Effects of substituents on aryl groups during the reaction of triarylphosphine radical cation and oxygen

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In a previous report (S. Yasui, S. Tojo and T. Majima, *J. Org. Chem.*, 2005, **70**, 1276), we presented the results from the laser flash photolysis (LFP) and product analysis of the 9,10-dicyanoanthracene (DCA)-photosensitized oxidation of triarylphosphine (Ar_3P) in acetonitrile under air, which showed that the photoreaction results in the oxidation of Ar_3P to give the corresponding phosphine oxide ($Ar_3P{=}O$) in a nearly quantitative yield, and that the reaction is initiated by the electron transfer (ET) from Ar_3P to DCA in the singlet excited state ($^1DCA^*$), producing the triarylphosphine radical cation $Ar_3P^{\bullet+}$. This radical cation decays through radical coupling with O_2 to afford the peroxy radical cation $Ar_3P^+–O–O^\bullet$, which we proposed to be the intermediate leading to the product $Ar_3P{=}O$. We now examined this photoreaction in more detail using ten kinds of Ar_3P with various electronic and steric characteristics. The decay rate of $Ar_3P^{\bullet+}$ measured by the LFP was only slightly affected by the substituents on the aryl groups of Ar_3P. During the photolysis of trimesitylphosphine (Mes_3P), the peroxy radical cation intermediate ($Mes_3P^+–O–O^\bullet$) had a lifetime long enough to be spectrophotometrically detected. The quantum yields of $Ar_3P{=}O$ increased with either electron-withdrawing or -releasing substituents on the aryl groups, suggesting that a radical center is developed on the phosphorus atom during the step when the quantum yield is determined. In addition, the *o*-methyl substituents in Ar_3P decreased the quantum yield. These results clearly indicated that $Ar_3P^+–O–O^\bullet$ undergoes radical attack upon the parent phosphine Ar_3P that eventually produces the final product, $Ar_3P{=}O$.

Introduction

Trivalent phosphorus compounds Z_3P are good electron donors and are easily converted to the corresponding radical cations $Z_3P^{\bullet+}$ when treated with a one-electron acceptor.[1–10] In principle, $Z_3P^{\bullet+}$ can act either as a cation or as a radical, but this class of radical cations is in fact quite labile toward a nucleophile mainly showing the reactivity as a cation. Thus, $Z_3P^{\bullet+}$ easily undergoes an ionic reaction with a small amount of alcohol or water in the solvent to eventually afford the corresponding pentavalent oxo-compounds $Z_3P{=}O$. One of the few examples of the radical reactions by $Z_3P^{\bullet+}$ is the radical coupling of $Z_3P^{\bullet+}$ with the aryl radical $Ar^\bullet$ taking place in competition with the ionic reaction with an alcohol upon treatment of Z_3P with a diazonium salt in an alcoholic solvent.[1]

We have found that the 9,10-dicyanoanthracene (DCA)-photosensitized oxidation of triarylphosphine (Ar_3P) quantitatively affords the corresponding triarylphosphine oxide ($Ar_3P{=}O$), in which the reaction is initiated by the electron transfer (ET) from Ar_3P to DCA in the singlet excited state ($^1DCA^*$) to generate the triarylphosphine radical cation $Ar_3P^{\bullet+}$.[7,11] Quite interestingly, the mechanism depends on the reaction conditions. When the photoreaction is carried out in aqueous acetonitrile (MeCN) under an argon atmosphere, the initially generated radical cation $Ar_3P^{\bullet+}$ undergoes an ionic reaction with water to produce $Ar_3P{=}O$.[7] On the other hand, the photoreaction under aerobic conditions in the absence of nucleophiles affords $Ar_3P{=}O$ through the radical coupling of $Ar_3P^{\bullet+}$ with molecular oxygen (O_2) in the solvent.[11] Thus, we performed the product analysis and the laser flash photolysis (LFP) on the DCA-photosensitized oxidation of Ar_3P under aerobic conditions to show the mechanism which includes the radical coupling of $Ar_3P^{\bullet+}$ with O_2. This was the first finding that the trivalent phosphorus radical cation $Z_3P^{\bullet+}$ undergoes radical coupling with O_2 in the ground state. This mechanism suggests the peroxy radical cation $Ar_3P^+–O–O^\bullet$ as an intermediate, but it is not clear how this intermediate produces the observed product $Ar_3P{=}O$. To determine this, it is quite informative to examine the effect of the substituents of aryl groups in Ar_3P on the quantum yield of $Ar_3P{=}O$.

