Synthesis and Photochemistry of *trans,trans*-1,4-Diphenyl-1,3-butadiene-1-^{13}C

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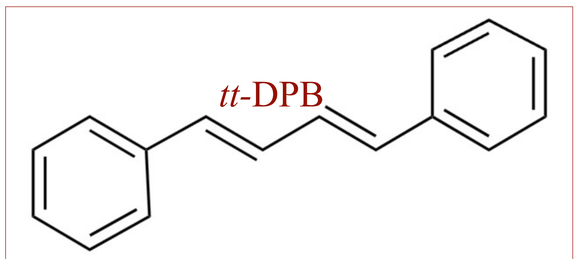
Abstract

The photochemistry and photophysics of the α,ω-diphenylpolyenes (DPPs) are of interest because they are considered to be models for the retinyl polyenes that are related to vitamin A and the visual pigments. ^{13}C substitution has a large effect on the photophysics of β-carotene. This work concerns the ^{13}C effect on photochemistry and photophysics of 1,4-diphenyl-1,3-butadiene (DPB). We are synthesizing *trans,trans*-1,4-diphenyl-1,3-butadiene-1-^{13}C (*tt*-DPB-^{13}C) in order to compare its photochemistry and photophysics. to that of ordinary *tt*-DPB. Specifically, processes that will be compared are the efficiencies of photoisomerization to *ct*-DPB isomer under direct and triplet sensitized excitation conditions, the fluorescence quantum yield and the excited state lifetimes. The importance of kinetic isotope and nuclear hyperfine effects will be evaluated.

