) intensity = 1, 43.1 (br d) intensity = 3, 41.5 (d, J = 38 Hz) intensity = 3; ^{1}H NMR δ -6.79 (d, J = 74 Hz) intensity = 1, -13.4 (mult) intensity = 1.

(14) Two of these species have been identified as $[Au(PPh_3)_2]^+$ and $[Au_9(PPh_3)_8]^{3+}$ by ^{31}P NMR, and a new polyhydride species is observed by ^{1}H NMR [(acetone) δ -7.80 (t, J = 54.9 Hz), -23.6(s)].

(15) Compound **3**·3$CHCl_3$ (unstable in the absence of solvent, $C_{81}H_{81}AuIr_3P_6NO_3BF_4Cl_9$, M_c = 2471.04) crystallizes in the triclinic space group $P\bar{1}$, with a = 13.656(3), b = 14.310 (3), c = 13.234 (2) Å; α = 95.88 (2), β = 116.06 (3), γ = 71.77 (2)°; Z = 1, V = 2205 (1) Å^3; ρ_c = 1.861 g cm^{-3}. 9607 independent reflections were collected (up to $2\theta_{max}$ < 54°), of which 7048 were considered as observed [$F_o^2 \geq 3.0\sigma(F_o^2)$] and subsequently used. The structure converged to the present conventional R factor of 0.061 by using anisotropic thermal parameters of Au, Ir, and P atoms and isotropic for the others. Compound **4** ($C_{90}H_{75}Au_3IrP_6NO_3F_6$, M_c = 2301.54) crystallizes in the monoclinic space group $P2_1/c$, with a = 14.042 (3), b = 13.309 (2)8 c = 43.58 (1) Å; β = 91.07 (2)°; Z = 4, V = 8143 (5) Å$_3$; ρ_c = 1.877 g cm^{-3}. 8689 independent reflections were collected (up to $2\theta_{max}$ < 42°), of which 4896 were considered as observed [$F_o^2 \geq 2.0\sigma(F_o^2)$] and subsequently used. The structure converged to the present conventional R factor of 0.056 by using anisotropic thermal parameters for Au, Ir, P, and F atoms. Data for both compounds were collected on an Enraf Nonius CAD 4 diffractometer at room temperature (Mo K$\bar{\alpha}$ λ = 0.71069 Å, graphite monochromated) by using an $\omega/2\theta$ scan for **3** and an ω scan for **4**. Both structures were refined using full-matrix least-squares analysis, and data were corrected for the effects of absorption and anomalous dispersion Scattering factors were taken from the "International Tables for X-ray Crystallography", Vol. IV.

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Synthesis and Transilience of a 1,3-Diazabiphenylene

Marc d'Alarcao and Nelson J. Leonard*

Roger Adams Laboratory, Department of Chemistry
University of Illinois, Urbana, Illinois 61801

Received May 17, 1983

In the course of our studies of coenzyme-enzyme interactions using dimensional probes,[1] we became interested in the synthesis and chemical properties of 1,3-diazabiphenylenes. We recently reported[1a] the first synthesis of this ring system by a thermal (780 °C) nitrogen extrusion in the gas phase, and we now wish to communicate an alternative synthesis via a diethynylpyrimidine utilizing the cobalt-catalyzed cooligomerization methods developed by Vollhardt.[2] We also wish to report an unusual, high-yield structural rearrangement of this diazabiphenylene to an isoquinoline with formal elimination of HCN.

The synthesis begins with 4,6-dichloro-5-formylpyrimidine, which is readily available from 4,6-dihydroxypyrimidine.[3] Elaboration of the aldehyde to the dibromoalkene **1** with CBr_4/

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(3) Klotzer, W.; Herberz, M. *Monatsh. Chem.* **1965**, *96*, 1567-1578.

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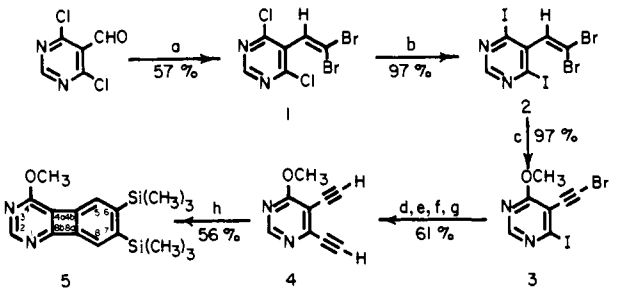
Scheme I



[a] CBr_4, Zn, Ph_3P, CH_2Cl_2. [b] 47% HI, 5 h. [c] $2NaOCH_3$, CH_3OH, 2 h. [d] *n*-BuLi, −78 °C, THF. [e] $(CH_3)_3SiCl$, −78 → 25 °C, THF. [f] $HC{\equiv}CSi(CH_3)_3$, $(Ph_3P)_2PdCl_2$–CuI, $(CH_3CH_2)_3N$. [g] NaOH, CH_3OH. [h] $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$, $CpCo(CO)_2$, xylenes.

