Synthesis and Characterization of Novel 6-Substituted 4-Phenyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorins

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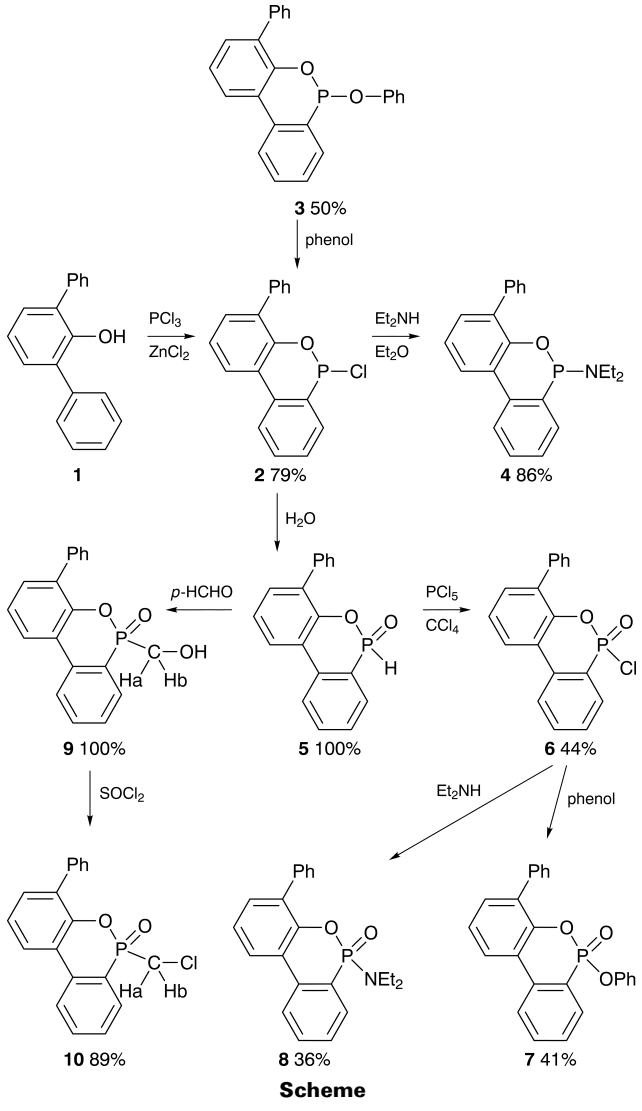
A series of novel 6-substituted 4-phenyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorins are synthesized, starting from the reaction of 2,6-diphenylphenol with phosphorus trichloride using zinc chloride as catalyst.

New phosphorus containing materials useful as additives or stabilizers in flame retardants constantly appear in the literature.[1–4] Only a few percent of phosphorus is needed in a polymer (1–2%) to suppress flammability.[5] One approach towards the synthesis of phosphorus containing materials has been described by Pastor and co-workers[9a] who studied the synthesis of the 6-chloro-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin ring system and its reaction with benzenethiols and phenols. In continuation of our work on 2,6-diphenylphenol (**1**) and its derivatives,[10] it was decided to synthesize 6-chloro-4-phenyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin (**2**). The reaction of alcohols with phosphorus trichloride is well known and has been used for many years in the synthesis of various materials,[11] but to the best of our knowledge this reaction has not been applied to 2,6-diphenylphenol. We herein report on the results of this study.



Scheme

The preparation of 6-chloro-4-phenyl-6*H*-dibenz[*c*,*e*][1,2]-oxaphosphorin (**2**) was attempted under a variety of conditions. The reaction was observed to proceed most efficiently when a $CaSO_4$ guard tube was employed as opposed to using an inert atmosphere; presumably the HCl formed during the course of the reaction aids in reaction catalysis when it is not blow away by N_2 or Ar.

We decided to concentrate our efforts on the synthesis of amino and phenoxy derivatives of 6-chloro-4-phenyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin (**2**). The reaction with phenol proceeded smoothly under a nitrogen atmosphere at 210 °C without catalyst to yield 6-phenoxy-4-phenyl-6*H*-dibenz-[*c*,*e*][1,2]oxaphosphorin (**3**), whilst with the reaction of diethylamine (Scheme) the order of addition is crucial to obtaining the required product, 6-diethylamino-4-phenyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin (**4**). 6-Chloro-4-phenyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin (**2**) must be added to excess diethylamine in diethyl ether, as the reverse reaction, addition of diethylamine to **2** results in liberation of gas, an indication that some decomposition may be taking place.

Reaction of **2** with boiling water yielded **5**, a further intermediate for several other derivatives. By extending this methodology to bisphenols, which are readily synthesized from 2,6-diarylphenols, it is feasible that new phosphorus containing bifunctional compounds can potentially be synthesized for the preparation of flame retardant materials.

Techniques used: HPLC, ^1H, ^{13}C, ^{31}P NMR, MS Schemes: 4
Refs: 17 Figs: 1 Tables: 3 (^1H, ^{13}C, ^{31}P NMR data)

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References cited in this synopsis

1 C. S. Reed, K. S. TenHuisen, P. W. Brown and H. R. Allcock, *Chem. Mater*., 1996, 8440.
2 G. Lapienis and S. Penczek, *Macromolecules*, 1977, **10**, 1301.
3 Y. Kawakami, K. Miyata and Y. Yamashita, *Polym. J*., 1979, **11**, 175.
4 (*a*) F. Millich and L. L. Lambing, *J. Polym. Sci., Polym. Chem. Ed*., 1980, **18**, 2155; (*b*) D. Derouet, T. Piatti and J. C. Brosse, *Eur. Polym. J*., 1987, **23**, 657; (*c*) F. Millich and C. E. Carraher Jr, *J. Polym. Sci. Part A, Polym. Chem*., 1970, **8**, 163.
5 S. Penczek and G. Lapienis, in *Handbook of Polymer Synthesis, Part B*, ed. R. Kricheldorf, Marcel Dekker Inc., New York, 1992.
9 (*a*) S. D. Pastor, J. D. Spivack and L. P. Steinhuebel, *Phosphorus Sulfur*, 1987, **31**, 71.
10 (*a*) A. S. Hay and R. F. Clark, *Macromolecules*, 1970, **3**, 533; (*b*) H. Yang and A. S. Hay, *Synthesis*, 1992, 467; (*c*) W-G. Kim, *PhD Dissertation*, 1992; (*d*) H. Yang, *PhD Dissertation*, 1992; (*e*) G. Barbiero, W-G. Kim and A. S. Hay, *Tetrahedron Lett*., 1994, **35**, 6199; (*f*) *ibid*, 5833; (*g*) A. S. Hay, H. Yang, W-G. Kim and G. Barbiero, *Polym. Prep., Jn*, 1994, **43**, 73; (*h*) G. Barbiero and A. S. Hay, *J. Polym. Sci. Part A, Polym. Chem*., 1996, **34**, 507.
11 G. W. Brown, in *The Chemistry of the Hydroxyl Group. Part 1*, Interscience, New York, 1971, 595.

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