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Chemistry of singlet oxygen with arylphosphines

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Abstract—The chemistry of singlet oxygen with a variety of arylphosphines has been studied. Rates of singlet oxygen removal by *para*-substituted arylphosphines show good correlation with the Hammett σ parameter ($\rho=-1.53$ in $CDCl_3$), and with the Tolman electronic parameter. The only products for the reactions of these phosphines with singlet oxygen are the corresponding phosphine oxides. Conversely, for *ortho*-substituted phosphines with electron-donating substituents, there are two products, namely a phosphinate formed by intramolecular insertion and phosphine oxide. Kinetic analyses demonstrate that both products are formed from the same intermediate, and this allows determination of the rate ratios for the competing pathways. Increasing the steric bulk of the phosphine leads to an increase in the amount of insertion product. VT NMR experiments show that peroxidic intermediates can only be detected for very hindered and very electron-rich arylphosphines.

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1. Introduction

The chemistry of singlet dioxygen with heteroatoms, i.e., organic sulfides[1–5] and, more recently, phosphines[5–9] has been the subject of numerous papers, as these reactions posses rather complicated mechanisms. Elucidation of the nature of reactive intermediates, and, ideally, their direct observation, have been a major goal of these studies. Such intermediates are of fundamental interest, as they should be even better oxidants than singlet dioxygen itself. In particular, many kinetic and trapping studies have been carried out to determine the nature of the peroxidic intermediates formed during the photooxidation of organic sulfides. The oxidation of phosphines has attracted somewhat less attention. An early paper by Bolduc and Goe[11] suggested an open zwitterionic species formed as a primary intermediate, but trapping studies by Sawaki and co-workers[7] indicated that the primary intermediate in the photooxidation of triphenyl phosphines and tributyl phosphite is electrophilic. This is in contrast with the nucleophilic behavior of the persulfoxide intermediate in the photooxidation of organic sulfides.[1] Ab initio calculations by Foote and co-workers[8] suggested a cyclic phosphadioxirane intermediate, which would indeed be expected to behave as an electrophile. Arylphosphines have also been investigated as fuel-stabilizers for jet fuels, and very recently Beaver and co-workers have provided strong evidence that phosphadioxiranes may play a key role during this antioxidant activity.[12,13] Arylphosphines represent an interesting target for studying reactive intermediates and reaction channels, since their electronic and steric parameters are well defined and can be varied in a systematic manner. Electronic parameters that can be used to assess the donor abilities of arylphosphines include Hammett constants as well as the Tolman electronic parameter.[14] The latter parameter is given by the CO stretching frequency of the carbonyl group trans to the phosphine in a Ni complex of the type $Ni(CO)_3(PR_3)$. The stronger the electron-donating ability of the phosphine, the stronger the backbonding to the trans CO ligand, and hence the lower the CO stretching frequency. Chemical properties of arylphosphines are also influenced by the steric bulk of the aryl groups, and the cone angle of a phosphine ligand has long been used as a measure of its bulk.[14] The cone angle is obtained by taking a space-filling model of the $MP(R_3)$ group. The metal is the apex of the cone, and the entire ligand forms the actual cone.[4,5] We have reported the special case of tris(*ortho*-methoxyphenyl)phosphine: the exceptionally large steric bulk of this phosphine (cone angle of 205°)[15] slows down the reactions of peroxidic intermediate so that it can be directly observed at very low temperatures by VT NMR. ^{31}P and ^{17}O NMR measurements at $-80°$ strongly suggest that the peroxidic intermediate is a three-membered ring containing a phosphorus and two oxygen atoms, that is, a phosphadioxirane.[10] We report herein, the products for the reaction of a variety of arylphosphines with singlet oxygen, kinetic data, as well as attempts to observe and characterize products and peroxidic intermediates of these reactions. Electronic parameters for the different arylphosphines were simply varied by using different substituents in the *para* position; the cone angle is the same for all of these *para*-substituted phosphines, namely 145°.

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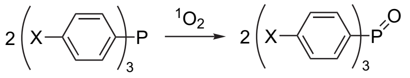
Conversely, steric parameters were changed by employing different substituents in the *ortho* position. All of these arylphosphines are unreactive with triplet oxygen, thus allowing kinetic investigations of their reactions with singlet oxygen.

