Received: 11 August 2021 | Revised: 3 October 2021 | Accepted: 4 October 2021

DOI: 10.1002/poc.4298

Journal of Physical Organic Chemistry WILEY

SPECIAL ISSUE ARTICLE

Wavelength-dependent photochemistry of 1-phenyl-1-diazopropane

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Funding information
National Science Foundation, Grant/Award Number: NSF CHE- 1900643

Abstract

1-Phenyl-1-diazopropane (**PDP**) was photolyzed in acetonitrile/methanol mixtures using either 520-nm light or 350-nm light. The main photoproducts were 1-methoxypropylbenzene and **E,*Z***-1-phenylpropene. With 520-nm light, a plot of (1-methoxypropylbenzene)/(**E,*Z***-1-phenylpropene) versus methanol concentration was linear. These results are consistent with the visible light induced fragmentation of **PDP** to dinitrogen and closed shell singlet (S_0) ethyl, phenylcarbene (**^{1}EPC**) which partitions between 1,2 hydrogen migration to form alkene, and reaction with methanol to form ether. The same plot generated with 350-nm light significantly deviates from linearity. It is proposed that 350-nm light generates the carbene in a vibrationally excited, open shell S_1 excited state (**^{1}EPC***). This state rearranges to ***E,Z***-1-phenylpropenes in competition with relaxation to ground state **^{1}EPC** over a few tens of ps. As a result, methanol cannot completely suppress alkene formation upon photolysis of **PDP** with 350-nm light. The carbene excited state is a “non-trappable carbene” route to alkenes.

KEYWORDS

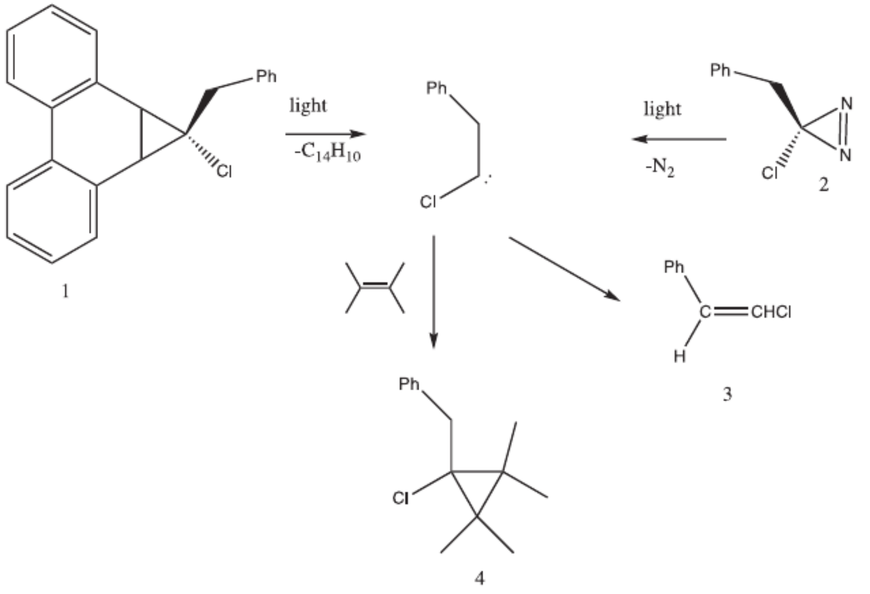
carbene, excited states, wavelength dependent

