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CONVENIENT UNIMOLECULAR SOURCES OF ARYLOXYL RADICALS.
III – PHOTOLYSIS OF BIS(ARYLOXY)PHOSPHINE AZIDES.

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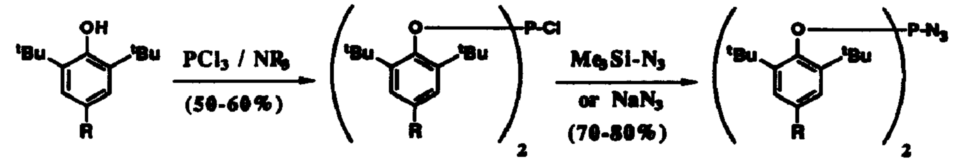
Abstract: Photolysis of sterically hindered bis(aryloxy)phosphine azides in solution, frozen matrix, or neat solid states leads to facile unimolecular production of aryloxyl radicals.

While many methods exist for generation of aryloxyl radicals by bimolecular chemistry, few unimolecular methods exist. We have previously described the use of aryloxyoxalyl chlorides and *tert*-butyl-peroxides,[1] as well as diaryl oxalates,[2] for unimolecular generation of aryloxyl radicals of various structure. Togo *et al.*[3] subsequently described a related process based on the photochemical Barton reaction. These methods give varying degrees of photochemical efficiency, side reactions, and ability to be used in non-fluid media. A primary goal of investigating these compounds is to maximize precursor stability and efficiency in generating aryloxyl radicals. In this paper, we describe the photolysis of sterically hindered bis(aryloxy)phosphine azides (BAPAs) as an effective method for generating aryloxyl radicals.

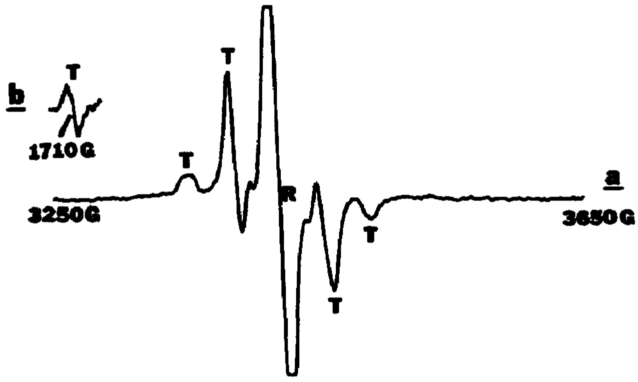
The BAPAs 1-3 were synthesized by reaction of the appropriate 2,6-di-*tert*-butyl-phenols with PCl3 in trialkylamine solvents, followed by treatment with trimethylsilyl azide in benzene or sodium azide in ethanol, followed by careful crystallization in the absence of direct light with wavelength <300 nm. Sterically demanding groups were important in stabilizing any radicals generated under solution conditions. Synthesis of BAPAs without sterically demanding groups on the phenol was impeded by both hydrolytic and thermolytic instability of the intermediate bis(aryloxy)chlorophosphines (BACPs) during isolation, a limitation upon which we are continuing to work in an effort to generalize this methodology.



(BACPs)

1 R = *tert*-Butyl
2 R = Me
3 R = OMe

Figure 1. X-band ESR spectrum from photolysis of BAPA **1** at 77 K.

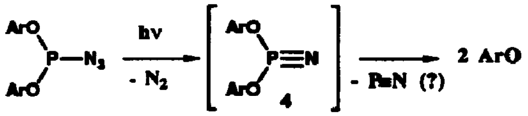


Curve a is from 77 K photolysis of neat powdered 1 at 254 nm through quartz. Spectrum at 77 K, 9.58 GHz; peaks marked T attributed to radical pair triplet signals, peak marked R assigned to monoradical signal. Inset curve b is the half-field region from the spectrum in curve a, with the same abscissa scale, but offset by 1560 G, and with a five-fold expansion of the ordinate (signal intensity) axis.

BAPAs **1-3** are crystalline solids,[4] and are stable in the absence of strong direct light. Upon heating, **1** gave a slightly bluish melt, which upon resolidification showed a strong, asymmetric electron spin resonance (ESR) peak at $g \approx 2$. The same result was obtained from 2 min of photolysis of solid **1** with 254 nm light either at room temperature or at 77 K. The ESR peak was stable for weeks, which in combination with the observed blue color suggested formation of 2,4,6-tri-*tert*-butylphenoxyl radical. This was confirmed by photolysis of **1** in degassed isopentane to give an azure solution with the typical ESR spectrum previously observed for 2,4,6-tri-*tert*-butylphenoxyl radical ($g = 2.0053$, $a_{meta} = 1.9$ G).[5] Photolysis of **2** at 77 K in glassy isopentane gave a blue-green matrix with the ESR spectrum[1,6] as expected for 2,6-di-*tert*-butyl-4-methylphenoxyl radical ($g = 2.0055$, $a_{methyl} \approx 11$ G, $a_{meta} < 2$ G). Photolysis of **3** in glassy isopentane at 77 K, followed by thawing, gave a magenta solution with an ESR radical spectrum at $g = 2.0044$ as typically observed[7] for 2,6-di-*tert*-butyl-4-methoxyphenoxyl radical. We saw no conclusive evidence of phosphorus-centered radicals, although such radicals have been generated from BACPs in other work via reduction by alkali metals.[8]