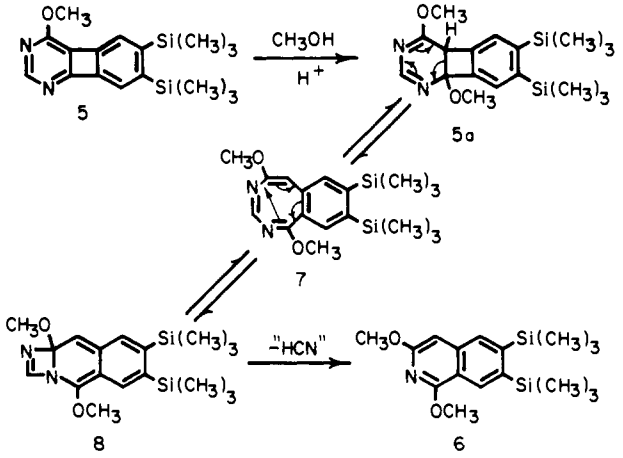
Ph_3P/Zn in CH_2Cl_2 by the general method of Corey and Fuchs[4] proceeded in 57% yield (Scheme I). Exchange of the ring chlorine atoms with concentrated HI at room temperature gave the diiodopyrimidine **2** in nearly quantitative yield. Addition of 2.0 equiv of $NaOCH_3$ to a methanolic solution of **2** effected both a dehydrobromination to generate the bromoalkyne moiety and a nucleophilic substitution of one of the iodo substituents. This reaction proceeds without complication (97% yield of **3**), presumably because upon substitution of the first iodide by a methoxyl group, the ring becomes deactivated toward further reaction. Halogen–metal exchange with *n*-butyllithium at −78 °C followed by trapping of the resulting acetylide with excess chlorotrimethylsilane gave the trimethylsilyl-protected acetylene, which was not isolated but was subjected immediately to reaction with trimethylsilylacetylene in triethylamine catalyzed by $(Ph_3P)_2PdCl_2$–CuI.[5] The resulting bis[(trimethylsilyl)ethynyl]pyrimidine was also not isolated, but the evaporated reaction mixture was passed rapidly through a silica gel column ($CHCl_3$) before deprotection, since the unprotected compound **4** is quickly decomposed by the chromatographically immobile residue of the earlier reactions. Removal of the trimethylsilyl protecting groups was accomplished by stirring with dilute methanolic NaOH at room temperature (30 min), affording **4** in 61% yield (over four steps, based on **3**).

The solid diethynylpyrimidine **4**, which is to our knowledge the first aromatic heterocycle carrying two ortho-disposed acetylenic functionalities, is moderately thermally unstable and darkens within a few hours at room temperature. If the solid is kept at −20 °C, however, no decomposition is evident for several weeks. It should be noted that although **4** is not shock sensitive, it decomposes violently with a release of gas when a sample is placed on a hot plate.

The synthesis of diazabiphenylene **5** was completed by treatment of **4** with bis(trimethylsilyl)acetylene (BTMSA) in the presence of $CpCo(CO)_2$. In a typical run, a solution of **4** (0.50 g, 3.16 mmol) in 50 mL of xylenes (distilled under N_2 from Na–benzophenone) was injected into an argon-purged, refluxing solution of BTMSA (50 mL) in xylenes (50 mL) containing $CpCo(CO)_2$ (2.0 mL). The reaction was stirred at reflux under irradiation by a 250-W floodlight for 10 min, then exposed to the air, and allowed to cool. The reaction solution was stirred vigorously in an open vessel for 4 h to decompose much of the catalyst and then chromatographed on silica gel (200 g, elution with 1:9 ether–petroleum ether, $R_f = 0.13$) to afford compound **5** as a pale yellow solid (0.58 g, 56% yield). An analytically pure sample was obtained by two recrystallizations (EtOH–H_2O): mp 95.5–96 °C.

The ^1H NMR and UV spectra of **5** are typical of biphenylene-like ring systems. Thus, the protons of **5** resonate at slightly higher field than would be expected in the absence of an induced paramagnetic ring current,[6] and the UV spectrum exhibits the three-band pattern between 300 and 400 nm characteristic of biphenylenes.[8]