1 | A PERSONAL NOTE

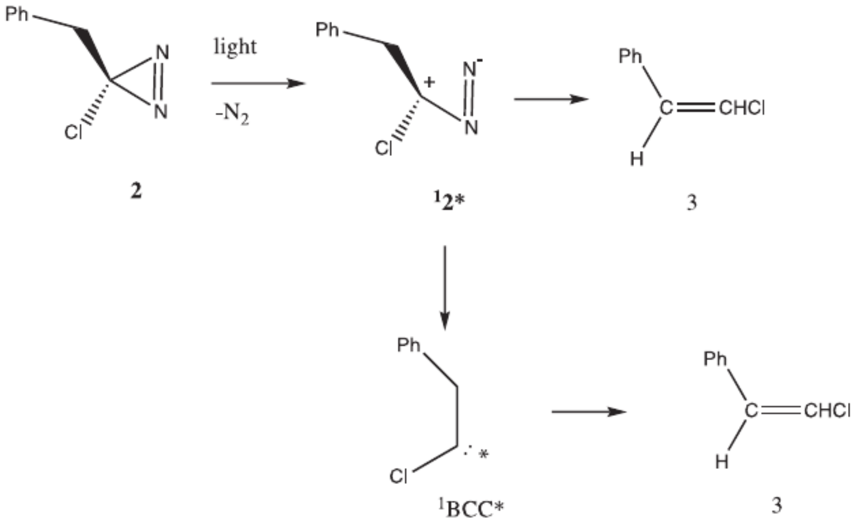
In the autumn of 1973, one of the authors (MSP) began his graduate studies in the laboratory of Professor Jerome Berson at Yale University. Luckily, for MSP, his desk was adjacent to that of a brilliant post-doctoral student, Dr. Barry K. Carpenter, who became a lifelong friend and inspiration. Barry's towering intellect was immediately obvious as he was the only student that could solve Professor Berson's chemistry problems during Monday night group meetings. If not for Barry, we might still be working on those problems 48 years later! Even more impressive than his intellect is Barry's integrity and belief in doing science for its own sake, devoid of the pursuit of personal fame or fortune, or recognition of any kind. For MSP, Barry has always been the consummate scientist and gentleperson scholar. We thank the organizers for making this special issue a reality and inviting us to participate.

2 | INTRODUCTION

One can economically write carbene mechanisms as shown in Scheme 1 wherein the combination of a thermally stable precursor and light is a clean, simple and efficient means of releasing a carbene of interest for detailed study.[1] For example, UV photolysis of **1** induces its fragmentation to phenanthrene and benzylchlorocarbene (**BCC**) in its closed shell singlet ground state. This carbene isomerizes to ***E,Z*-3** or can be intercepted with tetramethylethylene to form **4**.[2] A plot



SCHEME 1 A simple mechanism involving a single product forming, relaxed carbene intermediate



SCHEME 2 A mechanism involving two product forming intermediates

of **4/(*E,Z*-3)** versus tetramethylethylene concentration is linear, as predicted by Scheme 1. The same plot is decidedly non-linear when diazirine **2** is used as the photochemical precursor as first discovered by Tomioka and Liu (with cis-4-methyl-2-pentene) and later by Liu and Bonneau with tetramethylethylene.[2–4] The diazirine data requires the involvement of a second alkene product forming intermediate. That intermediate has been associated with a carbene-alkene complex.[3,4] The second intermediate is now generally thought to be an excited state of either the diazirine (first proposed by La Villa and Goodman on the basis of photoacoustic calorimetry[5]) or the carbene. Either a diradical or zwitterion like singlet excited state of the diazirine suffers rearrangement to alkene with loss of nitrogen, or the diazirine excited state loses nitrogen to form an excited state of the carbene which isomerizes rapidly to alkene product. The non-linear plot obtained with the diazirine precursor can be explained if an excited state of the precursor or the excited carbene forms alkene faster than it relaxes to **BCC**. In this mechanism, tetramethylethylene cannot completely suppress alkene formation (Scheme 2). There is a “non-trappable carbene” route to alkene!