Photolysis of BAPAs also can give rise to triplet radical pair spectra, as is observed[9] for diaryl oxalates. Irradiation of **1** as a neat powder at 254 nm and 77 K gave a typical triplet ESR spectrum with $g_{\perp} = 2.0018$, $g_{\parallel} = 2.0033$, $|D/hc| = 0.0065\ \mathrm{cm}^{-1}$, $|E/hc| < 0.0003$ G, (in addition to a central monoradical resonance, Figure 1). The relative intensities of the central radical peak and the outer triplet peaks depends upon the photolysis duration and conditions. Also, the triplet spectrum is stable for weeks in the absence of oxygen at room temperature. Such remarkable stability is observed only in a very few cases[9-10] from photochemically generated radical pairs. Presumably the triplet spectrum is due to interaction between two 2,4,6-tri-*tert*-butylphenoxyl radicals generated from the same molecule of 1, but trapped in proximity by the crystalline matrix. The zero field splitting (zfs) parameter $|D/hc|$ is given by $(1.299\ g_e\ \mathrm{cm^{-1}\text{-}Å^3})/r_{ij}^3$ in the simple dipolar approximation, where "g_e" is the free electron g-value, and r_{ij} is the interelectronic distance in angstroms. By this formula, a pair of interacting electrons 7.35 Å apart would give the observed zfs. The situation is actually not so simple, since the phenoxyl radicals are delocalized.[9] Efforts to fit the observed zfs to our previously used model[9] for interacting delocalized radicals were unsuccessful. Our model assumes that the phenoxyl groups released by photolysis of 1 do not move from the positions they occupy in the unphotolyzed precursor. For all energetically reasonable starting conformers of 1, we found that any no-motion placement of phenoxyl moieties predicts a zfs much larger than observed. Apparently, substantial relative movement of the phenoxyl moieties occurs in the lattice after photocleavage of 1, although the nature of this movement is not yet clear.

Deazetation of the BAPAs should lead to an intermediate phosphonitrile 4. We carried out IR and ^{31}P-NMR studies aimed at determining the nature of the phosphorus containing species formed in this process. Photolysis of 1 as a Nujol or Fluorolube mull at 10 K (using an APD Cryogenics Displex setup) led to disappearance of the -N_3 peak in the IR spectrum. In addition to peaks attributable to *tert*-butylphenoxy, we found a very weak peak at 1350 cm^{-1} which is similar to the position reported[11] for P≡N. Upon warming the matrix, the peak at 1350 cm^{-1} disappeared, and the fingerprint region of the spectrum became indistinct and broadened. Studies of P≡N in krypton have shown a similar behavior upon warming,[11] attributed to formation of polymers and oligomers of P≡N. Although this evidence is suggestive of formation of P≡N, the IR spectra were difficult to interpret due to their complexity and the weakness of the peak at 1350 cm^{-1}. As a result, although formation of P≡N seems to be required in this chemistry, we could not confidently identify it as a photolysate.



Attempts to identify phosphorus-containing products in the photolysate by ^{31}P NMR were not successful. Compound 3 was irradiated in glassy methylcyclohexane at 77 K and thawed to allow decay of the product radicals. There was a distinct diminution of the NMR signal for **3** at δ160, but the only new signal was a very broad band centered near δ0, which provided no clue to the nature of the by-products. If phosphonitrile **4** were present, a signal downfield of δ200 would have been expected based on the value of δ246 for $((iso\text{-Pr})_2\text{-N})_2P\equiv N$.[12] $P\equiv N$ is expected to have a signal downfield of δ100 (δ275[13] and δ122[14] have been proposed). However, $P\equiv N$ would have only a fleeting existence in fluid media,[11] and no ^{31}P NMR data have been found for its decomposition products. The search for phosphorus-containing products in this photochemical process will be continued.

The use of azidophosphines and related functional groups offers a promising new method for the photochemically efficient generation of aryloxyl radicals under a variety of unimolecular conditions. We hope to develop the scope of this photogeneration chemistry further in future work.

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4. Physical characterization of azides, recrystallized from spectral grade acetone. (1) mp 157-158°C, Anal. Calcd for $C_{36}H_{58}N_3O_2P$: C 72.57 H 9.81 N 7.05. Found C 72.10 H 9.62 N 6.52. ^{31}P-NMR ($CDCl_3$, 32.4 MHz) δ 158.5. IR(KBr) 2100 cm^{-1}. UV-VIS (λ_{max}(log[ε]),EtOH): 206 nm (4.75). (2) mp 117-118 °C, Anal. Calcd for $C_{30}H_{46}N_3O_2P$: C 70.42 H 9.06 N 8.21. Found C 70.07 H 8.94 N 8.00. ^{31}P-NMR ($CDCl_3$, 32.4 MHz) δ 160.0. IR(KBr): 2110 cm^{-1}. UV-VIS (λ_{max}(log[ε]),MeCN): 203 nm (4.74). (3) mp 118-119°C, Anal. Calcd for $C_{30}H_{46}N_3O_4$: C 66.30, H 8.47 N 7.73. Found C 65.81, H 8.71 N 7.65. ^{31}P-NMR(acetone-d_6), 32.4 MHz) δ 161. IR(KBr): 2105 cm^{-1}. UV-VIS (λ_{max}(log[ε])], MeCN]): 210 nm (4.79), 286(3.65).
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