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Transforming Triplet Vinylnitrene into Triplet Alkylnitrene at Cryogenic Temperatures

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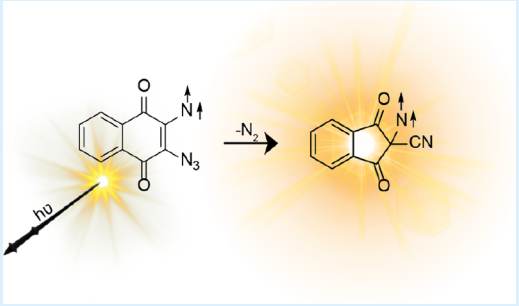
Supporting Information

ABSTRACT: Photolysis of 2,3-diazidonaphthalene-1,4-dione (**1**) in methyltetrahydrofuran matrices forms 2-(λ^1-azaneyl)-3-azidonaphthalene-1,4-dione (vinylnitrene ^{3}**2**), as confirmed by electron paramagnetic resonance spectroscopy. The zero-field splitting (zfs) parameters for ^{3}**2** (D/hc = 0.5338 cm^{-1}, and E/hc = 0.0038 cm^{-1}) reveal significant 1,3-biradical character. Irradiating ^{3}**2** yields 2-(λ^1-azaneyl)-1,3-dioxo-2,3-dihydro-1*H*-indene-2-carbonitrile (alkylnitrene ^{3}**3**), which has zfs parameters typical of a cycloalkylnitrene (D/hc = 1.57 cm^{-1}, and E/hc = 0.00071 cm^{-1}). Photolysis of **1** in argon matrices verifies that ^{3}**2** forms ^{3}**3**.

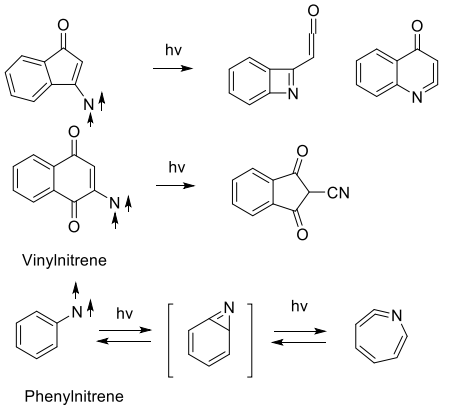


The quest for sustainable chemistry has sparked interest in light as a traceless synthesis reagent.[1] For example, vinyl azides, versatile building blocks in numerous synthetical applications,[2] have been used in visible-light-driven reactions to prepare heterocyclic compounds.[3] However, widespread employment of photoreactive vinyl azides requires an improved understanding of their complex reaction mechanisms, which depend on several factors, including vinyl azide structure, irradiation wavelength, and whether light is absorbed directly or through sensitizers.[4] Irradiation of cyclic vinyl azides at cryogenic temperatures yields stable triplet vinylnitrenes, which have been characterized in detail.[5] As cyclic vinylnitrenes are stable, they undergo secondary photoreactions (ring contraction and/or expansion) to form products (Scheme 1). Thus, cyclic vinylnitrenes are similar to triplet phenylnitrene, which undergoes ring expansion upon irradiation at cryogenic temperatures.[6] In contrast, noncyclic vinyl azides do not yield vinylnitrenes at cryogenic temperatures, presumably because they are unstable and form ketenimine products.[4a,7]

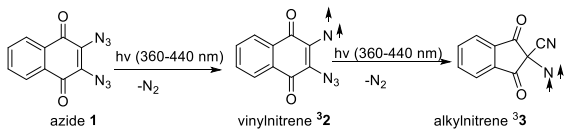
However, simple phenyl and vinyl azides exhibit different photochemistry in solution; phenyl azides form polymeric tars,[8] whereas cyclic and noncyclic vinyl azides yield heterocyclic products. Understanding the factors that control the photoreactivity of vinyl azides and the corresponding triplet vinylnitrenes will aid their general use in synthetical applications.