2. Results and discussion

2.1. Photooxidation of *para*-substituted arylphosphines

Reaction of singlet oxygen at room temperature with *para*-substituted arylphosphines **1**–**5** leads to the corresponding phosphine oxides in quantitative yield (Eq. 1).



1 X = MeO
2 X = H
3 X = F
4 X = Cl
5 X = CF_3

(1)

Total rate constants of singlet oxygen removal (k_T) by phosphines **1**–**5** have been measured by luminescence quenching experiments in a deuterated benzene and chloroform. The k_T values and the corresponding σ values as well as the Tolman electronic parameters for various phosphines are summarized in Table 1.

The logs of the k_T values (k_{Subst}/k_H) yield a good correlation with the Hammett σ parameters; the Hammett plot gives a negative slope of −1.53 in $CDCl_3$ (Fig. 1), and −1.93 in C_6D_6 (r^2=0.987). Since there are three aryl rings per phosphine, the actual ρ values for the electronic effect of one aryl ring are −0.51 and −0.64, respectively. The reason for the larger value in benzene is unclear at the moment, although it may simply be caused by the smaller dielectric constant of benzene, similar to what has recently been predicted by ab initio calculations for solvent effects on ρ values in benzhydryl cations.[16] The negative ρ value is in agreement with the electrophilic character of the initial singlet oxygen attack on the arylphosphine. The magnitude of ρ for one arylphosphine is smaller than that for the corresponding attack of singlet oxygen on aryl sulfides in thioanisoles.[17]

A plot of the k_T values versus the Tolman electronic parameter also gives a good linear correlation (r^2=0.971) for phosphines **1**–**4** (the Tolman electronic parameter for phosphine **5** has not been determined). Since the Tolman electronic parameter is a measure of the σ-donating ability of the phosphine, it is apparent that in the absence of steric variation, the σ-donation of the arylphosphine to the empty degenerate π* MO of the singlet oxygen molecule determines the reaction rate of singlet oxygen with the *para*-substituted arylphosphines.

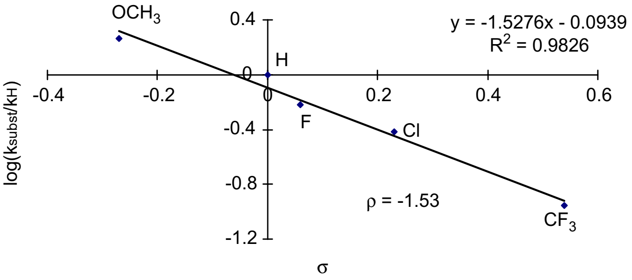


Figure 1. Hammett plot for the reaction of *para*-substituted arylphosphines with singlet oxygen.

In the absence of physical quenching, the value of k_T is the rate of formation of the peroxidic intermediate (i.e., the phosphadioxirane). For all *para*-substituted arylphosphines, the corresponding phosphine oxide was the only major product observed by ^{31}P NMR (other products such as the corresponding phosphinates[7] were 1% or less). In order to determine whether or not all of the peroxidic intermediates lead to the formation of the reaction products or whether loss of dioxygen from the intermediate (indirect physical quenching) is a major process, competition experiments have been carried out. These competition experiments are done under continuous irradiation of a solution containing a singlet oxygen acceptor with a known chemical reaction rate constant and the arylphosphine that is being studied. Thus the two substrates compete for one reactive intermediate (i.e., singlet oxygen) that is produced under steady-state conditions. 9,10-Dimethylanthracene (DMA) was used as a singlet oxygen acceptor in these experiments. DMA is known to interact with singlet oxygen by chemical reaction only. As reference values, we have used k_T values for the reaction of DMA with singlet oxygen from the recent literature,[9] namely $2.5\pm0.1\times10^7\ M^{-1}\,s^{-1}$ in $CDCl_3$ and $2.9\pm0.2\times10^7\ M^{-1}\,s^{-1}$ in deuterated benzene. Loss of DMA and compounds **1**–**5** was monitored by ^1H and ^{31}P NMR. The relative reaction rate ratio for the k_r values of

Table 1. Summary of kinetic data, electronic, and steric parameters for phosphines

