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Extending the Scope of Bis(acyl)phosphane Oxides: New Derivatives

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Abstract: A series of novel bis(acyl)phosphane oxide (BAPO) photoinitiators has been synthesized and tested with respect to their efficiency in the initiation step of radical photopolymerizations. The transient absorption spectra of the phosphanoyl radicals obtained upon laser-flash photolysis reveal maxima at ca. 450 - 460 nm. Rate constants for the addition of these radicals to the double bonds of butyl acrylate, methyl methacrylate, 1-vinyl-2-pyrrolidone and styrene have been determined. All phosphanoyl radicals have been found to react most rapidly with styrene and slowest with butyl acrylate. Low fluorescence quantum yields of 0.1-0.3% reveal, that the studied BAPOs undergo efficient intersystem crossing followed by α -cleavage. The heat profiles of selected photo-polymerizations have been observed using a high-resolution infrared camera. Thermal imaging experiments show substantial monomer-dependent exothermicity. All BAPO derivatives can additionally act as electron acceptors as indicated by cyclic voltammetry and EPR spectroscopy.

Introduction

Bis(acyl)phosphane oxides (BAPOs) have been among the most successful initiators for photo-induced radical polymerizations.^[1–5] Photolysis of BAPOs leads to the formation of a phosphanoyl and a mesitoyl radical via triplet-state α -cleavage with high quantum yields (Scheme 1).^[6,7] Both radicals are efficient in initiating radical polymerizations. Still, enhancing the scope of BAPOs in terms of specific excitation wavelengths and solubility remains a challenge. To this end, several modifications, particularly at the phenyl substituents of the benzoyl moieties have been introduced.^[1] Advanced synthetic protocols however allow to attach various groups directly at the phosphorus atom of BAPOs.^[5,8–11] Here, we introduce five novel BAPO derivatives and besides describing their synthesis, we report on their optical

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spectra, α -cleavage reactions, the kinetics of their addition to double bonds, reduction potentials, and the EPR spectra of selected one-electron reduced species.



Scheme 1. Photolysis of BAPO derivatives 1–5 to give phosphanoyl radicals 1Pe–5Pe and the mesitoyl radical Mese. For the substituents R, see Scheme 2.

Results and Discussion

Synthesis and Characterization of BAPOs 1–5

The new BAPO derivatives 1-5 were synthesized as shown in Scheme 2 using a synthesis method which we reported briefly in a previous communication.^[5] The readily available sodium bis(mesitoyl)phosphide, Na[P(COMes)₂] (Mes 2,4,6-= trimethylphenyl) is reacted with a hydrocarbon halide, R-X, in dimethoxyethane (DME) as solvent in a temperature range between 25 °C and 60 °C to give cleanly the corresponding bis(acyl)phosphanes, R-P(COMes)₂, which are characterized by their characteristic ³¹P NMR chemical shifts in the range from 40 - 70 ppm [R = 1-phenylethyl: ³¹P NMR δ = 71.1 ppm; R = 1naphtylmethyl: ³¹P NMR δ = 52.9 ppm; R = 2-(2methoxyethoxy)ethyl: ³¹P NMR δ = 44.9 ppm; R = 3-bromopropyl: ³¹P NMR δ = 48.5 ppm; R = 3-(triethoxysilyl)propyl: ³¹P NMR δ = 50.8 ppm]. In some cases, longer reaction times are needed in order to achieve complete conversion. These bis(acyl)phosphanes were subsequently oxidized without prior isolation to give the bis(acyl)phosphane oxides 1-5 in mostly excellent overall yields. The oxidation of (EtO)₃Si-(CH₂)₃-P(COMes)₂ with H₂O₂ requires a solvent change from DME to toluene and careful removal of sodium iodide by extraction of the organic with aqueous potassium carbonate in order to achieve a satisfactory yield (63%) of 5 as wax-like yellow solid. The BAPO derivatives 1 and 2 are yellow solids with melting points at 178 °C and 119 °C, respectively, while 3-4 are obtained as yellow viscous oils. All compounds are thermally stable at least up to 150 °C.

The molecular structure of the 1-phenylethylderivative **1** was determined by X-ray diffraction with single crystals. A plot is shown in Figure 1. The unit cell of **1** contains both enantiomers of which only the R-enantiomer is shown. These two molecules interact via intermolecular π -stacking between the mesityl rings

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which are at about 3.7 Å distance from each other. As also observed for other BAPOs^[5] and the commercially available Irgacure[®] 819^[12] the distances between the carbon centers of the COMes groups and the phosphorus atom are unusually long [P1-C11 1.905(2) Å, P1-C1 1.895(1) Å] and even longer than the P-C21 bond [1.832(2) Å] although the latter contains a sp³ valence electron hybridized carbon center while the acyl groups contain sp² carbons to which shorter bonds are expected. In contrast to other BAPO derivatives which show skewed arrangements between the P=O unit and the COMes groups, the COMes groups in **1** are in almost parallel arrangement and point to the opposite direction with respect to the central P=O unit.



Scheme 2. Synthesis and skeletal diagrams of BAPOs 1–5 and of commercially available BAPO Irgacure® 819 (6).



Figure 1 Plot of the structure of **1**. Thermal ellipsoids are shown at a 50% probability level. For clarity, hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: P1-O1 1.476(1), P1-C21 1.832(2), P1-C11 1.905(2), P1-C1 1.895(1), O2-C1 1.217(2), O3-C11 1.214(2), O1-P1-C21 115.82(8), O1-P1-C11 114.89(8), O1-P1-C1 118.13(8), O3-C11-P1 115.5(1), O2-C1-P1 114.7(1), C21-P1-C11 102.54(8), C21-P1-C1 102.66(8), C11-P1-C1 100.42(8); torsion angles: O2-C1-P1-O1 165.3(1), O3-C11-P1-O1 172.3(1), O2-C1-P1-C21 36.6(2), O3-C11-P1-C21 45.8(2).

Spectroscopic Investigations

Absorption and Emission Spectra.