Herein, we describe the photoreactivity of 2,3-diazido-1,4-naphthoquinone (**1**) at cryogenic temperatures. EPR and IR spectroscopy along with quantum calculations revealed that light transforms azide **1** into vinylnitrene ^{3}**2**, which absorbs another photon to yield alkylnitrene ^{3}**3** (Scheme 2)

Scheme 1



Scheme 2



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EPR spectroscopy revealed that irradiation of azide **1** results in the formation of vinylnitrene ^{3}**2**. In detail, irradiating (λ = 360−440 nm) azide **1** in a glassy methyltetrahydrofuran (mTHF) matrix at 10 K gave an EPR signal at 5358 G (Figure 1) with the following zero-field splitting (zfs) parameters,

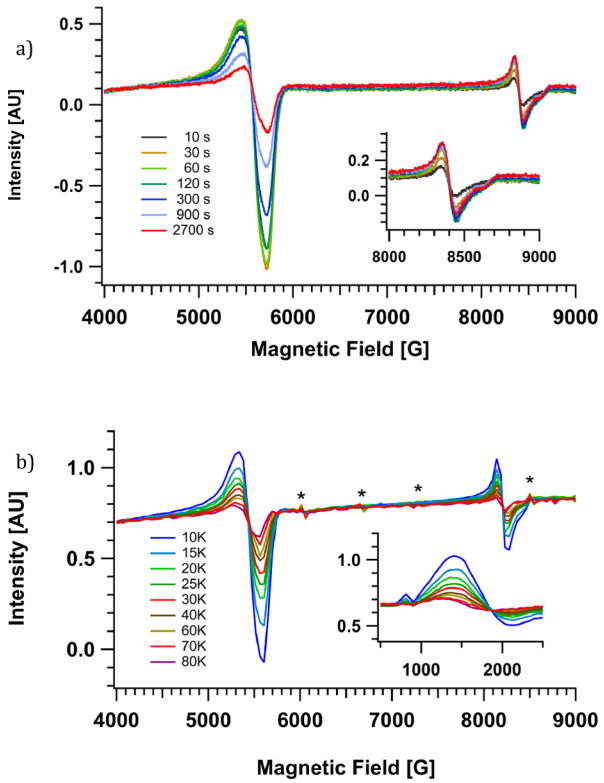
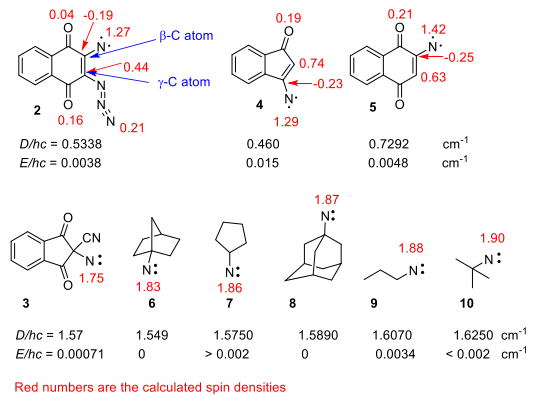


Figure 1. EPR spectra obtained by irradiation of **1** (high-pressure Hg lamp, 360−440 nm band filter) in THF matrices as a function of (a) irradiation time and (b) temperature (noise reduction was performed on the traces; original traces are in the Supporting Information). The signals labeled with asterisks are from the cavity of the EPR spectrometer.

calculated using Wasserman's equations: D/hc = 0.5338 cm^{-1}, and E/hc = 0.0038 cm^{-1}.[9] We assign this signal to vinylnitrene ^{3}**2** because the zfs values are comparable to those reported for vinylnitrenes ^{3}**4** and ^{3}**5** (Scheme 3).[5] Wentrup reported a linear relationship between D/hc values and the calculated spin

Scheme 3. zfs Parameters and Calculated Spin Densities of Nitrenes Calculated at the EPR III Level of Theory



density on the N atom of triplet nitrenes.[10] The calculated spin density [B3LYP/6-31G+(d)][11] of vinylnitrene ^{3}**2** places the unpaired electrons mainly on the N (1.27) and β-carbon [0.44 (Scheme 3)] atoms. As the calculated spin density on the N atom fits the trend observed for other triplet nitrenes and correlates well with the D/hc value, vinylnitrene ^{3}**2** is best described as a delocalized nitrene with significant 1,3-biradical character. Because of conjugation with the azido moiety, vinylnitrene ^{3}**2** has less 1,3-biradical character than vinylnitrenes ^{3}**4** and ^{3}**5**.