The Moss group has discovered several additional examples[6] of “Rearrangements in the Excited State” (RIES) mechanisms in diazirine photochemistry and the subject has been reviewed by Merrer and Moss.[7]

3 | RESULTS

Aromatic diazo compounds absorb strongly in the UV and more weakly in the visible region.[8] This allows for convenient wavelength dependent study of the

photochemistry of 1-phenyl-1-diazopropane (**PDP**).[9] Photolysis of **PDP** with visible light[10] in aerated methanol/acetonitrile mixtures produces known alkenes **A** and ether **E.**[11] Small amounts of propiophenone (ketone) are formed when the methanol content is low due to capture of triplet carbene (^{3}**EPC**).[12] A plot of (**E/A[*E*,*Z*]**) versus methanol concentration is linear (Figure 1).[13] The data is reminiscent of that obtained with **1**, the phenanthrene precursor to benzylchlorocarbene (**BCC**), Scheme 1.[3,4] The product ratios[14] are consistent with the presence of a single reactive intermediate, closed shell singlet ethylphenylcarbene (^{1}**EPC**) as shown in Scheme 3. The ***Z/E*** ratio is $\sim 0.35 + -0.4$ throughout the methanol range. This result is also consistent with the presence of a single reactive intermediate that forms both **E** and **A**.

Very different results are obtained when PDP is excited with 350-nm light (Figure 2).[15] At low methanol concentrations the **E/A** ratio is linear with a slope comparable to that of Figure 1 but the yield of ether **E** becomes saturated around 10 M methanol. The ***Z/E*** ratio of the alkenes is roughly twice that obtained with 520-nm light. These results are similar to those obtained with diazirine **2** (Scheme 2)[2–4] suggesting a more complex mechanism, one involving a "non-trappable" excited state species, that forms alkene product **A**.

4 | DISCUSSION

The data shown in Figure 2 is consistent with Scheme 4. Based on calculations[16,17] we posit that 350-nm photolysis promotes **PDP** to the S_2 excited state[18,19] of the diazo compound, ^{1}**PDP*** which can relax to the S_1 excited state or extrude nitrogen. Zhang, Vyas, and Hadad's

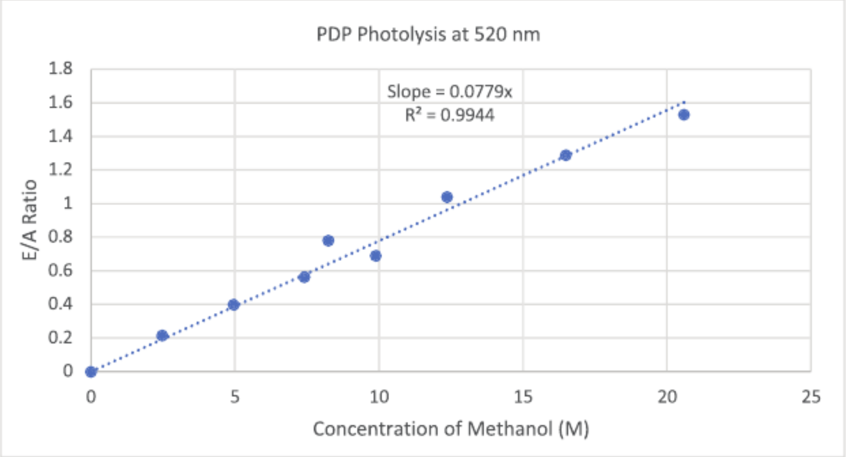
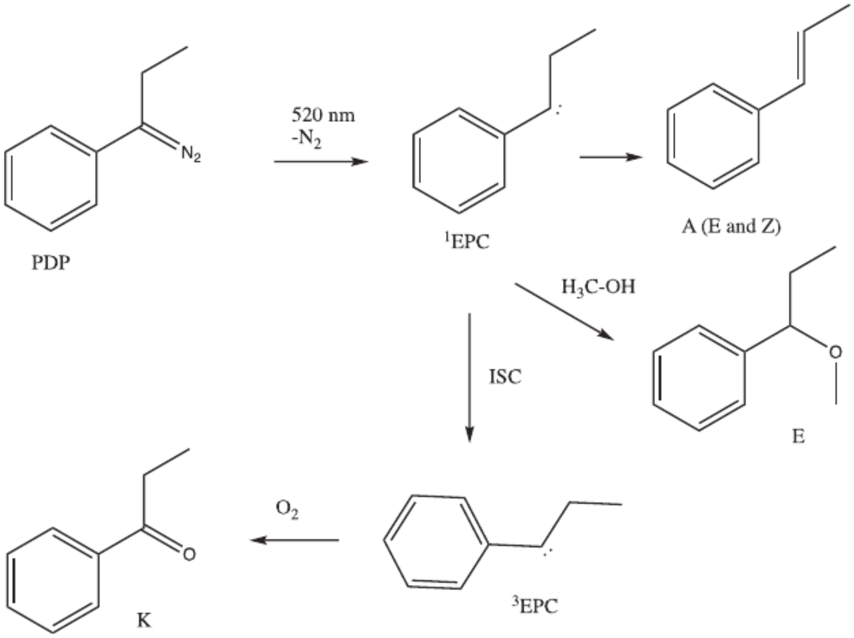