Phosphine	k_T in $CDCl_3$ $(M^{-1}\,s^{-1})\times10^6$	k_r in $CDCl_3$ $(M^{-1}\,s^{-1})\times10^6$	k_T in C_6D_6 $(M^{-1}\,s^{-1})\times10^6$	k_r in C_6D_6 $(M^{-1}\,s^{-1})\times10^6$	k_o/k_i in $CDCl_3$	σ_p	Cone angle (deg)[d]	Tolman electronic parameter (cm^{-1})[d]
$(p\text{-}CH_3OC_6H_4)_3P$[a]	14.9±1.6	32.4±1.2	33.1± 4.3	59.4±0.9		−0.27	145	2066.1
$(C_6H_5)_3P$[b]	8.1±0.3	16.2±1.6	10.5± 0.6	21.5±1.1		0	145	2068.9
$(p\text{-}FC_6H_4)_3P$[b]	4.9±0.2	11.0±1.0	5.5±0.2	11.0±0.8		0.06	145	2071.3
$(p\text{-}ClC_6H_4)_3P$[b]	3.1±0.2	7.1±0.7	3.3±0.3	8.0±0.8		0.23	145	2072.8
$(p\text{-}CF_3C_6H_4)_3P$[c]	0.9±0.05	2.2±0.3	0.9±0.06	2.6±0.6		0.54	145	
$(o\text{-}CH_3C_6H_4)_3P$[b]	5.4±0.5		8.0±0.2		80±7		194	2066.6
$(o\text{-}CF_3C_6H_4)_3P$[c]	0.1±0.01	Not measurable		Not measurable			205	
$(o\text{-}CH_3OC_6H_4)_3$[a]	2.8±0.4		5.0±0.2		25±3		205	2058.3

[a] Ref. 9.
[b] This work.
[c] Ref. 10.
[d] Ref. 14.

the phosphine and the singlet oxygen acceptor (i.e., DMA) was obtained from the equation of Higgins and co-workers.[18]

$$\frac{\log\left\{[\text{Arylphosphine}]^{\mathrm{f}}/[\text{Arylphosphine}]^{0}\right\}}{\log\left\{[\text{DMA}]^{\mathrm{f}}/[\text{DMA}]^{0}\right\}} = \frac{k_{\mathrm{r}}(\text{Arylphosphine})}{k_{\mathrm{r}}(\text{DMA})} \qquad (2)$$

For all of the *para*-substituted arylphosphines (compounds **1**–**5**), the rate of formation of the corresponding phosphine oxides (k_r) is twice the rate of singlet oxygen removal k_T, both in benzene and chloroform. Thus indirect physical quenching (loss of dioxygen from the periodic intermediate) is not detectable, and all of the phosphadioxirane intermediates are converted to product. We also conducted competition experiments in benzene (Table 1), and found that the reaction rates (i.e., k_r values) follows the same trend, but are somewhat larger than in chloroform. The reason for this increase is unclear at this time.

2.2. *ortho*-Substituted arylphosphines

Generally, k_T values are lower for these phosphines compared to their *para*-substituted counterparts. It is particularly instructive to compare the k_T values for tris(*ortho*-methoxyphenyl)phosphine (**6**), tris(*ortho*-tolyl)phosphine (**9**), and triphenylphosphine (**2**). Despite the fact that the electron density at the phosphorus atom is decreasing from **6** to **9** to **2** (cf. the Tolman electronic parameters), the corresponding k_T values are increasing. This illustrates the strong sensitivity of reactions of singlet oxygen with arylphosphines to steric effects, similar to what has been observed for organic sulfides.

We have recently reported an unusual intramolecular oxidation pathway during the photooxidation of tris(*ortho*-methoxyphenyl)phosphine (**6**). In addition to tris(*ortho*-methoxyphenyl)phosphine oxide (**7**), significant amounts of *ortho* methoxyphenyl di(*ortho*-methoxyphenyl)phosphinate (**8**) are obtained. In fact, at low concentration, this intramolecular oxidation product becomes the major reaction product. We have demonstrated that there exists a phosphine cone angle dependence for this reactive channel of the putative peroxidic intermediate by comparison with the corresponding *meta* and *para* isomers, which do not form the insertion product.[9] We now report that the behavior of the tris(*ortho*-tolyl)phosphine (**9**) is quite similar: reaction of singlet oxygen with **9** leads to the formation of tris(*ortho*-tolyl)phosphine oxide (**10**) and *ortho* tolyl di(*ortho*-tolyl)-phosphinate (**11**).