Figure 2 displays the UV-VIS absorption spectra of compounds 1–5 with intense π - π * absorptions around 315 -320 nm (1-4) and around 300 nm (5) and with distinct weak bands above 350 nm. The latter ones are attributable to $n-\pi^*$ transitions, responsible for an α -cleavage between the P(O)–C(O) bond leading to phosphanoyl (1P--5P-) and mesitoyl (Mes-) radicals (Scheme 1). Derivative 1 exhibits a band at 375 nm and the highestwavelength $n-\pi^*$ transition at 435 nm, higher than that of the wellestablished commercially available BAPO 6 (ca. 420 nm).[2] Naphthalene derivative 2 shows a somehow similar spectral shape as 1 whereas 3-5 possess less structured broad bands reaching to 430 nm. This observation shows that the substitution with a π system, which is separated from the P atom by a nonconjugating methylene group has a slight but not extended influence on the long-wave absorption of BAPOs. The substituents connected to the phosphorus center in 3-5 via sp³ carbon atoms behave essentially in an identical way (Figure 2, top). To test if the π substituents in **1** and **2** alter the photophysical reaction pathways in terms of allowing an extended reactivity in the singlet state, we have measured fluorescence spectra. Using an excitation wavelength of 373 nm, 1-4 show fluorescence with almost identical Stokes shifts at ca. 455 nm and very low quantum yields substantially below 0.4% (Figure 2, bottom and Table 1).



Figure 2. Top: UV-Vis absorption spectra of compounds 1-5 (two weak peaks in the spectrum of compound 5 at 486 nm and 582 nm are due to spectrometer artifacts); bottom: fluorescence emission spectra in acetonitrile normalized by absorbance at the excitation wavelength (373 nm). For fluorescence measurements, the absorbance of the solutions was kept at ca. 0.1 to avoid inner filter effects.

In contrast to **1–4**, BAPO **5** showed no detectable fluorescence, indicating that the excited singlet state of **5** preferentially reacts via intersystem crossing to the excited triplet state, or via internal conversion. Table 1 summarizes the fluorescence quantum yields (Φ_F) of **1–4** determined by comparison with the known quantum yield of 9,10-diphenylanthracene ($\Phi_{ST} = 0.95$ in cyclohexane) according to standard procedure.^[13] These results correspond to

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those obtained for related BAPOs and mono(acyl)phosphane oxides (MAPOs).^[6] Accordingly, for **1–5** efficient intersystem crossing and subsequent α -cleavage can be expected.

Table 1. Fluorescence quantum yields (Φ_F) of 1–5 in acetonitrile solutions
(A ≤ 0.1)

Compound ¹	Fluorescence quantum yield Φ_F (%)			
1	0.314 ± 0.026			
2	0.105 ± 0.001			
3	0.286 ± 0.003			
4	0.199 ± 0.005			
5 ^[a]	_			

[a] no detectable fluorescence

Phosporous-centered Radicals and their Reactivity.

Figure 3 shows transient optical absorption spectra obtained upon irradiation of **1–5** with a Nd-YAG laser at 355 nm.



Figure 3. Transient optical absorption spectra (absorbance change ΔA versus wavelength) of phosphanoyl radicals **1P**--**5P** · recorded 200 – 300 ns after laser excitation (355 nm, 8 ns) of **1–5** in argon-saturated acetonitrile solutions (absorbance at 355 nm ~ 0.3).

The bands centred at ca. 450 nm with lifetimes at a microsecond time scale are attributable to the phosphanoyl radicals **1P**•–**5P**•. Benzoyl-derived radicals like the mesitoyl radical **Mes**• do not reveal distinct absorptions in the VIS range and can only be observed by time-resolved IR and EPR spectroscopy.^[14,15] The absorption peaks around 450 – 460 nm are in agreement with the spectra of related BAPO-based phosphanoyl radicals.^[7,16]

The distinct absorptions of the phosphorus-centered radicals **1P--5P-** allowed us to determine the rate constants for their addition to butyl acrylate, methyl methacrylate, 1-vinyl-2-pyrrolidone and styrene via pseudo-first-order kinetic analysis.

Exponential fitting of the time decay traces obtained at various quencher concentrations, which were significantly higher than those of the radicals, yielded the pseudo-first-order rate constants (k_{exp}).^[7] The second order addition rate constants ($k_{monomer}$) are obtained from the slopes of their linear dependence on the monomer concentration. The corresponding curves are shown in Figure 4 for **1P**• (for **2P**•–**5P**• see the Supporting Information).



Figure 4. a) Decay traces for radical **1P**• in the presence of methyl methacrylate at three different concentrations (0.1 M, 0.3 M and 0.5 M) recorded following LFP of argon-saturated solutions of **1** in acetonitrile (excitation wavelength: 355 nm, monitoring wavelength: 465 nm; absorbance at 355 nm ~ 0.3). Experimental rate constants are obtained from exponential fitting of the time traces. b) Plots of the experimental rate constants k_{exp} of **1P**• versus monomer concentrations. Second order addition rate constants $k_{monomer}$ are obtained from the slopes.

The addition rate constants for **1P•-5P•** are summarized in Table 2 and Figure 5. Generally, the reactivity toward the monomers increases in the following order: butyl acrylate < methyl methacrylate < 1-vinyl-2-pyrrolidone < styrene. The highest reactivity with the most electron-rich alkene (styrene) suggests that phosphanoyl radicals show electrophilic behavior and prefer to react with electron rich quenchers.

In Table 2, the data for the novel compounds 1P - 5P are compared with the rate constants previously determined for radicals 6P and $Ph_2P(O)$, which are obtained by photolysis of

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commercially available Irgacure[®] 819 and Lucirin TPO[®], respectively.

Table 2. Second-order rate constants for the addition of phosphanoyl radicals **1P--5P**• to monomers and comparison with radicals **6P**• and Ph₂PO•. Errors are reported as twice the standard deviation from least squares analysis of the data.

	<i>k</i> monomer / 10 ⁷ (M ⁻¹ s ⁻¹)				
	butyl acrylate	methyl methacrylate	1-vinyl-2- pyrrolidone	styrene	
1P•	0.58 ± 0.02	1.01 ± 0.01	1.83 ± 0.04	4.45 ± 0.02	
2P•	1.28 ± 0.02	2.73 ± 0.02	5.42 ± 0.04	12.0 ± 0.10	
3P•	0.92 ± 0.10	1.63 ± 0.02	3.23 ± 0.06	6.19 ± 0.04	
4P•	0.93 ± 0.05	2.88 ± 0.06	6.07 ± 0.08	11.1 ± 0.13	
5P•	0.94 ± 0.01	2.19 ± 0.01	$3,64 \pm 0.07$	8.69 ± 0.09	
6P•	1.1 ^[a] 0.87 ± 0.02 ^[b]	-	-	-	
Ph₂PO•	2.8 ^[a] 1.98 ± 0.06 ^[b]	-	-	-	

[a] Reference [7]. [b] Reference [17]



Figure 5. Second-order rate constants $k_{monomer}$ for the addition of the phosphanoyl radicals **1P**•-**5P**• to butyl acrylate, methyl methacrylate, 1-vinyl-2-pyrrolidone, and styrene.