Scheme II



6,7-Bis(trimethylsilyl)-4-methoxy-1,3-diazabiphenylene (**5**) underwent an unforeseen rearrangement on treatment with acid in an alcohol solvent. Thus, a solution of **5** in CH_3OH containing excess trifluoroacetic acid (i.e., more than 1 mol equiv with respect to **5**) was converted quantitatively within 30 min at room temperature to a highly fluorescent product to which we were able to assign the structure **6**, namely 6,7-bis(trimethylsilyl)-1,3-dimethoxyisoquinoline. Formally, this overall conversion involves addition of CH_3OH and loss of the elements of HCN. The initial stage may be related to the observation[9] that biphenylene itself undergoes ring opening to a substituted benzocyclooctatetraene under conditions of nitration in acetic anhydride. We suggest that the sequence in Scheme II represents a reasonable pathway from the diazabiphenylene **5** to the isoquinoline **6**. Acid-catalyzed addition of CH_3OH to **5**, followed by electrocyclic ring opening, could produce the substituted benzodiazocine **7**. This type of valence isomerization is known in cyclooctatetraene[10] and azocine[11] chemistry. Compound **8** could then be formed in a second thermally allowed electrocyclic reaction. Any distribution of isomers **5a**, **7**, and **8** (Scheme II) could be altered by irreversible loss of the elements of HCN from **8**, thereby driving the reaction to completion (→**6**).[12] Preliminary kinetic data are consistent with this sequence but do not exclude other formal mechanisms.[13]

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(8) For examples of carbocyclic biphenylenes and their spectroscopic properties see: Cava, M. P.; Mitchell, M. J. "Cyclobutadiene and Related Compounds"; Academic Press: New York, 1967; Chapter 10. For biphenylenes containing ring nitrogens see: Kramer, J.; Berry, R. S. *J. Am. Chem. Soc.* **1972**, *94*, 8336–8347. Barton, J. W.; Walker, R. B. *Tetrahedron Lett.* **1975**, 569–572. MacBride, J. A. H. *J. Chem. Soc., Chem. Commun.* **1974**, 359–360. Kanoktanaporn, S.; MacBride, J. A. H. *J. Chem. Res.*, Miniprint **1980**, 2941–2949. MacBride, J. A. H.; Wright, P. M. *Tetrahedron Lett.* **1981**, *22*, 4545–4548.

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(12) Electrocyclic ring contractions followed by the loss of HCN or nitrile fragments have been suggested in the rearrangements of some seven-membered (8-π-electron) heterocycles: Nair, V. *J. Heterocycl. Chem.* **1975**, *12*, 183–184. Sindler-Kulyk, M.; Neckers, D. C. *J. Org. Chem.* **1983**, *48*, 1275–1281.

Recently, careful labeling studies and an independent synthesis provided strong evidence for the intermediacy of a 1,3-diazocine in the transformation of uracil-alkyne photoadducts to pyridones under strongly basic conditions.[14] Conclusions concerning a reaction in alkoxide solution may not be directly applicable to our rearrangement in strongly acidic medium; nevertheless, that study demonstrates the facility of valence isomerizations of the 1,3-diazocine system.

While we were not initially elated to observe the conversion of the exotic diazabiphenylene ring system, once constructed, to the more common isoquinoline system, we are now becoming interested in the valence isomerizations apparently available to its addition products, and we anticipate utilization of this reaction sequence that generates in situ a fluorescent product from a nonfluorescent precursor.

Acknowledgment. This work was supported by Research Grant GM-05829 from the National Institutes of Health.

Supplementary Material Available: Listing of physical and spectral data for compounds **1–6** (2 pages). Ordering information is given on any current masthead page.

(13) The reaction appears to be first order in **5** and first order in trifluoroacetic acid with an obsesrved rate constant of ~0.015 M^{-1} s^{-1} at 20 °C when the reaction is performed in CD_3OD and monitored by ^1H NMR. This is consistent with a preequilibrium involving protonation of **5** before the rate-determining step. The kinetics suggest that the reaction is specific acid catalyzed since as the acid is consumed (presumably by protonation of product) the reaction slows appropriately.

(14) Kaminski, V. V.; Swenton, J. S.; Cottrell, C. E. *Tetrahedron Lett.* **1982**, *23*, 4207-4210.

1-Phenylphosphonin Oxide as an Unstable Valence Tautomer of 9-Phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene 9-Oxide

Nandakumar S. Rao and Louis D. Quin*

Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706

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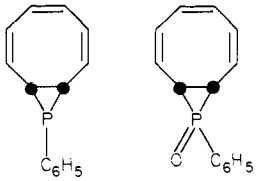
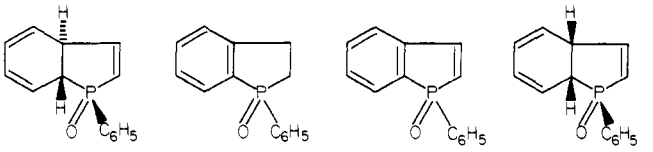
Scission of the 1,8-bond in bicyclo[6.1.0]nonatriene has been employed in the synthesis of cyclononatetraene;[1] the oxygen and nitrogen analogues (oxonin[2,3] and azonine[4]) have been prepared similarly. This conversion, however, has not been successful when a sulfide[5] or phosphine[6] group is present in the three-membered component of the bicyclic ring system. We have discovered that the 1,8-bond in the *P*-oxide (**2**) of 9-phenyl-9-phospha[6.1.0]-nona-2,4,6-triene[7] (**1**) has drastically reduced stability; rearrangement of **2** accompanies formation from **1** at −20 °C or above, and this has allowed us to observe the first monocyclic phosphonin oxide, of structure **3**.



