Angewandte Chemie International Edition

Photopolymerizations

DOI: 10.1002/anie.201203648

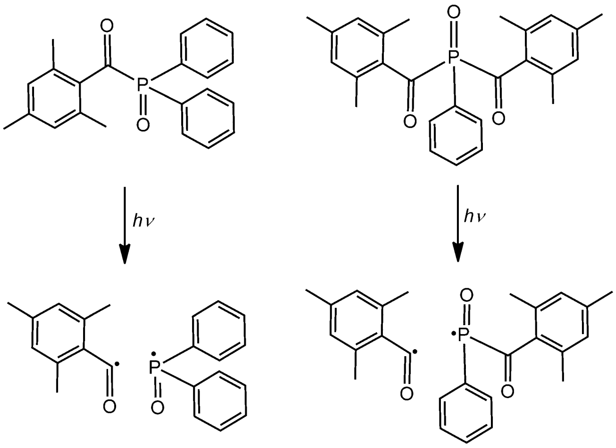
Novel Synthetic Pathways for Bis(acyl)phosphine Oxide Photoinitiators**

*Luca Gonsalvi and Maurizio Peruzzini**

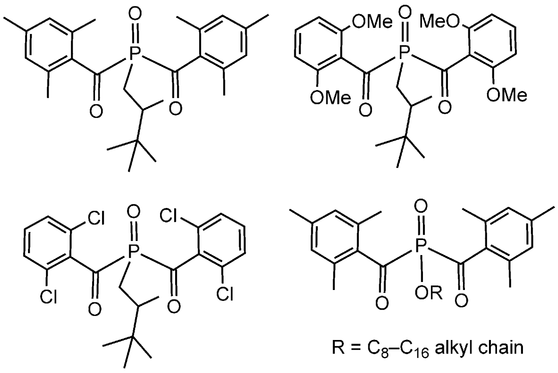
fabrics · phosphorus · photoinitiators · polymers · radical polymerization

For more than 30 years, photoinitiated polymerization has been widely used in industry for several applications, ranging from coatings, adhesives, inks, optical waveguides, microelectronics.[1] More recently, the development of high-tech materials, such as laser videodiscs, curing of acrylate dental fillings, and the manufacture of 3D objects has been possible also thanks to the discoveries of novel photoinitiators endowed with tailored properties, such as fast polymerization rates, high activity at room or lower temperatures, biological compatibility, and the possibility to use solar light instead of UV light to produce radicals in high quantum yields. This last issue is important for application on humans (dentistry, bone replacement), where UV light is known to cause damage to healthy tissues.[2] Of particular interest for industrial applications is also the possibility to use radiation curing of clear coatings, for example where a high degree of whiteness is required. One of the issues that needed to be solved is the shelf-life of these lacquering agents as no yellowing of the cured film is tolerated especially in the finished article and after prolonged exposure to solar light.[3]

A class of photoinitiators responding to most of the above-mentioned requirements is represented by monoacylphosphine oxides (MAPOs) and even more by the bis(acyl) analogues (BAPOs). These phosphorus-based compounds (Scheme 1) easily generate an acyl and a phosphinoyl radical by light irradiation, according to a Norrish type I cleavage mechanism, that is, the photochemical cleavage of aldehydes and ketones into two free radical intermediates. In this type of reaction, the carbonyl group accepts a photon and is excited to a photochemical singlet then triplet state through spin crossing. On cleavage of the α-carbon–carbon bond from either state, two radical fragments are obtained. BAPOs show superior efficiencies as photoinitiators as their molar extinction coefficients at 400 nm are usually higher than those of the corresponding MAPOs. Some of the most well-known BAPOs are solids, such as bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, commercialized by Ciba (now BASF) with the trade name IRGACURE 819.[4] This class of compounds is characterized by the presence of bulky substituents in *ortho* position, which is necessary to increase the solvolytic stability by shielding the carbonyl group from nucleophilic attack. Some examples of BAPOs based on this concept are shown in Scheme 2. The issues related to solubility, crystallization, or fine dust hazards have been solved either by introduction of alkyl groups directly onto the P atom, as in the case of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-



Scheme 1. Radical cleavage pathways of a MAPO (left) and a BAPO (right).



Scheme 2. Examples of BAPO structures.