TR-EPR and ³¹P CIDNP-NMR Spectroscopy.

The structure-reactivity relationship of phosphanoyl radicals is influenced by the s-orbital character at the phosphorus center as well as by steric factors.^[7,17–20] The ³¹P hyperfine coupling constants (hfc), determined by (time-resolved) EPR, present insights into the s-orbital of the P center. Generally, the bigger the ³¹P hfc gets, the higher the s-orbital character of the spin carrying orbital and the more efficient is the addition of the P-centered radical to an acrylate double bond. This can be traced back to a correlation between the s-orbital character of the P-centered radical and the ³¹P hfc.^[17,21] BAPOs with alkyl substituents at the phosphorus atom generally reveal ³¹P hfcs of *ca.* 25–27 mT.^[17] Upon laser-flash photolysis (355 nm) of **1**, we have obtained the time-resolved EPR (TR-EPR, CIDEP) spectrum shown in Figure 6. It closely resembles the CIDEP spectra of related BAPOs

recorded in the 50 ns time regime.^[7,14,17,22] The phosphorus centred radical **1P**• gives rise to a doublet signal with a ³¹P hfc of 24.3 mT (g = 2.0042; calc. ³¹P hfc: 21.6 mT, see Supporting Information), whereas the mesitoyl radical **Mes**• appears as a rather narrow unresolved signal (g = 2.0005) in between the lines of the ³¹P doublet (Figure 6).

DFT calculations indicate that P-centered radicals **2P--5P**possess electronic structures rather closely resembling those of **1P**- (see Supporting Information). We therefore assume that the differences of the addition constants for **1P--5P**- (Figure 5) can be traced back to steric factors. Radical **1P**- is very likely the sterically most congested radical, caused by the methyl and phenyl substituent at the sp³ carbon center next to the phosphorus atom, contributing to the lower reactivity toward double bonds.



Figure 6. TR-EPR spectrum observed between 200-300 ns after laser flash photolysis (355 nm) of 1 (15 mM solution in toluene), ³¹P hfc: 24.3 mT (microwave frequency: 9.474 GHz).

The α -cleavage of the photoinitiators **1–5** and the corresponding follow-up reactions can be conveniently followed using ³¹P CIDNP spectroscopy. This NMR-based method provides information about reaction products formed via radical pairs.^[22] Radical-pairbased phenomena lead to enhanced absorptive or emissive NMR signals of reaction products, caused by a non-Boltzmann population of magnetic energy levels. Figure 7 illustrates the products detected via ³¹P CIDNP after photolysis of **2**.





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The radical pair **Mes**•/**P2**• can recombine regenerating the parent compound **2**. The benzoyl and the phosphanoyl radical may also form product **a** via P–O bond formation. Two phosphanoyl radicals **P2**• either yield **b** or **c** when reacting either via P,P or P,O recombination (Scheme 3). This reactivity pattern is general for all derivatives **1–5** (see Supporting Information for further spectra) and follows that reported for related photoinitiators.^[4,23]



Scheme 3. Reaction pattern of the primary radicals P. and Mes.

Following Polymerizations with a Thermal Camera

Another approach to explore the reactivity of BAPOs **1–5** was to follow the development of heat produced during polymerization reactions using a high-resolution infrared camera.^[24] Argon-saturated samples were successively irradiated with UV light pulses (1s, 5s and 10s) while thermal videos were recorded. The lamp was positioned above the sample to avoid the heating of the glass vial along the path of the camera. Selected thermograms of the polymerization of butyl acrylate initiated by compound **3** are shown in Figure 8a,b.



Figure 8. a,b) Glass vial containing a 1 mM solution of **3** in acetonitrile and butyl acrylate (1:1 v/v ratio) before (a) and after (b) 10 s irradiation with a Hg-Xe UV lamp. The line in the middle of the sample is caused by reflection. c) Plots of temperature change ΔT versus time t ($\Delta T = T_t - T_{initial}$). The three line styles represent the temperatures at the top, the center and the bottom of the sample volume, where the temperature was sampled. The irradiation times are indicated in the plot.

For comparison, a reference sample containing only butyl acrylate in acetonitrile was prepared, showing a basically uniform low temperature upon irradiation (see the Supporting Information). However, when the sample contains the photoinitiator and butyl acrylate, substantial heating is detected (red, yellow color, Figure 8a,b). The corresponding heat profiles (temperature change vs. time, Figure 8c) show an increase in temperature with increasing irradiation periods (1s, 5s and 10s). Three positions in the solution volume (top, center and bottom) were chosen to monitor the temperature change. Figure 8c shows that the heat distribution within the sample is almost uniform. This might be due to the short light path of approximately 2 cm. The temperature changes are significantly more pronounced for the sample containing butyl acrylate than for methyl methacrylate, which is in line with the enthalpy for the addition of butyl acrylates to C-centered radicals being higher than for methyl methacrylate.^[25] This indicates that the observed heat development is mainly caused by the exothermic polymerization chain growth rather than by the initiating process.

One-Electron Reduction Reactions of 1-5.

Beside serving as photoinitiators, BAPO and MAPO derivatives have been shown to serve as electron-transfer-active agents, in particular revealing (quasi) reversible one-electron reductions.^[26] Accordingly, we have recorded cyclic voltammograms of **1–5** (see Figure 9 and the Supporting Information). For all derivatives, we were able to observe quasi-reversible reduction steps (except **5**, see Table 3), whereas no distinguishable signals occurred in the oxidative region.



Figure 9. Cyclic voltammogram of **1** (1 mM in acetonitrile, supporting electrolyte: 0.1 M tetrabutylammonium tetrafluoroborate), recorded using a Pt working electrode, Pt counter electrode and Ag pseudo-reference electrode (100 mVs⁻¹ scan rate). Potentials are given vs. Fc⁺/Fc. The direction of the potential sweep is indicated by the arrow.