Now, with ten electronically and sterically tuned Ar_3P (**1**) available, we analyzed the DCA-photosensitized oxidation of **1** based on the results from LFP and product analysis (Scheme 1). Our major findings in the present study are that (1) both electron-withdrawing and -releasing substituents on the aryl ligands increased the relative quantum yield of $Ar_3P{=}O$, and that (2) on the other hand, the decay rate of $Ar_3P^{\bullet+}$ was not affected by the substituents in this way. These findings along with other evidence strongly suggest that the peroxy radical cation $Ar_3P^+–O–O^\bullet$ undergoes radical attack on **1** to produce a dimeric radical cation $Ar_3P^+–O–O–P^\bullet Ar_3$. Our mechanism is different from that proposed for the O_2-mediated oxidation of Ar_3P in dichloromethane (CH_2Cl_2), for which the ET from Ar_3P to

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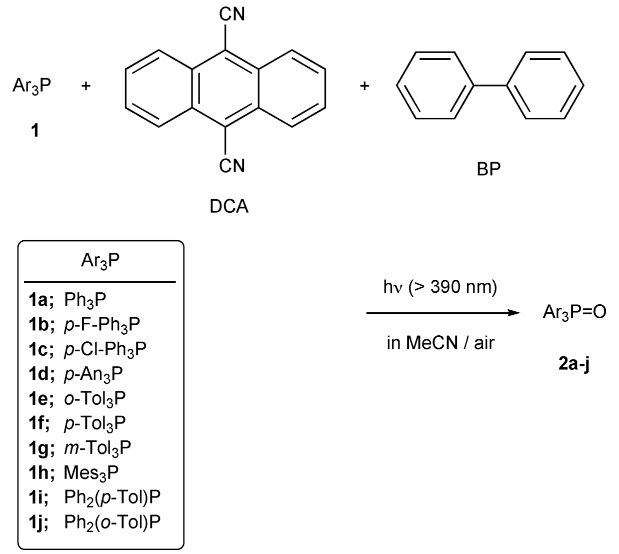


Scheme 1

Ar_3P^+–O–O$^\bullet$ has been assumed to construct a chain-reaction producing $Ar_3P{=}O$.[12] The difference in the stability of the intermediate well explains the diversity of the mechanism.

Results and discussion

Laser flash photolysis

When a mixture of **1**, biphenyl (BP) and DCA in MeCN was irradiated with a 355 nm laser, the transient absorption spectrum characteristic of the radical cation $\mathbf{1}^{\bullet+}$ was observed.[7] Clearly, $\mathbf{1}^{\bullet+}$ is generated from the ET from **1** to the biphenyl radical cation ($BP^{\bullet+}$). It is well established that the photoinduced ET from BP to the excited DCA occurs to give the DCA radical anion and $BP^{\bullet+}$, and the hole transfer from $BP^{\bullet+}$ to **1** is favorable because **1** has a lower oxidation potential than BP. We have found that the quantum yield of the product from **1** is one order lower when BP is absent.[7,11]

The absorption of $\mathbf{1}^{\bullet+}$ disappeared on the basis of the first-order kinetics in air. For each radical cation $\mathbf{1a\text{–}f}^{\bullet+}$, the disappearance of the absorption at 525–600 nm was analyzed in order to determine the decay rate constant k_{decay}(air) as summarized in Table 1. Even under an argon atmosphere, $\mathbf{1}^{\bullet+}$ spontaneously decayed at a slower rate. Table 1 also summarizes the pseudo-first order rate constants k_{decay}(Ar) for the decay under an argon atmosphere. Since $\mathbf{1}^{\bullet+}$ reacts with O_2 as reported in a previous article,[11] the second-order rate constant k_{O2} for the reaction of $\mathbf{1}^{\bullet+}$ with O_2 was calculated according to eqn (1).

$$k_{O2} = (k_{decay}(\text{air}) - k_{decay}(\text{Ar}))/[O_2] \qquad (1)$$

The LFP for trimesitylphosphine **1h** provided useful information with respect to the fate of the transient species during the photo-oxidation of Ar_3P. When **1h** was likewise subjected to the photolysis under an argon atmosphere, a transient absorption spectrum with a maximum at 600 nm assignable to the trimesitylphosphine radical cation ($\mathbf{1h}^{\bullet+}$) was observed at 100 ns after the laser flash, which disappeared on the time scale of a few μs (Fig. 1). Under air (where $[O_2] = 1.82 \times 10^{-3}$ M in MeCN), the transient absorption of $\mathbf{1h}^{\bullet+}$ disappeared on the time scale of 300 ns, and the absorption with a maximum at 560 nm appeared on the time scale of 1 μs. Furthermore, the LFP under an O_2 atmosphere gave the absorption spectrum with a maximum at 560 nm at 100 ns after the laser flash. The peak at 600 nm was observed only as a shoulder peak, which disappeared in the time scale of several tens of μs (Fig. 2). The spectral change seen in Fig. 2 is very similar to that reported for the reaction of an aromatic olefin radical cation