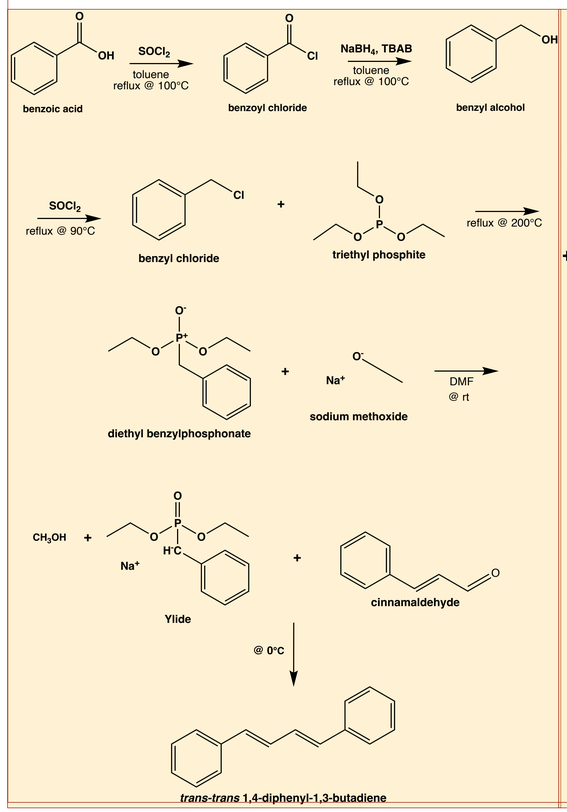


Introduction

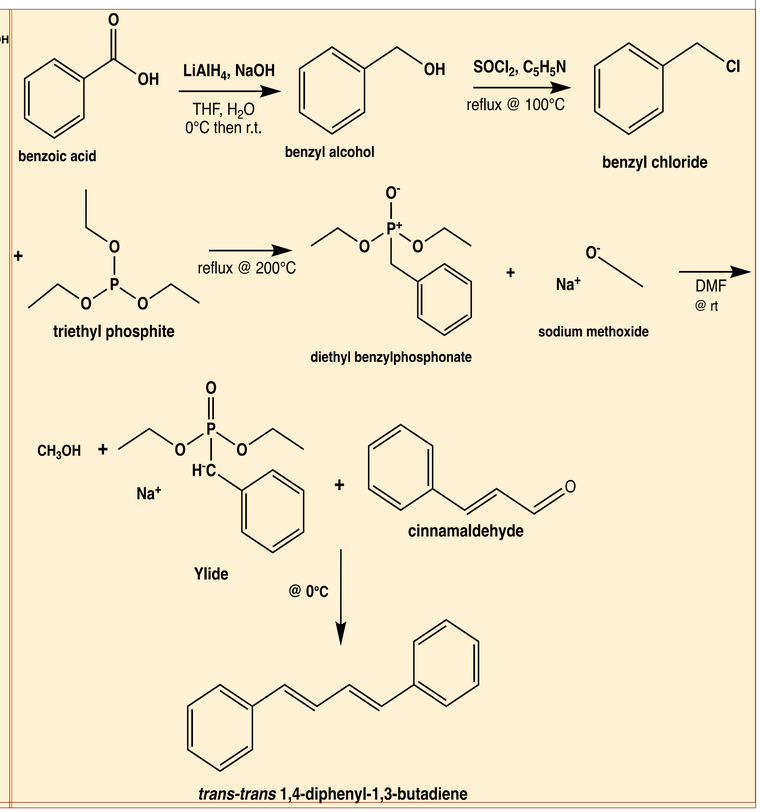
The final step of our *tt*-DPB synthesis is a Wittig reaction that employs cinnamaldehyde and benzyl chloride. ^{13}C benzoic acid substituted at the carbonyl C is commercially available and cinnamaldehyde is available in our laboratory. Thus, we need to convert the benzoic acid to benzyl chloride in order to prepare the Wittig reagent. The two synthetic schemes shown in Methods differ in the steps used to convert benzoic acid to benzyl chloride. We applied them first to ordinary benzoic acid.

Methods

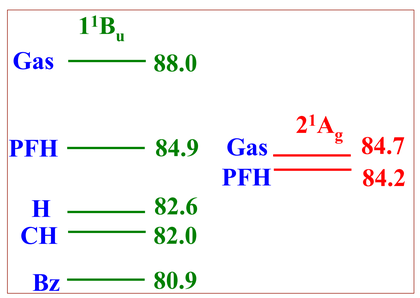
Synthetic Route 1



Synthetic Route 2

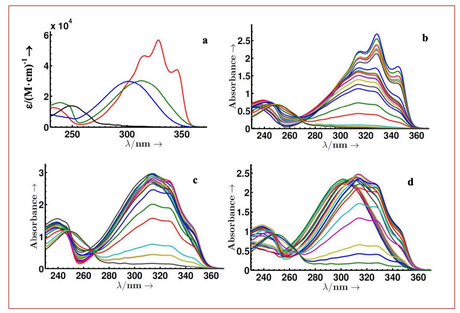


State Energy Diagram of tt-DPB in different media [1]



1. Saltiel et al. ACS Publications, **2006**, 1674-7

Photoisomerization Spectra of DPBs in EtOH [2]



2. Saltiel et al. ACS Publications, **2016**, 2832-40

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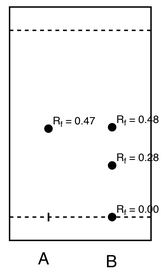
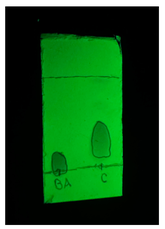
Results

- Synthetic route 1 gave a low yield of benzyl chloride (19% yield) and, consequently, a low yield of *tt*-DPB.
- A better yield of benzyl chloride (57% yield) was obtained using the synthetic sequence in synthetic route 2 and the led to an increased yield and the overall *tt*-DPB yield was satisfactory. We will use this approach for *tt*-DPB-^{13}C

Thin Layer Chromatography



KEY
A = Pure DPB in DCM
B = Synthetic Compound



KEY
BC = Benzoic Acid
C = Benzylic Alcohol

Future Work

This research is ongoing and the investigation of the photochemistry of ^{13}C substituted DPB will soon be conducted now that an improved synthetic route has been determined.

References

1. Saltiel, J.; Krishna, T. S. R.; Laohhasurayotin, S.; Ren, Y.; Phipps, K.; Yee, W. A.; Davis, P. H. Medium Effects on the Direct Cis-Trans Photoisomerization of 1,4-Diphenyl-1,3-butadiene in Solution. *J. Phys. Chem. A* **2011,** *115*, 2120-2129. http://dx.doi.org/10.1021/jp111482m
2. Saltiel, J.; Redwood, C. E. Photochemistry of the 1,4-Diphenyl-1,3-butadienes in Ethanol. Trapping Conical Intersections. *J. Phys. Chem. A* **2016**, *120*, 2832-2840. http://dx.doi.org/10.1021/acs.jpca.6b02330