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The one-electron reduction potentials of **1–4**, leading to the formation of the corresponding radical anions reveal a rather narrow range between -1.75 V and -1.81 V (vs. Fc⁺/Fc). Accordingly, the aromatic substituents, which are separated by sp^3 C-centers from the P atom hardly influence the electron donating/accepting properties of BAPOs.

Table 3. Reduction potentials and CV peak separations for 1--5 and comparison with BAPO 6 (all values vs. Fc+/Fc)

	1	2	3 ^[c]	4	5 ^[d]	6 ^[c]
E _{1/2} [V vs.	-1.80	-1.77	–1.81 ^b	-1.80	-	-1.86
$\Delta E_{\rho} [V]^{[b]}$	0.10	0.16	0.097 ^b	0.14	-	0.089

[a] $E_{1/2} = (E_{pc} + E_{pa})/2$, E_{pc} and E_{pa} are cathodic and anodic peak potentials, respectively. [b] $\Delta E_p = (E_{pa} - E_{pc})$. [c] Data from ref.^[26] [d] Reduction waves are not clearly distinguishable.

Reductions with a K-metal mirror in THF under high vacuum led to well distinguishable EPR spectra attributed to $1^{-}-5^{-}$ (Figure 10 and Supporting Information). The spectra are dominated by ³¹P hfc of *ca.* 2.2 mT for all radical anions (Table 4). These values closely resemble those obtained for **6** and related derivatives.^[26]. This reveals that, as in the case of the P-centered radicals **1P**--**5P**•, the delocalization of the charge and the spin in $1^{-}-5^{-}$ is basically confined to the acyl (mesitoyl) substituents and character of the additional substituents at the P(V) center does not have a marked effect on the electronic properties in **1**-**5** at the radical-anion stage.



Figure 10. EPR spectrum of **2** obtained after K-metal reduction in THF (T = 200 K), together with its simulation (microwave frequency: 9.473 GHz).

Table 4. ³¹ P hfcs and g factors determined for 1 -5 compared to 6						
	1	2	3	4∙-	5	6 ^[a]
³¹ P hfc [mT]	2.24	2.29	2.19	2.18	2.22	2.20
g factor	2.004 ±0.001	2.004 ±0.001	2.004 ± 0.001	2.004 ± 0.001	2.004 ± 0.001	2.004

[a] Taken from ref.^[26].

Conclusions

We have shown that the presented synthetic procedure allows a very convenient access to a variety of new P-substituents in bis(acyl)phosphane oxides. This approach can be used to adjust the hydrophilicity or lipophilicity of BAPO derivatives or allows introducing groups which can be utilized as anchors to specific environments (e.g. polyoxyethylene groups, Si-containing substituents, possibly intercallating π systems). These modifications do not deteriorate the excellent photoinitiating and electron-donating properties of this class of compounds, sustaining the character of 1P--5P being decisive for their role as polymerization initiating P-centered radicals. The substitution patterns presented in this work have a slight effect on the positioning and the extinction coefficients of the $n-\pi^*$ bands, however a systematic behavior cannot be established. We plan now to investigate how to utilize the (photo)chemistry of the conveniently accessible radical anions 1'--5'-.

Experimental Section

General Instrumentation. NMR spectra were recorded on Bruker Avance 500 MHz spectrometer with respect to ¹H. Chemical shifts are reported in ppm relative to TMS and residual chemical shifts of the solvent as the secondary standard (for ¹H and ¹³C) and 85% H₃PO₄ (for ³¹P). Coupling constants (*J*) are given in Hertz (Hz) as absolute values. The multiplicity of the signals is indicated as s, d, t, or m for singlets, doublets, triplets, or multiplets, respectively.

IR-spectra were measured on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer using the ATR technique. The relative intensities of the signals are indicated as s = strong, m = medium and w = weak.

UV/VIS spectra were measured on a UV/VIS/NIR Lambda 19 spectrometer in 10 mm Quarz cuvettes (200 - 800 nm).

Mass spectra were taken by the MS-service center of the Institute of Organic Chemistry (LOC) of the ETH Zürich on a ESI-Q-TOF system (maXis, Brucker Baltonics, Germany) coupled to an Agilent 1200 system (Agilent Ltd., Deutschland). The data were analyzed and evaluated using the Data Analysis 4.0 software package of Bruker Daltonics, Germany. Highly resolved mass spectra confirm the purity of **1–5**, since elemental analysis did not give satisfactory results for BAPO derivatives.

The thermal properties of the compounds were investigated with simultaneous thermogravimetry (TG) and differential thermoanalysis (DTA) using a NETZSCH STA 409 apparatus. The measurements were performed under an atmosphere of argon in an Al₂O₃ crucibles. The heating rate was 2.0 or 10.0 °C/min within a temperature range from 20 to 500 °C.

Single crystals suitable for X-ray diffraction were protected with polyisobutylene oil in glovebox then transferred to the goniometer of an Oxford XCalibur, a Bruker SMART APEX or a Bruker APEX diffractometer;

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MoKa radiation (0.71073 Å). The structure was solved and refined using SHELXS.

Synthesis of 1-5. All manipulations with air or moisture sensitive compounds were performed in a Standard vacuum line using dried glass ware. All reactions were performed under an argon atmosphere in dried and argon saturated solvents. Sodium/benzophenone was used for drying toluene, diethylether and sodium, benzophenone, tetraglyme was used for drying DME. Air sensitive compounds were stored and weighed in a glove box from M Braun (Lab master 130 bzw. 150B-G). Chemicals were used as purchased from ABCR, Acros, Aldrich or Fluka.