---

[*] Dr. L. Gonsalvi, Dr. M. Peruzzini
Consiglio Nazionale delle Ricerche (CNR)
Istituto di Chimica dei Composti Organometallici (ICCOM)
Via Madonna del Piano 10, 50019 Sesto Fiorentino (Italy)
E-mail: maurizio.peruzzini@iccom.cnr.it
Homepage: http://www.iccom.cnr.it

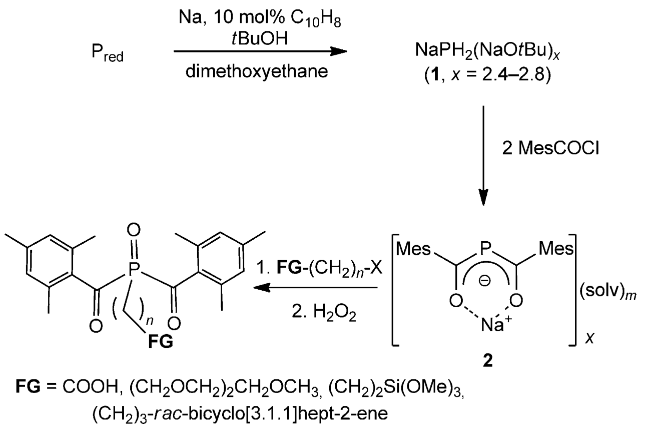
[**] We thank COST (Phoscinet) and MIUR (PRIN 2009) for supporting our research activity on phosphorus chemistry.

phosphine oxide and derivatives (Scheme 2),[5] or by using alkoxy groups with long alkyl chains, such as for bis(2,4,6-trimethylbenzoyl)-*n*-butoxyphosphine oxide or moving to superior analogues where the *n*-butyl group is replaced by $R = C_8–C_{16}$ alkyl chains.[6]

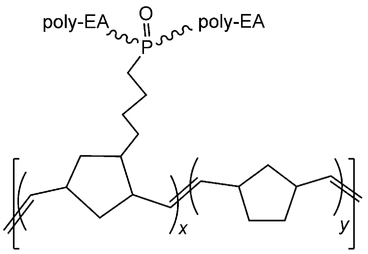
For the reasons explained above, a cheap, easy, and widely applicable synthetic pathway to a library of substituted BAPOs would be highly desirable.

The groups of Grützmacher and Levalois-Grützmacher have been interested in the chemistry of phosphorus derivatives and in coating technology during the last few years.[7] In their recent contribution,[8] a novel synthetic route to BAPOs is disclosed, together with examples of application of such compounds to stain-resistant fabrics and photopolymerization. The common approach requires the reaction of either a primary phosphine RPH_2 or the corresponding metalated derivative $RPH_{2-x}M_x$ with an acyl chloride; this approach has inherent safety problems and a low functional-group compatibility. Instead, it was shown that a useful phosphorus synthon such as $NaPH_2(NaOtBu)_x$ (**1**, $x = 2.4–2.8$) can be easily obtained by reaction of elemental phosphorus, sodium, and *tert*-butanol and can be used without prior isolation to react with mesitoyl chloride to give sodium bis(mesitoyl)phosphide (**2**) in high yields and purity as a crystalline solid. In a following step, **2** is reacted with a series of alkyl halides carrying suitable functional groups (FG) to give the intermediates FG-$(CH_2)_n$-$P(COMes)_2$, which are finally converted in very good yields to the corresponding BAPOs by oxidation with aqueous hydrogen peroxide (Scheme 3).

Examples of BAPOs so obtained include 2-[bis(2,4,6-trimethylbenzoyl)phosphoryl]acetic acid (BAPO-AA), bis(2,4,6-trimethylbenzoyl)-{[2-(2-methoxyethoxy)ethoxy]-ethyl}phosphine oxide (BAPO-PEG, water-soluble), bis(2,4,6-trimethylbenzoyl)-[3-tri(methoxysilyl)propyl]phosphine oxide (BAPO-TMESI) and bis(2,4,6-trimethylbenzoyl)-(*rac*-5norbornen-2-butyl)phosphine oxide (BAPO-NOR). Interesting examples of the versatility of such new BAPOs were also described. For example, BAPO-TMESI was grafted to cotton textile, then allowed to stand in an *n*-hexane solution of 1*H*,1*H*,2*H*,2*H*-perfluorodecylacrylate and irradiated for one hour, after which the stain-proof white cotton fabric so obtained showed hydrophobic and lipophobic properties, stable for more than half a year. In a second example, BAPO-NOR was used in a ring-opening metathesis polymerization (ROMP)-type polymerization reaction using a Grubbs catalyst, and a film-forming photoactive polymer was obtained. This compound is endowed of further reactivity upon irradiation, as it would be expected. By reacting a droplet of a solution of such material with ethyl acrylate (EA) on a silicon wafer and protecting the thin film with a copper grid, by SEM it was possible to demonstrate that radical EA polymerization occurred only where the light hit the film, in the form of cubic polymer blocks of about 100 μm width (Scheme 4).