If the phosphine oxides and phosphinates are formed from the same intermediate (i.e., a phosphadioxirane), we can use a simple steady-state treatment to obtain the rate ratio for the intramolecular (k_i) and intermolecular (k_o) reaction rates: according to Scheme 1, the rate of formation of the phosphinates (compounds **7** and **10**) is given by Eq. 3:

$$\mathrm{d}[\text{Phosphinate}]/\mathrm{dt} = k_{\mathrm{i}}[\text{Phosphadioxirane}] \qquad (3)$$

Likewise, the rate of formation of the phosphine oxides (compounds **8** and **11**) can be expressed by Eq. 4:

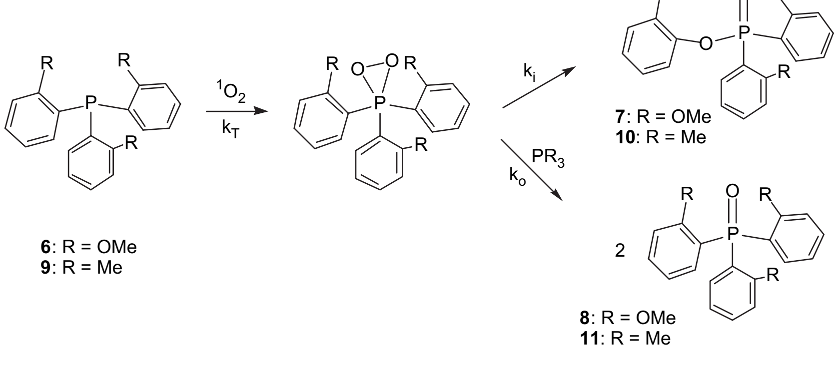
$$\mathrm{d}[\text{Phosphine oxide}]/\mathrm{dt} = 2k_{\mathrm{o}}[\text{Phosphadioxirane}][\text{Phosphine}] \qquad (4)$$

Assuming a steady-state concentration of the phosphadioxirane, and working at low conversion of the starting phosphine, we can combine Eqs. 3 and 4 to obtain an integrated expression for the rate ratio of intramolecular versus intermolecular oxidation:

$$[\text{Phosphine oxide}]/[\text{Phosphinate}] = (2k_{\mathrm{o}}[\text{Phosphine}])/k_{\mathrm{i}} \qquad (5)$$

According to Eq. 5, a plot of the product ratio versus starting material concentration should be linear with a slope of twice the rate ratio k_o/k_i. A plot of the photooxidation product ratio (**11/10**) for tris(*ortho*-tolyl)phosphine versus starting concentration of tris(*ortho*-tolyl)phosphine (in $CDCl_3$) indeed gives a good linear correlation with a slope of 161±14 (Fig. 2).

The rate ratio of intermolecular versus intramolecular oxidation for tris(*ortho*-tolyl)phosphine is thus 80±7. This ratio is considerably larger than that of the reaction of phosphine **6** with singlet oxygen where k_o/k_i is 25±3 in $CDCl_3$. Intramolecular oxidation is thus less favorable for



Scheme 1. Reaction of electron-rich *ortho*-substituted arylphosphines with singlet oxygen.

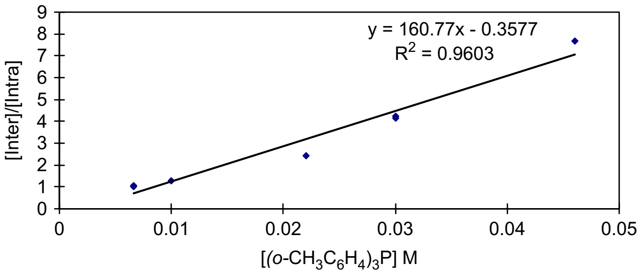


Figure 2. Product ratio of phosphine oxide (intermolecular product)/phosphinate (intramolecular product) versus starting phosphine concentration for the reaction of tris(*ortho*-tolyl)phosphine with singlet oxygen.