1-phenylethyl-PO(COMes)₂ (1). 5.016 g Na[P(COMes)₂] x 0.5 DME (12.721 mmol) and 1.7 mL 1-phenylethylbromide (2.295 g, 12.401 mmol) were dissolved in 10 mL DME in a 50 mL Schlenk flask. After heating the reaction mixture to 60 °C for 24 h, a complete conversion to the corresponding phosphane is indicated by ³¹P NMR spectroscopy (δ = 71.1 ppm). 10 mL toluene were added and the suspension was cooled in an ice bath. Subsequently, 4.5 mL 30% H₂O₂ (approx. 4 equivalents) were added to achieve the quantitative oxidation to the bis(acyl)phosphane oxide 1.30 mL Dichloromethane (DCM) were added and the resulting mixture was first extracted with 10 mL deionized water, then with 10 mL of a saturated aqueous Na₂CO₃ solution, then with 10 mL of a saturated aqueous NaCl solution, and finally again with 10 mL deionized water. The combined aqueous phases were extracted with 20 mL DCM. Afterwards the combined organic phases were dried over Na₂SO₄. After filtration and evaporation of all volatiles under vacuum at 60 °C (oil pump, 1 mbar) 4.927 g (11.035 mmol, 87 % yield) of BAPO 1 are obtained as yellow solid. 1H-NMR (400.13 MHz, C₆D₆): δ = 7.56–7.55 (m, 4H, Ph), 7.29–7.27 (m, 2H, Ph), 7.08-7.05 (m, 4H, Ph), 6.68 (s, 4H, Mes), 6.53 (s, 4H, Mes), 4.38-4.31 (m, 2H, CH), 2.50 (s, 12H, o-Me), 2.09 (s, 3H, p-Me), 2.04 (s, 12H, o-Me), 1.98 (s, 3H, p-Me), 1.62 (dd, ³J_{HH} = 7.20 Hz, ³J_{PH} = 16.01 Hz, 3H, CH₃). - ¹³C{¹H}-NMR (100.6 MHz, C₆D₆): δ = 215.8 (d, J = 50.0 Hz, CO), 215.3 (d, J = 54.6 Hz, CO), 141.5 (Mes-C⁴), 141.2 (Mes-C⁴), 138.5 (d, J = 4.4 Hz, Ph-C¹), 137.8 (d, J = 41.7 Hz, Mes-C¹), 136.5 (d, J = 40.0 Hz, Mes-C¹), 137.6 (Mes-C²), 136.5 (Mes-C²), 130.1 (d, *J* = 6.3 Hz, Ph-C²), 129.8 (Mes-C³), 129.6 (Mes-C³), 129.1 (Ph-C⁴), 127.8 (d, J = 1.8 Hz, Ph-C³), 38.8 (d, J = 52.7 Hz, PCH), 21.3 (p-CH₃), 21.2 (p-CH₃), 20.4 (o-CH₃), 19.7 (o-CH₃), 17.2 (d, J = 2.1 Hz, C<u>C</u>H₃). – ³¹P{¹H}-NMR (162.0 MHz, C₆D₆): δ = 31.1. – ³¹**P-NMR** (162.0 MHz, C₆D₆): δ = 31.1 (dq, ³J_{PH} = 8.8 Hz, ²J_{PH} = 15.7 Hz). - IR (ATR [cm⁻¹]): 2961.2 (w), 2928.3 (w), 2361.8 (w), 1662.3 (m), 1606.5 (m), 1493.5 (w), 1452.0 (m), 1420.3 (w), 1378.1 (w), 1261.7 (w), 1196.7 (s), 1146.3 (m), 1094.4 (m), 960.3 (w), 880.8 (m), 849.3 (s), 783.4 (s), 768.0 (s), 741.5 (m), 705.2 (s), 649.5 (m), 616.8 (m). - UV/VIS (ACN [nm], ε [l mol⁻¹cm⁻¹]): 416 (438, shoulder), 400 (469, max), 368 (790, max), 318 (2945, max), 245 (6845, shoulder), < 200 (42063, max). - MS (ESI): m/z = 447.2076 (MH+). - DTA/TG: melting point 178°C, decomposition > 210°C - X-Ray Diffraction: CCDC 1536239.

1-naphtyImethyI-PO(COMes)₂ (2). 3.893 g Na[P(COMes)₂] x 0.5 DME (9.896 mmol) and 1.726 g degassed chloromethyInaphthalin (9.771 mmol) were dissolved in 10 mL DME in a 50 mL Schlenk flask. After stirring the reaction mixture at room temperature for 4 hours, a complete conversion to the corresponding phosphane is indicated by ³¹P NMR spectroscopy (δ = 52.9 ppm). 10 mL toluene were added and the suspension was cooled in an ice bath. Subsequently, 5 mL 30% H₂O₂ (approx. 5 equivalents) were added. After 1 hour at 50 °C, the quantitative oxidation to the bis(acyl)phosphane oxide 2 was achieved. After addition of 50 mL DCM, the reaction mixture was first extracted with 20 mL deionized water, then with 20 mL of a saturated aqueous Na₂CO₃ solution, then with 20 mL of a saturated aqueous phases were extracted with 20 mL DCM. Afterwards the combined organic phases were dried over Na₂SO₄. After

filtration and evaporation of all volatiles under vacuum (oil pump, 1 mbar) 3.900 g (8.083 mmol, 82 % yield) of BAPO 2 are obtained as yellow solid. ¹**H-NMR** (300.13 MHz, C_6D_6): $\delta = 8.43$ (d, J = 8.43 Hz, 1H, Naph), 7.69– 7.60 (m, 3H, Naph), 7.44-7.18 (m, 3H, Naph), 6.55 (s, 4H, Mes), 4.23 (d, J = 12.31 Hz, 2H, PCH₂), 2.20 (s, 12H, o-Me), 2.00 (s, 6H, p-Me). -¹³C{¹H}-NMR (75.5 MHz, C₆D₆): δ = 216.3 (d, J = 51.3 Hz, CO), 140.9 (Mes-C⁴), 136.4 (d, J = 40.8 Hz, Mes-C¹), 136.2 (d, J = 0.6 Hz, Mes-C²), 134.1 (d, J = 2.1 Hz, Naph), 132.8 (d, J = 4.0 Hz, Naph), 129.8 (d, J = 6.3 Hz, Naph), 129.2 (Mes-C³), 128.4 (Naph), 128.2 (Naph), 127.1 (d, J = 8.5 Hz, Naph), 126.4 (Naph), 125.9 (Naph), 125.3 (d, J = 3.2 Hz, Naph), 125.2 (d, J = 1.2 Hz, Naph), 30.5 (d, J = 49.7 Hz, PCH₂), 20.7 (p-CH₃), 19.5 (o-CH₃). $-{}^{31}$ P{¹H}-NMR (121.5 MHz, C₆D₆): δ = 22.9. $-{}^{31}$ P-NMR (121.5 MHz, C_6D_6): $\delta = 22.9$ (t, J = 12.2 Hz). – IR (ATR [cm⁻¹]): 2922.7 (w), 1663.6 (m), 1634.9 (w), 1605.3 (m), 1509.0 (w), 1419.4 (w), 1377.3 (w), 1295.2 (w), 1264.0 (w), 1214.4 (m), 1195.9 (s), 1148.4 (w), 1030.8 (w), 965.0 (w), 893.0 (w), 857.4 (m), 820.4 (m), 795.1 (m), 775.9 (s), 743.9 (m), 730.2 (w), 720.2 (m), 707.8 (w), 678.0 (w), 660.8 (w), 621.6 (w). - UV/VIS (ACN [nm], ε [Imol⁻¹cm⁻¹]): 417 (269, shoulder), 396 (486, shoulder), 368 (757, max), 319 (3810, max), 292 (11676, shoulder), 282 (13081, max), 250 (9287, shoulder), 243 (11594, max), 239 (11588, max), 220 (60579, max), < 215 (< 60000, max). -MS (ESI): m/z = 483.2084 (MH⁺). - DTA/TG: melting point 119 °C, decomposition > 170 °C.