As the second EPR signal at 8151 G is consistent with reported triplet alkylnitrene signals, it is assigned to alkylnitrene ^{3}**3** (Figure 1; D/hc = 1.57 cm^{-1}, and E/hc = 0.00071 cm^{-1}).[12] This D/hc value is similar to those reported for secondary and tertiary cycloalkylnitrenes, including cyclopentylnitrene ^{3}**8**, norbornylnitrene ^{3}**9**, and adamantylnitrene ^{3}**10** (Scheme 3).[13] In comparison, acyclic alkylnitrenes typically have slightly larger D/hc values (1.60−1.74 cm^{-1}).[10,13b] The calculated spin density for alkylnitrene ^{3}**3** is localized on the N atom (1.75), correlating with the D/hc value. Furthermore, the simulated EPR spectra of vinylnitrene ^{3}**2** and alkylnitrene ^{3}**3** are displayed in the Supporting Information, and they fit well with the observed spectra.

Both EPR signals were present after the initial 10 s irradiation, but their intensities changed differently with irradiation time. Further irradiation decreased the intensity of the 5358 G signal but increased the intensity of the 8151 G signal, implying that vinylnitrene ^{3}**2** is the precursor of alkylnitrene ^{3}**3**. Both signals broadened as the matrix was warmed to 80 K. However, the intensity was recovered upon cooling, verifying that both nitrenes are thermally stable to at least 80 K.

To clarify how alkylnitrene ^{3}**3** forms from vinylnitrene ^{3}**2**, the photoreactivity of azide **1** in argon matrices was studied with IR spectroscopy. After irradiation for 35 s (xenon lamp, 360−440 nm band filter), the intensities of the characteristic azido bands of azide **1** at 2135, 2124, 2117, and 2105 cm^{-1} were reduced (Figure 2). The multiple azido bands most likely correspond to azide **1** being trapped in different conformers or matrix sites. The intensities of the bands at 1682, 1674, 1564, 1367, 1344, and 1268 cm^{-1} were also reduced. Concurrently, new bands with contrasting time profiles appeared, suggesting primary and secondary photoreactions. Specifically, after irradiation for 20 s, new bands appeared at 1709 and 1330 cm^{-1} (Figure 2a), which are assigned to vinylnitrene ^{3}**2** by comparison with its calculated spectrum (Figure 2b; significant bands at 2147, 1694, and 1323 cm^{-1} after scaling by 0.9613).[14] We theorize that the azido band of vinylnitrene ^{3}**2** is buried under those of azide **1**. In addition, less intense bands were seen at 1644, 1608, 1418, 982, 978, 839, 798, 702, 677, and 657 cm^{-1} and scaled bands of vinylnitrene ^{3}**2** at 1604, 1572, 1406, 964, 928, 833, 776, 691, 667, and 650 cm^{-1}.

Irradiation for 35 s further increased the intensity of the bands of vinylnitrene ^{3}**2**. Concurrently, new bands appeared at 1778, 1766, 1758, 1747, 1206, and 941 cm^{-1}. These bands are assigned to alkylnitrene ^{3}**3** by comparison with its calculated and scaled spectrum (2261, 1776, 1743, 1210, and 964 cm^{-1}). The multiplicity of the symmetric and antisymmetric carbonyl bands at 1778, 1766, 1758, and 1747 cm^{-1} is assigned to different matrix sites for alkylnitrene ^{3}**3**.