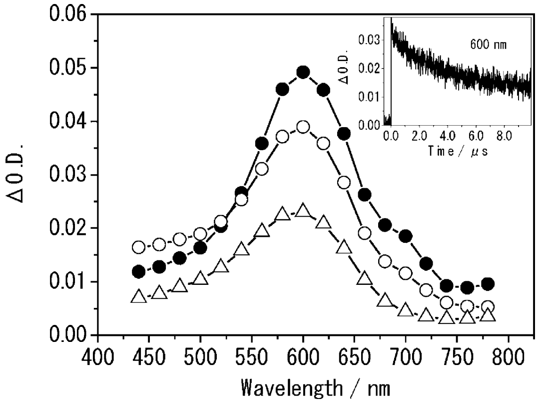


Fig. 1 Transient absorption spectra recorded at 100 ns (●), 1 μs (○), and 5 μs (△) after a laser flash during the 355 nm LFP of **1h** under an argon atmosphere. Inset: time profile of the transient absorption at 600 nm showing the decay of $\mathbf{1h}^{\bullet+}$.

Table 1 Rate constants for the decay of $\mathbf{1}^{\bullet+}$ determined by transient absorption measurements[a]

Radical cation ($\mathbf{1}^{\bullet+}$)	$k_{decay}(\text{air})^b/10^6\ s^{-1}$	$k_{decay}(\text{Ar})^c/10^5\ s^{-1}$	$k_{O2}{}^d/10^8\ M^{-1}\ s^{-1}$	$\lambda_{max}{}^e$/nm
$\mathbf{1a}^{\bullet+}$	1.82	2.19	8.80	525
$\mathbf{1b}^{\bullet+}$	1.57	3.65	6.65	530
$\mathbf{1c}^{\bullet+}$	5.15	6.54	24.7	550
$\mathbf{1d}^{\bullet+}$	2.39	2.39	14.8	600
$\mathbf{1e}^{\bullet+}$	2.30	4.55	10.1	550
$\mathbf{1f}^{\bullet+}$	1.95	2.86	9.12	550
$\mathbf{1g}^{\bullet+}$	1.82	4.35	7.60	550
$\mathbf{1h}^{\bullet+}$	2.57	3.25	12.3	600
$\mathbf{1i}^{\bullet+}$	2.78	4.29	12.9	535
$\mathbf{1j}^{\bullet+}$	1.89	3.12	8.69	535

[a] The LFP of **1** with the third harmonic generation (355 nm, 5 ns) from a Q-switched Nd^{3+}:YAG laser: $[\mathbf{1}] = 1.00 \times 10^{-2}$ M, $[BP] = 1.00 \times 10^{-1}$ M and $[DCA] = 5.00 \times 10^{-5}$ M in MeCN. [b] Pseudo-first order rate constant determined in air, $[O_2] = 1.82 \times 10^{-3}$ M in MeCN. [c] Pseudo-first order rate constant determined under an argon atmosphere. [d] Second order rate constant. [e] Wavelength monitored for the $\mathbf{1}^{\bullet+}$ transient absorption.

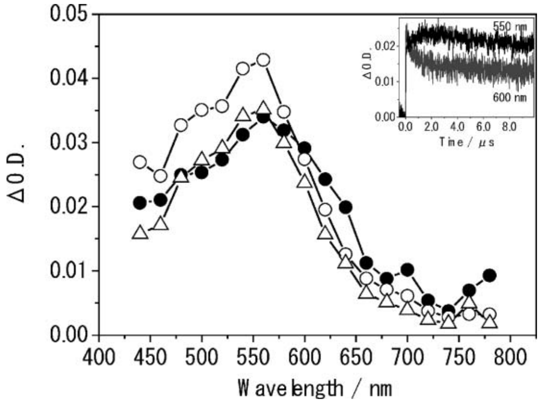
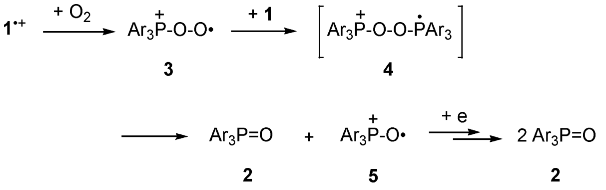


Fig. 2 Transient absorption spectra recorded at 100 ns (●), 1 μs (○), and 5 μs (△) after a laser flash during the 355 nm LFP of **1h** under an O_2 atmosphere, showing the reaction of $\mathbf{1h}^{\bullet+}$ with O_2. Inset: time profiles of the transient absorptions at 600 (black) and 550 nm (grey), showing the decay of $\mathbf{1h}^{\bullet+}$ and the formation of the peroxy radical cation ($Mes_3P^+–OO^\bullet$).