tris(*ortho*-tolyl)phosphine as compared to tris(*ortho*-methoxyphenyl)phosphine (**6**). This could be due to the smaller cone angle of this phosphine (194° compared to 205° for phosphine **6**, see Table 1) or due to a combination of the smaller cone angle and an electronic effect, i.e., decreased electron density at the phosphorus atom. The latter effect can be quite drastic, as illustrated by the behavior of tris(*ortho*-trifluoromethyl)phenyl phosphine (**12**). The cone angle of phosphine **12** is similar to that of **6**, but tris(*ortho*-trifluoromethyl)phenyl phosphine obviously is highly electron deficient. Phosphine **12** does quench singlet oxygen with a rather slow rate constant $k_T=1\times10^5\ M^{-1}\ s^{-1}$, as determined by a singlet oxygen luminescence quenching experiment. However, we were unable to detect any products either at room temperature or temperatures as low as −80 °C. Phosphine **12**, therefore, represents the first known example of *physical* quenching of singlet oxygen by a phosphine. It is quite possible that the quenching mechanism involves a transient dioxygen–phosphine complex, i.e., indirect physical quenching.[19] The lack of reactivity of **12** is not merely an electronic effect, since the corresponding *para* isomer tris(*para*-trifluoromethyl)phenyl phosphine (**5**) reacts with singlet oxygen to form phosphine oxide, albeit at a low rate ($k_T=9\times10^5\ M^{-1}\ s^{-1}$, see Table 1), and without any concomitant physical quenching. It, therefore, appears that electron-rich substituents in the *ortho* position are needed for the intramolecular oxygen atom insertion reaction to become a major pathway.

2.3. Low temperature photooxidation of arylphosphines

We were unsuccessful in detecting any peroxidic intermediates at temperatures as low as −80 °C for the *para*-substituted phosphines **1**–**5**. It appears that the cone angle of these phosphines (145 °C) is simply too small to prevent the reaction with starting material even at such low temperatures from being too fast to allow spectroscopic detection of any peroxidic intermediate.

In contrast to the *para*-substituted arylphosphines **1**–**5**, the reaction of tris(*ortho*-methoxyphenyl)phosphine (**6**) and singlet dioxygen at −80 °C in methylene chloride or methylene chloride/toluene mixtures leads to the rapid formation of a new phosphine species, namely tris(*ortho*-methoxyphenyl)-phosphadioxirane.[10] This phosphadioxirane can be identified by its ^{31}P NMR signal at −45 ppm. The only other peak observed in the ^{31}P NMR spectrum during the low temperature photooxidation of **6** is the signal for the corresponding tris(*ortho*-methoxyphenyl)phosphine oxide (**8**) (26 ppm at −80 °C).[9] Compound **8** is formed due to the reaction of phosphadioxirane with unreacted starting material. Formation of **8** relative to phosphadioxirane is diminished in CH_2Cl_2/toluene mixtures compared to neat CH_2Cl_2 solution. In the present work, we noted that tris(*ortho*-tolyl)phosphine (**9**) shows similar behavior compared to **6** at room temperature. We, therefore, reasoned that phosphine **9** might also form a phosphadioxirane that can be directly detected at low temperature. However, despite numerous attempts, we were unable to observe any peroxidic intermediate for phosphine **9** at −80 °C, and only the corresponding phosphine oxide **11** was obtained, regardless of solvent. It appears that the relatively small decrease in the cone angle of **9** compared to **6** and possibly the decrease in the electron density at the phosphorus atom are sufficient to make the phosphadioxirane intermediate too short-lived for direct observation. Interestingly, formation of the phosphinates **7** and **10** is greatly diminished if the photooxidation is carried out at low temperature and completely suppressed below −60 °C. This appears to be in agreement with the very recent observation by Beaver and co-workers[13] who noted that the phosphinate–phosphine oxide ratio is actually increased at elevated temperatures.

3. Experimental

3.1. Materials

All solvents and materials were the purest commercially available products and used as received, except for tris-(*ortho*-trifluoromethylphenyl)phosphine, which was synthesized according to a literature method.[20]

3.2. Instrumentation

^{1}H and ^{31}P NMR spectra were obtained on a Bruker AC300 and DRX400 instrument. Low temperature spectra were obtained by standard VT NMR techniques. Absorption spectra were recorded on a Carey 300 UV–vis spectrophotometer.

3.3. Time-resolved singlet oxygen measurements

A nanosecond Nd:YAG laser (model MiniLaseII/10 Hz; New Wave Research Inc., USA) doubled (532 nm) or tripled (355 nm) in frequency is used as an excitation source. Singlet oxygen luminescence is monitored at right angle. The detector is a cryogenic germanium photodiode detector (model 403HS; Applied Detector Corp., USA) cooled by liquid nitrogen and specialized for detection of near-infrared radiation. Three different filters are used to remove undesired radiation. A Schott color glass filter (model RG850; cut-on 850 nm; Newport, USA) is taped to the sapphire entrance of the detector to block any additional ultraviolet and visible light from entering. The port opening to the detector contains the remaining filters. The long wave pass filter (silicon filter model 10LWF∼1000; Newport, USA) transmits in the range of 1100–2220 nm and blocks in the range of 800–954 nm. A band pass filter (model BP-1270-080-B*; CWL 1270 nm; Spectrogen, USA) blocks in the UV, visible, and IR regions and only transmits in the range of 1200–1310 nm with maximum transmission of 60% at 1270 nm. Signals were digitized on a LeCroy 9350CM 500 MHz oscilloscope and analyzed using Origin software. Generally, four to six runs were conducted per phosphine, and errors are reported as one standard deviation.