MeO(CH2CH2O)2-PO(COMes)2 (3). 4.048 g Na[P(COMes)2] x 0.5 DME (10.290 mmol) and 1.7 ml degassed bromodiethylene glycol (2.290 g, 11.885 mmol) were dissolved in 10 mL DME in a 50 mL Schlenk flask. After stirring the reaction mixture at 80 °C for 5 days, ³¹P NMR spectroscopy (δ = 44.9 ppm) indicates the complete conversion to the corresponding phosphane. The suspension was concentrated under vacuum (oil pump, 1 mbar), the residue suspended in 20 mL of ethanol, and the reaction mixture cooled to 0 °C in an ice bath before 1.2 mL 30% H_2O_2 (approx. 1 equivalent) were added to achieve quantitative oxidation. The reaction mixture was concentrated to dryness under vacuum and suspended in 20 mL of diethylether. Na₂SO₄ was added to remove residual water, the mixture filtered, and the clear filtrate concentrated under vacuum and 60 °C. The product 3 was obtained in 96 % yield (4.407 g, 9.915 mmol) as yellow oil. ¹H-NMR (300.13 MHz, C₆D₆): δ = 6.68 (s, 4H, Mes), 3.74 (dt, J_{PH} = 15.31 Hz, J_{HH} = 6.45 Hz, 2H, PCH₂CH₂), 3.34 (t, J = 4.95 Hz, 2H, CH₂), 3.17 (t, J = 4.95 Hz, 2H, CH₂), 3.11 (s, 3H, OMe), 2.59-2.51 (m, PCH₂), 2.51 (s, 12H, o-Me), 2.09 (s, 6H, p-Me). - ¹³C{¹H}-NMR (75.5 MHz, C₆D₆): δ = 215.9 (d, J = 55.8 Hz, CO), 140.7, (Mes-C⁴), 136.5 (d, J = 41.7 Hz, Mes-C¹), 136.4 (Mes-C²), 129.2 (Mes-C³), 71.5 (<u>CH</u>₂OMe), 70.11 (<u>CH</u>₂CH₂OMe), 63.6 (d, J = 4.8 Hz, PCH₂CH₂), 58.2 (OMe), 28.2 (d, J = 55.1 Hz, PCH₂), 20.8 (p-Me), 19.9 (o-Me). $- {}^{31}P{}^{1}H{}$ -NMR (121.5 MHz, C₆D₆): δ = 25.0. – ³¹**P-NMR** (121.5 MHz, C₆D₆): δ = 25.2–24.8 (m). – IR (ATR [cm-1]): 2921.3 (w), 2868.2 (w), 1721.0 (w), 1672.8 (m), 1607.3 (s), 1451.8 (m), 1421.4 (m), 1380.4 (w), 1295.8 (w), 1245.8 (w), 1196.2 (s), 1105.1 (s), 1034.0 (m), 957.6 (w), 886.5 (m), 849.9 (s), 770.6 (m), 741.4 (m), 699.8 (w), 619.2 (m). - UV/VIS (ACN [nm], ε [Imol⁻¹cm⁻¹]): 394 (477, shoulder), 361 (603, max), 316 (18689, max), 291 (8021, max), 239 (6221, shoulder), < 200 (30299, max). - MS (ESI): m/z = 445.2157 (MH+). -**DTA/TG**: decomposition > 150 °C.

3-bromopropyI-PO(COMes)₂ (4). 5.312 g Na[P(COMes)₂] x 0.5 DME (13.502 mmol) and a tenfold excess of 15 ml degassed 1,3-dibromopropane (29.835 g, 147.786 mmol) were dissolved in 20 mL DME in a 50 mL Schlenk flask. After stirring the reaction mixture at 60 °C for 16 hours, ³¹P NMR spectroscopy (δ = 48.5 ppm) indicates the complete conversion to the corresponding phosphane. Oxygen (5.0, Pangas) was