1 2 3

Phosphirane **1** was first oxidized by exposure for 12 h to a 5–10-fold excess of a 1:1 mixture of 30% H_2O_2 and methanol at 0 °C. This provided a product with $\delta(^{31}P)$ + 46.9 in about 95% purity, which was further purified by chromatography on alumina with elution by 10% methanol in benzene. The hygroscopic solid had a mass spectrum suggestive of either **2** or **3** (calcd and found for $M^+ - 1$ *m/e* 227.0625, base peak), but the ^{13}C NMR spectrum[8] eliminated both possibilities, especially by the presence of two different methine carbons, with one showing the characteristic large coupling for direct attachment to ^{31}P. The data suggested the product to possess one (**4**) of the 3a,7a-dihydrophosphindole



4 5 6 7

oxide structures, and this was proved by rearrangement to the known[9] 2,3-dihydrophosphindole oxide **5** (10 h in 15% NaOH, 25 °C) and by air oxidation to the known[9] phosphindole oxide **6**. The formation of a 3a,7a-dihydrophosphindole derivative during oxidation of **1** can only be explained by assuming the intermediacy of a a phosphonin oxide, which undergoes intramolecular [4 + 2] cycloaddition. Since the 3a,7a-dihydrophosphindole oxide differed from the two known[10] forms with cis-fused rings ($\delta(^{31}P)$ + 61.9, +71.1), trans ring fusion was suspected and was confirmed by conducting partial epimerization (7.5% NaOH, 2 min at 25 °C) to the cis,cis isomer **7** with $\delta(^{31}P)$ +61.9. The trans ring fusion in **4** was also indicated by the H_{3a}–H_{7a} coupling constant (at 250 MHz), which was approximately 20 Hz in an ABX (X = ^{31}P) spectrum; this abnormally large value has been observed for trans protons in related systems (e.g., 20 Hz in *trans*-3a,7a-dihydroindene[11]). The cis isomer **7** had a H_{3a}–H_{7a} coupling of 12–14 Hz. The stereochemistry at phosphorus in **4** could not be directly determined but was revealed in the corresponding phosphine ($\delta(^{31}P)$ −16.4, formed with retention[12] using $C_6H_5SiH_3$; methiodide mp 105–115 °C dec, giving the correct C, H, P analyses). The magnitude of $^2J_{PH}$ in phosphines is related to the proximity of the lone pair on phosphorus to the proton on the sp^3 carbon.[13] The absence of ^{31}P coupling to H-7a (as observed in the H-coupled ^{31}P spectrum) suggests the *P*-phenyl and H-7a to have the cis arrangement shown in the corresponding phosphine oxide **4**.

The trans ring fusion in **4** implies that the initially formed phosphonin oxide precursor must have had the trans structure at the C-2,C-3 double bond (as in **3**) for the subsequent thermally induced [4 + 2] cycloaddition to be allowed by orbital symmetry considerations.[14] This is consistent with observations made in the cycloadditions with cyclononatetraene[1] and oxonin.[3] The trans double bond in **3** is also predicted by orbital symmetry conservation in the thermal opening of the cis-fused three-membered ring in

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(8) ^{13}C NMR ($CDCl_3$, 22.5 MHz, FT ^1H-decoupled, J_{PC} in parentheses) δ 42.6 (C-3a, 14.7), 46.7 (C-7a, 79.1), 122.0 (C-4 or C-7, s), 125.3 (C-4 or C-7, s), 126.0 (C-2, 87.9), 128.4 (C-5, s), 128.5 (phenyl meta, 11.7), 128.6 (phenyl ipso, 91.6), 129.1 (C-6, 12.2), 130.2 (phenyl ortho, 10.2), 131.8 (phenyl para, 2.9), 151.4 (C-3, 10.3); ^1H NMR ($CDCl_3$, 250 MHz, FT) δ 3.06–4.04 (H-3a and H-7a, five-line ABX m), 5.9–6.4 (H-4, H-5, H-6, and H-7, m), 6.43 (H-2, d of d, $^2J_{PH}$ = 25.9, $^3J_{H\text{-}2,H\text{-}3}$ = 8.5), 7.22 (H-3, d of d, $^3J_{PH}$ = 39.2, $^3J_{H\text{-}2,H\text{-}3}$ = 8.5), 7.33–7.84 (C_6H_5, m).

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