Triarylphosphonium Salts as Radical Precursors Using Photoredox Catalysis

Andrew Boldt, Jonathan Ramirez, and Susan Stevenson*

Department of Chemistry, Carthage College
2001 Alford Park Drive, Kenosha WI 53140

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1. Background

- Traceless Activation Groups (TAGs) are currently studied with the use of photoredox catalysis conditions as an approach to access carbon radicals.

- Some previous research that has been conducted on the reactivity of specific TAGs such as phthalimides and *N*-hydroxyphthalimide esters.

Pratsch, G. P.; Lackner, G. L.; Overman, L. E. *J. Org. Chem.* **2015**, *80*, 6025-6036.

Chenneberg, L.; Baralle, A.; Daniel, M.; Fensterbank, L.; Goddard, J.-P.; Ollivier, C. *Adv. Synth. Catal.* **2014**, *356*, 2756-2762.

- Precedent for proposed reaction using triarylphosphonium salts as radical precursors.

Hedstrand, D. M.; Kruizinga, W. H.; Kellogg, R. M. *Tetrahedron Lett.* **1978**, *19*, 1255-1258

- Carbon-Phosphorous radical homolytic cleavage has yet to be thoroughly investigated and it opens a new scope of possible traceless activation groups.

2. Preliminary Experiments

- This result suggested that the triphenylphosphonium salts could act as radical precursors.

3. Reaction Optimization

Photocatalyst	equiv. Hünig's Base	Light Source	Counterion	Yield (%)
Ir[(dtbbpy)(ppy)2]PF6	6	Blue LED	Br-	56
5,10-Di(2-Naphthyl)-5,10-dihydrophenazine	6	Blue LED	Br-	15
Ru(bpy)3(PF6)2	6	Blue LED	Br-	8
3,7-Di(4-biphenyl)-1-naphthalene-10-phenoxazine	6	Blue LED	Br-	23
Ir[(dtbbpy)(ppy)2]PF6	1	Blue LED	Br-	65
Ir[(dtbbpy)(ppy)2]PF6	2	Blue LED	Br-	59
Ir[(dtbbpy)(ppy)2]PF6	4	Blue LED	Br-	<5
Ir[(dtbbpy)(ppy)2]PF6	6	Blue LED	Br-	75
Ir[(dtbbpy)(ppy)2]PF6	8	Blue LED	Br-	50
Ir[(dtbbpy)(ppy)2]PF6	6	White Light	Br-	43
Ir[(dtbbpy)(ppy)2]PF6	6	UV Light	Br-	8
Ir[(dtbbpy)(ppy)2]PF6	6	House Light	Br-	<5
Ir[(dtbbpy)(ppy)2]PF6	6	Blue LED	Br-	75
Ir[(dtbbpy)(ppy)2]PF6	6	Sunlight	Br-	33
Ir[(dtbbpy)(ppy)2]PF6	6	Blue LED	BF4-	69
Ir[(dtbbpy)(ppy)2]PF6	6	Blue LED	Cl-	75
Ir[(dtbbpy)(ppy)2]PF6	6	Blue LED	Br-	75
Ir[(dtbbpy)(ppy)2]PF6	6	Blue LED	I-	45

4. Purification with Merrifield Resin

Mechanism of Merrifield Resin and NaI interacting with triphenylphosphine.

5. Substrate Scope

6. Proposed Mechanism

7. Natural Product

Brittonin A

8. Reactivity of Benzyl Bromide

Electron Withdrawing Group Substrates

70% Dimerization
13% Reduction

48% Dimerization
22% Reduction

Electron Donating Group Substrates

84% Dimerization
< 1% Reduction

64% Dimerization
< 1% Reduction

81% Dimerization
< 1% Reduction

61% Dimerization
< 1% Reduction

9. Conclusions

- Substrates with electron withdrawing groups tend to favor a reduction reaction.

86% yield

- Substrates with electron donating groups favor a dimerization reaction.

89% yield

- The benzyl bromide substrates with electron withdrawing groups performed both reduction and dimerization reaction while the triphenylphosphonium salt substrates tended to only do the reduction.
- The benzyl bromide substrate with the electron donating groups tended to, overall, yield lower dimerization amounts than the triphenylphosphonium salt substrates.

10. Acknowledgements

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