Scheme 3. A novel synthetic route to functionalized BAPOs X = halogen, solv = solvent.



Scheme 4. Drawing of a photoactive branched polymer obtained by ROMP polymerization of BAPO-TMESI and EA at room temperature in the presence of Grubbs' catalysts $[RuCl_2(PCy_3)_2(CHPh)]$ (1 mol%).

These results open the way to a new class of BAPO-type photoinitiators bearing functional groups, which can be chosen for many different applications, as photoactive polymers and surfaces. The mildness of the applied synthetic method and the choice of widely available starting materials, which are safe and easy to handle, as well as the fact that purification or isolation of unstable reaction intermediates can be avoided, make this method highly competitive for use in the production of commodities on both small and large scale.

Received: May 11, 2012

---

[1] a) Y. Yagci, S. Jockusch, N. J. Turro, *Macromolecules* **2010**, *43*, 6245–6260; b) K. Dietliker, T. Jung, J. Benkhoff, H. Kura, A. Matsumoto, H. Oka, D. Hristova, G. Gescheid, G. Rist, *Macromol. Symp.* **2004**, *217*, 77; c) K. Dietliker, *A compilation of photoinitiators commercially available for UV today*, Sita Technology Ltd, Edinburgh, London, **2002**; d) J.-P. Fouassier, J. F. Rabek, *Radiation curing in Polymer Science and Technology*, Elsevier Applied Science, London, **1993**.

[2] a) K. Ikemura, T. Endo, *Dent. Mater. J.* **2010**, *29*, 481–501; b) K. Ikemura, K. Ichizawa, M. Yoshida, S. Ito, T. Endo, *Dent. Mater. J.* **2008**, *27*, 765–774; c) Y. J. Park, K. H. Chae, H. R. Rawls, *Dent. Mater. J.* **1999**, *15*, 120–127; d) K. D. Jandt, R. W. Mills, G. B. Blackwell, S. H. Ashworth, *Dent. Mater. J.* **2000**, *16*, 41–47.

[3] a) W. Rutsch, G. Berner, R. Kirchmayr, R. Hüsler, G. Rist, N. Bühler in *Organic Coatings—Science and Technology, Vol. 8* (Eds.: G. D. Parfitt, A. V. Patsis), Marcel Dekker, New York, **1986**, p. 175.

[4] a) S. Jockusch, I. V. Koptyug, P. F. McGarry, G. W. Sluggett, N. J. Turro, D. W. Watkins, *J. Am. Chem. Soc.* **1997**, *119*, 11495 – 11501; b) T. Sumiyoshi, W. Schnabel, A. Henne, P. Letchken, *Polymer* **1985**, *26*, 141 – 146; c) R. Shergill, M. Haberler, C. B. Vink, H. V. Patten, J. R. Woodward, *Phys. Chem. Chem. Phys.* **2009**, *11*, 7248 – 7256.

[5] a) W. Rutsch, K. Dietliker, D. Leppard, M. Köhler, L. Misev, U. Kolczak, G. Rist, *Prog. Org. Coat.* **1996**, *27*, 227 – 239.

[6] a) T. E. Bishop (DSM), World Patent WO 2012/012067A1, **2012**; b) G. Ullrich, B. Ganster, U. Salz, N. Moszner, R. Liska, *J. Polym. Sci. Part A* **2006**, *44*, 1686 – 1700.

[7] a) M. J. Tsafack, J. Levalois-Grützmacher, *Surf. Coat. Technol.* **2006**, *201*, 2599 – 2610; b) K. Kamlangkla, S. K. Hodak, J. Levalois-Grützmacher, *Surf. Coat. Technol.* **2011**, *205*, 3755 – 3762.

[8] A. Huber, A. Kuschel, T. Ott, G. Santiso-Quinones, D. Stein, J. Bräuer, R. Kissner, F. Krumeich, H. Schönberg, J. Levalois-Grützmacher, H. Grützmacher, *Angew Chem.* **2012**, *124*, 4726 – 4730; *Angew Chem. Int. Ed.* **2012**, *51*, 4648 – 4652.