FIGURE 1 Photolysis of PDP with 520-nm light and the ratio of ether (E) to alkenes (A) formed. Trendline fitted for all data points. The ratios are GC peak integrations[11,13,14]



SCHEME 3 An economical mechanism describing the 520-nm photolysis of 1-phenyl-1-diazopropane (PDP)

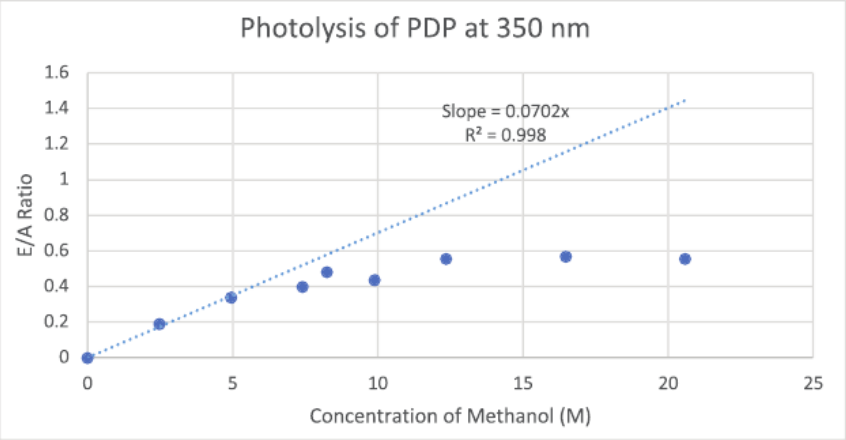
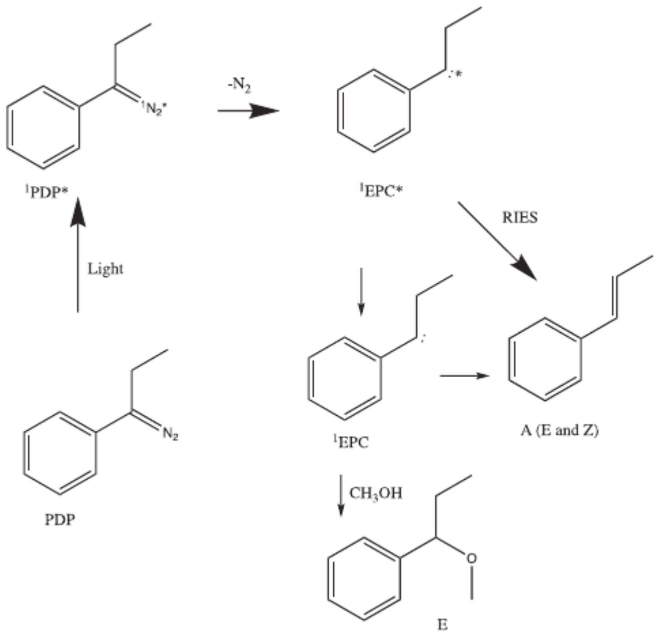


FIGURE 2 Photolysis of PDP with 350-nm light and the ratio of ether (E) to alkenes (A) formed. Trendline fitted for methanol concentrations from 0 M to about 5 M to emphasize the end of the linear region and the saturation in yield of ether. Ratios are GC peak integrations[12–14]