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bubbled through the solution for 30 minutes at room temperature. Subsequently, 50 mL of diethylether were added and this mixture was extracted first with 15 mL distilled water, then two times with 15 mL of a saturated aqueous Na₂CO₃ solution, and finally with 15 mL distilled water. The combined aqueous phase was extracted once with 50 mL diethylether and the combined organic phases were dried over Na₂SO₄. After filtration, the filtrate was concentrated to dryness on the vacuum at 60 °C. The residue was purified by flash-chromatography using hexane/ethylacetate 1:2 as eluent to give 5.2 g (83%) of product 5 as yellow oil. ¹H-NMR $(300.13 \text{ MHz}, C_6D_6): \delta = 6.66 \text{ (s, 4H, Mes)}, 2.95 \text{ (t, } J = 6.30 \text{ Hz}, 2\text{H}, CH_2Br),$ 2.46-2.30 (m, 2H, PCH2), 2.41 (s, 12H, o-Me), 2.15-1.98 (m, 2H, PCH₂CH₂), 2.08 (s, 6H, *p*-Me). $- {}^{13}C{}^{1}H$ -NMR (75.5 MHz, C₆D₆): $\delta = 216.4$ (d, J = 54.0 Hz, CO), 141.0, (Mes-C⁴), 136.5 (d, J = 40.9 Hz, Mes-C¹), 135.8 (Mes-C²), 129.3 (Mes-C³), 33.4 (d, J = 14.4 Hz, CH₂Br), 25.1 (d, J = 54.1 Hz, PCH₂), 25.0 (d, J = 3.4 Hz, PCH₂CH₂), 20.8 (p-Me), 19.6 (o-Me). $-{}^{31}P{}^{1}H{}$ -NMR (121.49 MHz, C₆D₆): $\delta = 26.1. - {}^{31}P$ -NMR (121.49 MHz, C₆D₆): δ = 26.4–25.9 (m). – **IR** ATR [cm⁻¹]): 2922.7 (w), 1735.7 (w), 1672.0 (m), 1607.3 (s), 1431.9 (m), 1378.6 (w), 1295.9 (w), 1241.6 (m), 1212.6 (s), 1193.9 (s), 1147.3 (m), 1035.5 (m), 958.6 (w), 888.0 (m), 849.7 (s), 757.1 (m), 736.9 (m), 619.0 (m). - UV/VIS (ACN [nm], ε [Imol⁻¹cm⁻¹]): 394 (466, shoulder), 364 (552, max), 315 (2330, max), 294 (7283, max), 241 (5858, shoulder), < 200 (30959, max). - MS (ESI): m/z = 463.1037 (MH⁺). - DTA/TG: decomposition > 170 °C.

Synthesis of 3-(triethoxysilyl)propyl-PO(COMes)₂ (5). 4.995 g Na[P(COMes)₂] x 0.5 DME (12.697 mmol) and 4.228 g 1,3iodopropyltriethoxysilane (4.228 g, 12.726 mmol) were dissolved in 20 mL DME in a 50 mL Schlenk flask. After stirring the reaction mixture at 60 °C for 2 hours, ³¹P NMR spectroscopy (δ = 50.8 ppm) indicates the complete conversion to the corresponding phosphane. The suspension was concentrated to dryness under vacuum and subsequently 10 mL toluene and 10 mL Diethylether were added. The resulting suspension was extracted two times with 10 mL of degassed aqueous K_2CO_3 (pH = 10). Then the mixture was cooled in an ice bath and a small amount of K₂CO₃ was added to assure saturation with K₂CO₃. Afterwards 1.8 mL H₂O₂ (30%, ca. 1.4 equiv.) were slowly added in order to oxygenate the phosphane to 5. 20 mL Diethylether were added before the suspension was extracted with two times 20 mL saturated aqueous Na₂CO₃, two times 10 mL saturated aqueous NaCl, and once with 10 mL of degassed aqueous K_2CO_3 (pH = 10). The combined aqueous phase were extracted once with 20 mL diethylether, the combined organic phases were dried over Na₂CO₃, all insoluble parts were filtered off, and the filtrate dried under vacuum at 60 °C. This treatment gave 4.367 g product 5 (7.988 mmol, 63%) in form of a yellow wax.¹H-NMR (400.13 MHz, C₆D₆): δ = 6.66 (s, 4H, Mes), 3.82 (q, J = 6.94 Hz, 6H, OCH₂CH₃), 2.55–2.45 (m, 2H, PCH₂), 2.48 (s, 12H, o-Me), 2.18–2.08 (m, 2H, PCH₂CH₂), 2.08 (s, 6H, *p*-Me), 1.23 (t, J = 7.00, 6H, OCH₂C<u>H</u>₃), 0.80 (t, J = 7.80 Hz, 2H, SiC<u>H</u>₂). - ¹³C{¹H}-NMR (100.6 MHz, C₆D₆): δ = 217.5 (d, J = 53.4 Hz, CO), 141.0 (Mes-C⁴), 137.3 (d, J = 40.2 Hz, Mes-C¹), 136.2 (Mes-C²), 129.6 (Mes-C³), 58.7 (OCH₂CH₃), 29.8 (d, J = 52.3 Hz, PCH₂), 21.2 (p-CH₃), 20.2 (o-CH₃), 18.7 (OCH₂<u>C</u>H₃), 16.2 (d, J = 4.3 Hz, PCH₂CH₂), 12.9 (d, J = 12.4 Hz, SiCH₂). $- {}^{31}P{}^{1}H$ -NMR (162.0 MHz, C_6D_6): $\delta = 29.0. - {}^{31}P-NMR$ (162.0 MHz, C_6D_6): $\delta = 29.1-28.9$ (m). - IR (ATR [cm⁻¹]): 2974.5 (w), 2920.0 (w), 2878.6 (w), 2359.5 (w), 1669.6 (w), 1608.7 (m), 1441.2 (w), 138131 (w), 1293.9 (w), 1253.1 (w), 1211.2 (m), 1197.7 (m), 1164.7 (w), 1149.0 (m), 1075.8 (s), 1033.3 (m), 956.7 (m), 887.3 (m), 863.0 (w), 849.0 (m), 804.0 (m), 781.5 (m), 748.4 (m), 732.2 (m), 698.5 (w), 645.3 (w), 618.1 (m). - UV/VIS (ACN [nm], ε [Imol⁻¹cm⁻¹]): 394 (359, shoulder), 365 (443, max), 303 (4643, max), 290

(5813, max), 243 (5486, shoulder), < 200 (33497 max). – **MS** (ESI): m/z = 547.2632 (MH⁺). – **DTA/TG**: melting point 37 °C, decomposition > 190 °C.

Materials and Solvents for Spectroscopic Investigations. The solvent acetonitrile was obtained from Roth (purity \ge 99.9 %). Butyl acrylate (purity \ge 99.0 %), methyl methacrylate (\ge 99.0 %), 1-vinyl-2-pyrrolidone (\ge 97.0 %) and styrene (\ge 99.5 %) were obtained from Fluka and used as received. The photoinitiator Irgacure® 819 (6) was obtained from BASF. All experiments were performed at ambient temperature.