As no new alkyl azido bands were explicitly observed, we conclude that vinylnitrene ^{3}**2** does not form alkyl azide precursors that need to absorb another photon to yield

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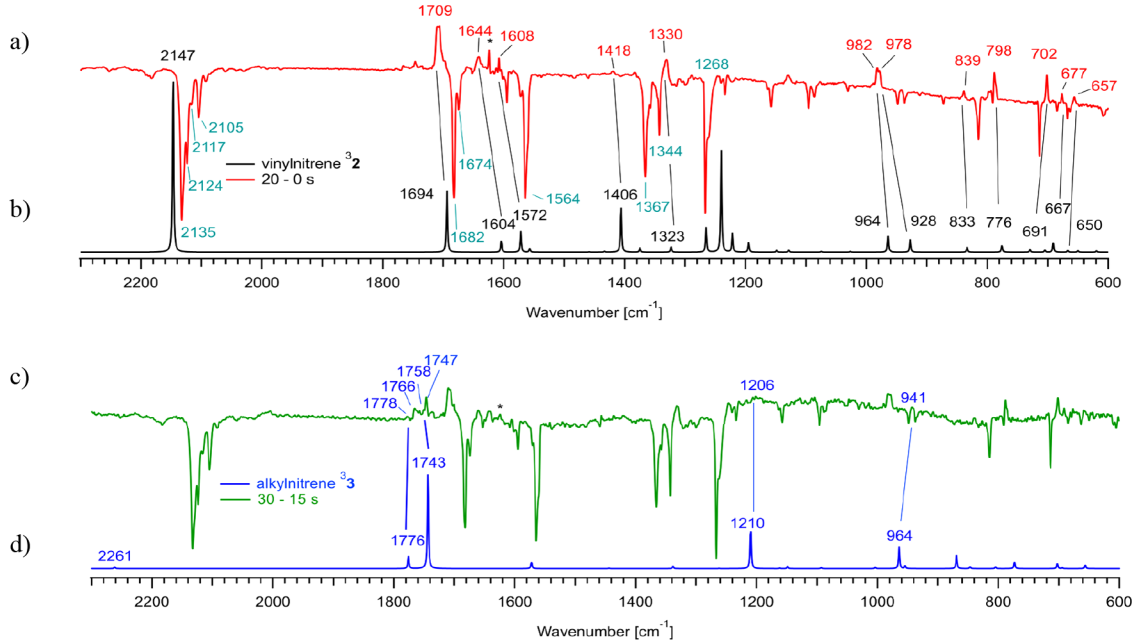
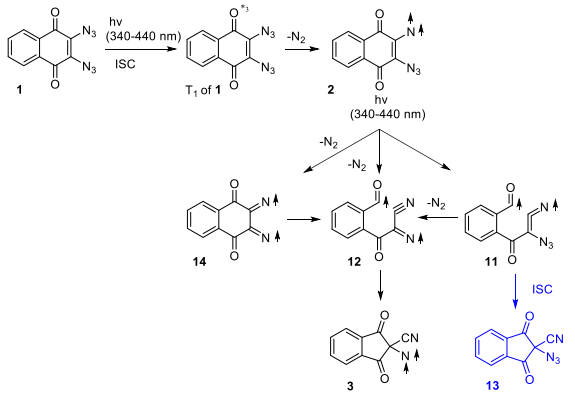


Figure 2. Differential IR spectra obtained after irradiating **1** (xenon lamp, 360−440 nm band filter) in an argon matrix at 10 K (a) from 20 to 0 s and (c) from 30 to 15 s. Calculated IR spectra [B3LYP/6-31+G(d) and scaled] for (b) ^{3}**2** and (d) ^{3}**3** (IR spectra after irradiation for 10, 15, 30, and 35 s are displayed in the Supporting Information; asterisks denote impurities).

alkylnitrene ^{3}**3**. Rather, we propose that alkylnitrene ^{3}**3** forms via α-cleavage of vinylnitrene ^{3}**2** (Scheme 4). Although,

Scheme 4. Proposed Mechanism for the Formation of 3 from 1



biradical ^{3}**11** could intersystem cross to form alkyl azides **13**, it is unlikely because we did not observe IR bands that can be assigned to alkyl azide **13**. It is also possible that vinylnitrene ^{3}**2** forms biradical ^{3}**12** concurrently with extruding N_2. Furthermore, it can be theorized that vinylnitrene ^{3}**2** forms diimino diradical ^{3}**14**, which could undergo α-cleavage to form biradical ^{3}**12**.