SCHEME 4 Photochemical product formation from 1-phenyl-1-diazopropane (PDP) using 350 nm light

calculations[17] predict that these states fragment to form the open shell singlet state of ethylphenylcarbene, ^{1}EPC*. We note in support of this claim that UV photolysis of 9-diazofluorene in acetonitrile produces the excited open shell singlet state of fluorenylidene.[20] The excited state of the carbene relaxes over 21 ps to the lower energy closed shell singlet form of the carbene. Experimentally distinguishing the diazo excited state versus carbene excited state route to alkene awaits a general solution, one that will likely involve direct, sub-ps observation of intermediates.

We further hypothesize in Scheme 4 that ^{1}EPC* is *both* electronically and vibrationally excited and isomerizes to a mixture of ***E,Z*** alkenes **A** in competition with relaxation to closed shell singlet carbene, ^{1}EPC, over a few tens of ps. Hot, open shell singlet carbene ^{1}EPC* is the "non-trappable carbene" source of propenes **A**.

Scheme 4 is consistent with Luk's finding of conical intersections (CIs) connecting vibrationally excited open shell singlet 2-butylidene with butenes.[19]

When **PDP** is excited with lower energy radiation (520 nm), the ^{1}EPC formed is born with insufficient energy to access a CI leading to alkenes **A**. This explains why the ***E,Z*** ratios of the 1-phenylpropenes produced by 350- and 520-nm light are not the same.

In future work we will further vary the photolysis wavelength and try to define the onset of "non-trappable" carbene contributions, and the excess energy needed to access this alkene forming route.

We propose that this mechanism explains numerous results of earlier workers who noted major differences in products formed depending on the mode of decomposition of carbene precursors and first recognized the existence of multiple product forming pathways.[21]

5 | CONCLUSIONS

The photochemistry of 1-phenyl-1-diazopropane **(PDP)** is wavelength dependent. The data obtained with 520-nm light are consistent with the presence of a single, relaxed, closed-shell singlet carbene intermediate, **^{1}EPC**, which isomerizes to 1-phenylpropenes and/or is captured with methanol to form an ether. The data obtained with 350-nm requires the presence of two alkene product forming intermediates; one that is methanol trappable (**^{1}EPC**) the other which is not. We propose that the non-trappable intermediate is hot, open-shell singlet carbene **^{1}EPC*** which traverses a conical intersection to form alkene products, in competition with relaxation to **^{1}EPC**, over a few tens of ps.

ACKNOWLEDGEMENTS

Support of this work by the National Science Foundation (NSF CHE- 1900643) is gratefully acknowledged. The authors also wish to thank Mr. Emmanuel Gonzalez for running various control experiments with trans-1-phenylpropene.

DATA AVAILABILITY STATEMENT

The data is available

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[9] In a typical experiment, 0.2 grams of propiophenone para toluene sulfonyl hydrazone was dissolved in 10 mL of anhydrous methanol in a 500 mL round bottom flask. To the flask was added one equivalent of 0.5M sodium methoxide in methanol solution. The methanol was removed by rotary evaporation leaving behind a white solid. The salt was heated under vacuum to produce **PDP** which collected on a cold finger. The red diazo compound was dissolved in anhydrous acetonitrile and used immediately in photochemical studies. PDP prepared this way produced H NMR and IR spectra consistent with the literature.

[10] Luzchem LED-GR lamp (https://www.luzchem.com/#)

[11] Trans 1-phenylpropene was identified by comparison with an authentic sample. The cis isomer and ether **E** were identified by comparison of the MS (obtained by GC-M) with literature spectra.

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[13] Samples were analyzed using an Agilent GC MS, model 5977B EI MS.

[14] Figures 1 and 2 report integrated GC peak areas and will be converted to absolute product ratios in the future.

[15] Southern New England Ultraviolet RPR 350 lamp.

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How to cite this article: J. Tokihiro, C. Fitzpatrick, M. S. Platz, *J Phys Org Chem* **2021**, e4298. https://doi.org/10.1002/poc.4298