Off the Beaten Path: Almost Clean Formation of Indene from the ortho-Benzylene + Allyl Reaction

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ABSTRACT: Polycyclic aromatic hydrocarbons (PAHs) play an important role in chemistry both in the terrestrial setting and in the interstellar medium. Various, albeit often inefficient, chemical mechanisms have been proposed to explain PAH formation, but few yield polycyclic hydrocarbons cleanly. Alternative and quite promising pathways have been suggested to address these shortcomings with key starting reactants including resonance stabilized radicals (RSRs) and o-benzylene. Here we report on a combined experimental and theoretical study of the reaction allyl + o-benzylene. Indene was found to be the primary product and statistical modeling predicts only 0.1% phenylallene and 0.1% 3-phenyl-1-propyne as side products. The quantitative and likely barrierless formation of indene yields important insights into the role resonance stabilized radicals play in the formation of polycyclic hydrocarbons.
(2a and 2b) are generated by flash pyrolysis of allyl iodide (3) and benzocyclobutenedione (1), respectively (see Schemes 1 and 2). The latter was synthesized according to the procedure described in the Supporting Information.

**Scheme 1. Benzocyclobutenedione (1) Pyrolysis to o-Benzyne (2a and 2b)**

**Scheme 2. Allyl Iodide (3) Pyrolysis to Allyl Radical (4a and 4b)**

Mass spectra were recorded on the basis of delayed coincidences between electrons and ions.29 Figure 1 shows the mass spectra of the two precursors introduced in the microreactor alone and combined.

A detailed description of peak assignments can be found in the Supporting Information and only peaks relevant to the o-benzyne + allyl reaction are discussed here. Figure 1A shows a strong signal at m/z 41, which is indicative of efficient conversion of allyl iodide to allyl radical, while Figure 1B contains a peak at m/z 76, corresponding to o-benzylene. Electron kinetic energy analysis and the time-of-flight mass analysis of the coincident photoion allow us to plot the photoion mass-selected threshold photoelectron spectrum, ms-TPES, which provides an isomer selective fingerprint to assign the m/z peaks. Contributions of the cis- and trans-1,5-hexadiyne-3-en, which are also C₆H₄ isomers, can thus be fully ruled out.

Lastly, Figure 1C shows the presence of a single new peak at m/z 116 associated with the mass corresponding to the addition of allyl to o-benzynel followed by the loss of a hydrogen atom according to Scheme 3.

**Scheme 3. o-Benzene (2) Addition to Allyl Radical (4) Yielding Indanyl Radical Intermediate (5) Followed by Hydrogen Loss To Form Indene (6)**

The m/z 116 ms-TPES was recorded in the 7.6–9.2 eV photon energy range to determine the isomeric composition of the C₉H₈ product (Figure 2). The clear vibronic structure matches the indene reference TPES recorded by West et al.30 at room temperature. The sharp resonance observed at 8.14 eV is in excellent agreement with the indene ionization energy, and the first electronically excited state of the ion is also clearly visible at 8.93 eV. The early ms-TPES signal onset before the main resonance is caused by vibrational hot and sequence bands as pointed out by Cunha de Miranda et al.31 Ionization energies of three isomeric products that potentially contribute, phenylallene (8.29 eV),32 3-phenyl-1-propyne (8.99 eV), and 1-phenyl-1-propyne (8.42 eV)33 are indicated using red tick marks and do not contribute to the ms-TPES significantly, if at all.

The C₉H₉ potential energy surface (PES) was sampled by scanning internal coordinates at the uB3LYP/6-311++G(d,p) level of theory to yield insights into the formation mechanism of the various C₉H₈ isomers. G4 calculations were subsequently carried out for the intermediates (INT) and transition states (TS) and a simplified summary of the PES is shown in Figure 3. Using uB3LYP, no entrance barrier to reaction is found, and the allyl radical readily adds to one of the two radical centers of o-benzynel, forming INT1. From

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**Figure 1.** Mass spectrum of (A) allyl iodide (16% in argon) taken at 9.0 eV and 1045 K, (B) benzocyclobutenedione (1% in argon) taken at 9.5 eV and 1080 K, and (C) allyl iodide (16% in argon) and benzocyclobutenedione (1% in argon) together at 9.0 eV and 1045 K. Masses and structures of key species are shown in the mass spectra.

**Figure 2.** TPES of product at m/z 116 taken from 7.6 to 9.2 eV at 930 K compared to reference TPES of indene provided by West et al.30 The red marks indicate the ionization thresholds of three possibly formed C₉H₈ isomers.

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INT1, ring closure proceeds via allyl rotation and through TS1, which is the rate limiting transition state for the formation of indene. A more detailed figure of the potential energy surface can be found in the Supporting Information. In addition, calculations on the initial reaction to form INT1 were performed using different methods, described in detail in the Supporting Information. From these calculations it was found that the association reaction of allyl with benzyne is likely barrierless, or nearly so, as a negligible barrier cannot be completely ruled out.

Pathways leading to the other potential products, phenylallene, 3-phenyl-1-propyne, and 1-phenyl-1-propyne, were also explored and are summarized in Figure 3 and the Supporting Information. These isomers all fall well below the energy of the reactants and their formation is, thus, energetically allowed. The rate-limiting transition states are TS2, TS3, and TS4, respectively, which are all substantially (>82 kJ/mol) higher in energy than TS1 on the path to indene.

Rice–Ramsperger–Kassel–Marcus (RRKM) theory was employed to estimate the branching over the various products.34 Rate constants for crossing the rate limiting barriers for each of the product species are calculated as a function of energy (Figure 4) and a 99.8% indene, 0.1% phenylallene, and 0.1% 3-phenyl-1-propyne branching is predicted at the entrance energy (indicated by the dotted line in Figure 4). The contributions of the fourth isomer, 1-phenyl-1-propyne, is found to be negligible. This supports the experimental observation that indene is the primary reaction product.

The bimolecular reaction of o-benzyne with allyl is found to produce bicyclic indene exclusively. The facile formation of the five-membered ring species is intriguing in the context of recent findings that pentagon-bearing species are important in both the growth and destruction of PAHs.18,35,36 Furthermore, the formation of a polycyclic species from o-benzyne + a RSR reaction confirms the computational findings of Matsugi and Miyoshi25 that multiring species are favored over open-chain species in these types of reactions. While estimates of pressure and temperature dependent rate constants are outside the scope of this Letter, on the basis of the computations, it is clear that the formation rate of INT1 will determine the production of indene for a large range of energies, as the reverse reaction of INT1 toward allyl and o-benzyne is hardly competitive. As a result, indene formation will be governed by collision rate and the impact factor, which while not estimated here, is expected to be high due to o-benzyne containing two sites of attack by either of the CH2 groups of allyl.

Such condensation reactions, i.e., those with little to no entrance barrier, may also play an important role in the formation of aromatic molecules in low-temperature environments, such as Titan’s atmosphere and in cold molecular clouds.37,38 After association, the forward condensation reaction is faster than the dissociation and is made irreversible by the loss of the hydrogen, which also allows thermal stabilization of the product indene. However, at high temperatures, further hydrogen loss from indene yields the indenyl RSR (see Supporting Information). Indenyl plays a critical role in the formation of large aromatic species.16,39 This suggests that reactions of o-benzyne and RSRs may play a central role in initiating PAH formation in high temperature environments, such as combustion engines and the outflow of carbon-rich stars, as well.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c00374.

Experimental procedures and characterization data for reaction (including ionization energies, mass spectra, ion signals vs pyrolysis temperature, fractional abundance vs temperature, potential energy surfaces and scans, and transition state structures). (PDF)

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