We performed density functional theory (DFT) calculations [B3LYP/6-31+G(d)] to further support the mechanisms in Scheme 4.[11] Optimization of azide **1** gave minimal energy conformers **1A** and **1B**, differing mainly in azide group orientation. Time-dependent density functional theory (TD-DFT) calculations of the lowest-energy conformer (**1A**) showed that the singlet excited state (S_1) of **1** is located 53 kcal/mol above its ground state (S_0), whereas the first and second triplet excited states (T_1 and T_2, respectively) are 30 and 58 kcal/mol, respectively, above S_0.

Following optimization, T_1 of **1** is located 30 kcal/mol above S_0. Thus, for azide **1**, the energy of optimized T_1 and that obtained from TD-DFT calculations are in good agreement. Spin density calculations showed that T_1 of **1** has a (π, π*) configuration, as the carbon atoms of the double bond have the highest spin density [0.33 (Figure 3)].

The optimized structure of vinylnitrene ^{3}**2** has the C_β−C_γ bond with single-bond character [1.45 Å (Scheme 1)]. As mentioned above, the unpaired electron density is mainly on the nitrene nitrogen (1.30) and β-carbon (0.45) atoms, with additional small contributions from the terminal nitrogen atom of the azido group (0.21) and the γ-carbonyl oxygen atom (0.16). The optimized structure of alkylnitrene ^{3}**3** is characteristic of triplet alkylnitrenes, as the C−N bond has single-bond character (1.42 Å). Similarly, spin density calculations confirmed that the unpaired electrons are centralized on the nitrogen atom, as expected for triplet alkylnitrenes.

Calculated stationary points on the pathway for forming vinylnitrene ^{3}**2** from azide **1** and its transformation to alkylnitrene ^{3}**3** are shown in panels a and b in Figure 3. The calculated transition state barrier for T_1 of **1** to release N_2 and form vinylnitrene ^{3}**2** is only 6 kcal/mol above T_1 of **1** and thus easily accessible. We propose that vinylnitrene ^{3}**2** undergoes α-cleavage to form biradical ^{3}**11**, which extrudes N_2 to give biradical ^{3}**12**, followed by ring closure to triplet alkylnitrene ^{3}**3**. As the calculated transition state barrier for forming biradical ^{3}**11** is located 24 kcal/mol above vinylnitrene ^{3}**2**, this process is feasible photochemically. As the calculated transition state barriers for forming biradical ^{3}**12** and alkylnitrene ^{3}**3** are smaller (12 and 0.3 kcal/mol, respectively), the calculations support the transformation of vinylnitrene ^{3}**2** into alkylnitrene ^{3}**3** as shown in Figure 3. It should be noted that we could not locate the transition state for vinylnitrene ^{3}**2** forming radical **12**

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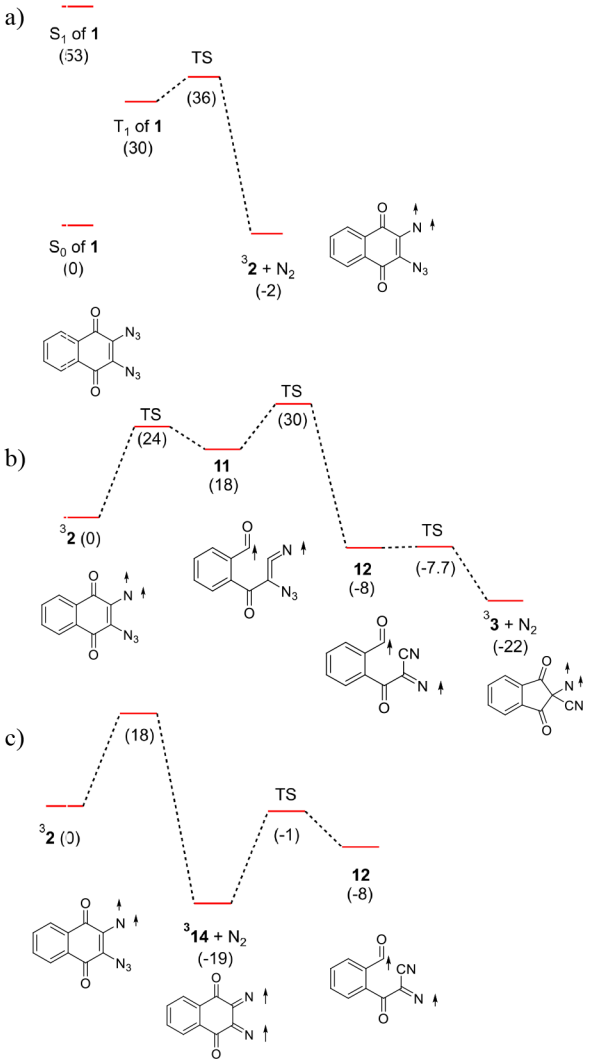