3.4. General procedures for arylphosphines photooxidation by singlet oxygen

Photooxidation reaction mixtures of 0.01–0.10 M in tris(*ortho*-methoxyphenyl)phosphine and singlet oxygen sensitizers (tetraphenylporphyrin or C_{70}, max absorption was generally kept between 0.5 and 0.6) were prepared in test tubes or NMR tubes. For NMR analyses, deuterated solvents were employed during the photooxidation. The samples were presaturated with oxygen for 1–2 min and then irradiated under a constant stream of oxygen with a 250 W tungsten–halogen lamp. A 492 nm cutoff filter was used so that the arylphosphines themselves were not irradiated.

3.5. Competition experiments between phosphines and 9,10-dimethylanthracene

The phosphine compounds were irradiated in the presence of a singlet oxygen acceptor namely 9,10-dimethylanthracene (DMA), which removes singlet oxygen by chemical reaction only so that $k_T = k_r = 2.5 \times 10^7\ M^{-1}\ s^{-1}$ in $CDCl_3$.[9] We used tetraphenylporphyrin (TPP) or C_{70} as sensitizers. Phosphine concentration ranged from 0.0005 to 0.003 M, and DMA concentration ranged from 0.0005 to 0.004 M. Irradiation times ranged from 5 to 30 min (for compound **5**). Conversion of each compound was generally kept between 20 and 80%. DMA concentrations were monitored by ^1H NMR while phosphine concentrations were monitored by ^{31}P NMR. All of the NMR peaks used to determine concentrations are summarized below.

Phosphine	^{31}P NMR in $CDCl_3$, ppm	^1H NMR in $CDCl_3$ (methyl) ppm
$(p\text{-}CH_3OC_6H_4)_3P$ (**1**)	−17.8	3.81
$(p\text{-}CH_3OC_6H_4)_3PO$	21.4	3.84
$(C_6H_5)_3P$ (**2**)	−13.0	
$(C_6H_5)_3PO$	21.2	
$(p\text{-}FC_6H_4)_3P$ (**3**)	−16.6	
$(p\text{-}FC_6H_4)_3PO$	18.9	
$(p\text{-}ClC_6H_4)_3P$ (**4**)	−16.0	
$(p\text{-}ClC_6H_4)_3PO$	19.0	
$(p\text{-}CF_3C_6H_4)_3P$ (**5**)	−13.7	
$(p\text{-}CF_3C_6H_4)_3PO$	17.7	
DMA		3.11
$DMAO_2$		2.16
$(o\text{-}CH_3C_6H_4)_3P$ (**9**)	−37.2	
$(o\text{-}CH_3C_6H_4)_3PO$ (**10**)	29.1	
$(o\text{-}CH_3C_6H_4)_3PO_2$ (**11**)	22.2	
$(o\text{-}CH_3OC_6H_4)_3P$ (**6**)	−39.2	3.76
$(o\text{-}CH_3OC_6H_4)_3PO$ (**7**)	26.0	3.58
$(o\text{-}CH_3OC_6H_4)_3PO_2$ (**8**)	27.0	3.60, 3.73

Generally, four to six runs were conducted per phosphine, and errors are reported as one standard deviation. A control experiment demonstrated that the DMA endoperoxide does not oxidize the arylphosphines during the timeframe of the competition experiments (i.e., 1 h or less).

3.6. Low temperature NMR studies

Samples were directly irradiated in NMR tubes placed in a transparent Dewar flask. Acetone/liquid N_2 and 80% acetone–20% methylene chloride/liquid N_2 were used for controlling the irradiation temperatures at −80 and −90 °C, respectively. After the photooxidation, the NMR tubes were frozen in liquid N_2 and subsequently placed into the precooled NMR spectrometer.

Acknowledgements

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