Emission Spectroscopy. Solutions of the photoinitiators in acetonitrile were prepared so that the absorbance at and above the excitation wavelength was ≤ 0.1 . The absorption spectra were recorded using a UV-3101 PC UV-VIS-NIR spectrometer (Shimadzu, Japan). Fluorescence emission spectra were recorded with a FluoroMax-2 spectral-fluorimeter (Horiba Scientific, Japan) at the excitation wavelength of 373 nm. Fluorescence quantum yields (Φ_F) of **1–5** were determined by comparison with the known quantum yield of 9,10-diphenylanthracene ($\Phi_{ST} = 0.95$ in cyclohexane).^[13] Emission spectra were measured for each compound and for the standard at four different concentrations. The wavelength integrated intensities of these spectra were plotted versus the absorbance at the excitation wavelength (A_{373}). From the slopes of these plots, the fluorescence quantum yields were calculated according to equation 1,^[13]

$$=\Phi_{ST}\frac{I}{I_{ST}}\frac{A_{ST}}{A}\frac{\eta^2}{\eta_{ST}^2}$$
(1)

where *I* is the integrated emission intensity, *A* the absorbance at 373 nm and η the refractive index of the solvent (acetonitrile for the BAPOs and cyclohexane for the standard ST).

 Φ_{F}

Laser Flash Photolysis Experiments. The experiments were performed on a LKS80 Laser Flash Photolysis Spectrometer (Applied Photophysics, UK). Samples were excited with the frequency tripled light from the Spitlight Compact 100 (InnoLas, Germany) solid state Nd:YAG laser at 355 nm (pulse duration: 8 ns, energy: 10 mJ/pulse). The concentration of the BAPOs in the acetonitrile solutions was adjusted to achieve the absorbance of ~ 0.3 at 355 nm. The solutions were purged with argon for 10 minutes before the measurement. The transient absorption spectra were recorded in a quartz cuvette (1 cm x 1 cm) using a flow system driven by a peristaltic pump (0.012 L min⁻¹). Rate constants for the addition of the phosphanoyl radicals to the monomer double bonds were determined in pseudo-first-order experiments; solutions of the compounds in acetonitrile containing monomer-concentrations in the range of 0.5 M to 0.025 M and providing absorbance of ~ 0.3 at 355 nm were prepared. Static solutions were saturated with argon and then measured. The decay of the phosphanoyl radicals was recorded at the absorption maximum determined from the transient absorption spectra.

TR-EPR Spectroscopy. Continuous-wave time-resolved (TR) EPR experiments were performed on a Bruker ESP 300E X- band spectrometer (unmodulated static magnetic field) equipped with a 125 MHz dual channel digital oscilloscope (Le Croy 9400). As the light source, the frequency triplet light of a Nd:YAG laser was used (InnoLas Spitlight 400, 355 nm, operating at 20 Hz, ca. 7 mJ/pulse, 8 ns). The setup is controlled by the fsc2 software developed by Dr. J. T. Toerring (Berlin). Spectra were recorded by acquiring the accumulated (50 accumulations) time responses to the incident laser pulses at each magnetic field value of the chosen field range (field steps: 0.5 G). Argon-saturated solutions in toluene (~ 15 mM in photoinitiator concentration) were pumped through a quartz flat cell

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positioned in the cavity of the EPR spectrometer using a flow system (flow rate: 2-3 mL min^-1).

³¹P CIDNP-NMR Spectroscopy. The experiments were carried out with a 200 MHz Bruker AVANCE DPX spectrometer equipped by a custom-made CIDNP probe head. A Quantel Nd-YAG Brilliant B (355 nm, ~60 mJ/pulse, pulse length ~8–10 ns) operating at 20 Hz served as light source. mJ/pulse, pulse length ~ 8–10 ns) operating at 20 Hz was employed as the light source. The timing sequence of the experiment consists of a series of 180° radiofrequency (RF) pulses (applied to suppress the normally present NMR intensities), the laser flash, the 90° RF detection pulse and the acquisition of the FID. The spectra were recorded with ¹H decoupling and "dummy" CIDNP spectra employing the same pulse sequence but without the laser pulse were always measured. Samples were prepared in deuterated benzene and deoxygenated by bubbling with argon before the experiment.

Thermal Imaging. Thermographic experiments were conducted with the VarioCAM high resolution infrared camera (InfraTec, Germany). Solutions of the photoinitiators in acetonitrile were mixed with the monomers in a 1:1 v/v ratio. The samples were purged with argon for 15 minutes. The polymerization was initiated by light pulses generated by a Hg-Xe-lamp (Hamamatsu, Japan) positioned above the vial containing the sample (see figure 5). Pulses of various durations (1s, 5s, 10s) were employed. Thermograms were recorded in order to monitor the heat profile of the reactions (recording frequency: 10 Hz). The data were evaluated using the IRBIS remote 3.0 software.

Cyclic Voltammetry. Cyclic voltammograms (CVs) were obtained with a PG580 potentiostat (Uniscan, UK) using a standard three-electrode electrochemical cell with platinum disk working (WE) and counter (CE) electrodes and a silver wire pseudoreference electrode (RE). Approximately 1mM sample solutions were prepared in acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate supporting electrolyte and purged with argon for 10 min before each experiment. CVs were recorded at 100 mV/s scan rate. All potentials are given vs. Fc*/Fc, which was used as internal reference and are uncorrected from Ohmic drop.

EPR Spectroscopy. Radical anions of **1-4** were prepared in a special three-compartment EPR sample tube connected to the vacuum line. K-metal mirror was sublimated to the wall of the tube and THF (ca. 0.4 mL) was freshly condensed to dissolve the investigated compound. The sample was successively degassed by three freeze-pump-thaw cycles and sealed under high vacuum. Reductions were performed by contact of the THF solution of the parent molecule with the K-metal mirror in the evacuated sample tube. A Bruker X-band spectrometers, ESP 300 (equipped with an ENDOR unit, 12.5 kHz field modulation), both with an EUROTHERM temperature control unit, was used to record the cw-EPR spectra. Typical experimental conditions for the EPR spectra were 2mW microwave power and 0.03 mT field modulation. Spectra were analyzed with WinEPR and SimFonia software provided by the manufacturer of the spectrometer as well as with WinSim a public domain program.^[27]

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Novel bis(acyl)phosphane oxide (BAPO) derivatives have been synthesized and tested with respect to their efficiency as radical photoinitiators and electron acceptors.

Phosphorous-based Photoinitiators*

Anna Eibel, Max Schmallegger, Michal Zalibera, Alex Huber, Yasmin Bürkl, Hansjörg Grützmacher,* and Georg Gescheidt*

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Extending the Scope of Bis(acyl)phosphane Oxides: New Derivatives