Figure 3. Calculated [B3LYP/6-31+G(d)] stationary points on the energy surface of (a) **1** forming ^{3}**2** and (b) ^{3}**2** forming ^{3}**3**. Energies are in kilocalories per mole.

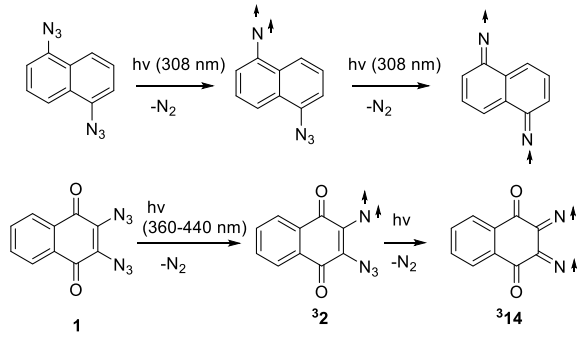
in a concerted manner. Although this does not rule out the concerted mechanism, it does not seem likely.

Figure 3c displays the calculated stationary points for the transformation of vinylnitrene ^{3}**2** to biradical ^{3}**12** through diimino diradical ^{3}**14**. The calculated transition state barrier for diimino diradical ^{3}**14** forming vinylnitrene ^{3}**2** is 18 kcal/mol, whereas the barrier for diimino diradical **14** yielding biradical ^{3}**12** is 18 kcal/mol. Although this transformation is feasible photochemically and could result in alkylnitrene ^{3}**3**, it is highly unlikely, because diimino diradical ^{3}**14** is more stable than vinylnitrene ^{3}**2** and it was not observed with IR (see the Supporting Information) or EPR spectroscopy.

This is the first reported transformation of a triplet vinylnitrene to a triplet alkylnitrene, which is remarkable as there are very few methods available to form triplet alkylnitrenes.[12c,15] This limitation stems from the fact that direct photolysis of alkyl azides does not yield singlet alkylnitrenes that intersystem cross to their triplet counterparts. Instead, the singlet excited state of alkyl azides is theorized to rearrange in a concerted manner to form imine products. Thus, our results open the possibility of forming alkylnitrenes via the phototransformation of triplet vinylnitrenes.

Interestingly, azide **1** reacts differently from diazido naphthalene and phenyl derivatives, which upon irradiation in cryogenic matrices form the corresponding triplet monoarylnitrenes but undergo secondary photolysis to release another N_2 molecule, yielding diimino diradicals (Scheme 5).[16]

Scheme 5. Diimino Diradicals



These diimino diradicals have singlet ground states, but as the singlet−triplet energy gap is small, the triplet states have been extensively characterized by EPR spectroscopy. We did not observe formation of triplet or singlet diimino diradical **14** from vinyl azide **1** (Scheme 5) because the carbonyl group makes α-cleavage of vinylnitrene ^{3}**2** feasible, resulting in rearrangement to triplet alkylnitrene ^{3}**3** rather than formation of diimino diradical **14**.

In conclusion, we have demonstrated that irradiation of azide **1** yields vinylnitrene ^{3}**2**, which is stable at cryogenic temperatures. However, ^{3}**2** transforms photochemically to triplet alkylnitrene ^{3}**3**, thus establishing a new method for forming triplet alkylnitrenes at cryogenic temperatures, which have potential in high-spin assemblies. However, for general use of vinyl azides in synthesis, secondary photolysis must be avoided. Further studies to characterize the fate of alkylnitrene ^{3}**3** at cryogenic temperatures will be undertaken by our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01950.

Experimental procedures, characterization of azide **1**, theoretical calculations, argon and mTHF matrices, and simulated EPR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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