with O_2, in which the olefin radical cation is converted to the corresponding peroxy radical cation ($R^1R^2C^+–CR^3R^4–OO^\bullet$).[13,14] Therefore, the spectral change observed in the LFP for **1h** supports our proposal that $\mathbf{1}^{\bullet+}$ decays through radical coupling with oxygen to produce the peroxy radical cation (**3** in Scheme 2). The second order rate constant for the bimolecular reaction between $\mathbf{1h}^{\bullet+}$ and O_2 was also calculated according to eqn (1) as listed in Table 1. This is the first direct observation of the reaction of $Ar_3P^{\bullet+}$ and O_2 to give $Ar_3P^+OO^\bullet$.[15]



Scheme 2

Product analysis

A mixture of **1**, DCA and BP in MeCN was irradiated with light from a xenon lamp (>390 nm with a glass filter) under aerobic conditions. The irradiated solution was analyzed by GC, indicating that **1** was gradually converted to the corresponding phosphine oxide (**2**) without other products in an appreciable amount. As has been previously observed,[11] the plot of the amount of the conversion of **1** *versus* the irradiation time was linear in each experiment. The slopes were sometimes slightly different values in the different experiments even for the same Ar_3P. This is probably due to the instability of the instrument and/or subtle differences in the concentration of the dissolved O_2. To more reliably perform the examination of the substituent effect, we prepared sample solutions of **1a** (as a standard) and of the particular Ar_3P from the common mother solution and then the resulting solutions were subjected to the photoreaction one after the other (see Experimental section). The value Q_{rel} was obtained by dividing the slope for the reaction of the particular Ar_3P by that for **1a** as listed in Table 2. The value Q_{rel} represents the relative value of the quantum yield of **2**.[16] Importantly, both the electron-withdrawing and -releasing substituents increase the Q_{rel} value.

Table 2 Relative quantum yield Q_{rel} of the DCA-photosensitized oxidation of **1** in air[a]

Ar_3P (**1**)	$\Sigma\sigma^{\bullet b}$	Q_{rel}
1a	0	1
1b	0.36	1.242
1c	0.54	1.561
1d	1.26	2.803
1e	1.17^c	0.564
1f	1.17	2.076
1g	^{d}	0.989
1h	3.51^c	0.289
1i	0.39	1.197
1j	0.39^c	1.367

[a] $[\mathbf{1}] = 1.00 \times 10^{-2}$ M, $[BP] = 1.00 \times 10^{-1}$ M and $[DCA] = 5.00 \times 10^{-5}$ M; under aerobic conditions in MeCN; irradiated with visible light (>390 nm) from a Xe lamp. [b] The sum of the $\sigma^\bullet$ values of the three substituents. The $\sigma^\bullet$ values are taken from ref. 17. [c] Assuming $\sigma^\bullet(o\text{-Me}) = \sigma^\bullet(p\text{-Me})$. [d] Not available.

Substituent effect

In Fig. 3, the logarithm of Q_{rel} was plotted *versus* $\Sigma\sigma^\bullet$, the sum of the Hammett substituent constants $\sigma^\bullet$ of the substituents on the aryl groups of Ar_3P (**1**). The linear correlation with the positive value of the slope ($\rho^\bullet = 0.33$; correlation coefficient $r = 0.97$) was found with the exception of **1e** and **1h**. The $\sigma^\bullet$ scale has been defined for the homolytic cleavage of dibenzylmercury as a measure of the spin density developing on the benzyl carbon atom in the transition state.[17] That is, the correlation in Fig. 3 strongly suggests that the spin is developed on the phosphorus atom in the transition state of the Q_{rel}-determining step. The phosphorus atom of **1** (or any intermediates) occupies the position equivalent to that of the benzyl carbon of dibenzylmercury with respect to the aryl moieties. It should be noted that the $\sigma^\bullet$ scale has been obtained by subtracting the polar effects from the total effects of the substituents for measuring the pure effect used to stabilize a radical center. The analysis has assumed that the *meta*-substituents exert only a polar effect on the radical center.[18] In our system, the reaction of tris(*m*-tolyl)phosphine (**1g**) gives Q_{rel} nearly identical to that for the unsubstituted phosphine (**1a**), which may indicate that there is a slight stabilization by the substituents through the polar effect in all stages during the reaction sequence.

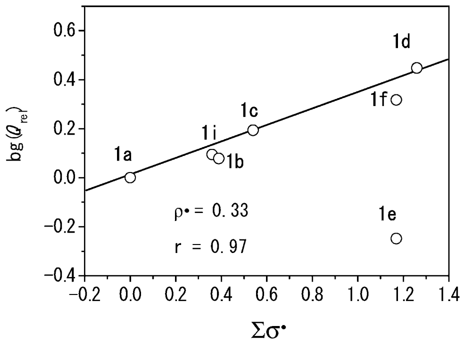


Fig. 3 Plot of logQ_{rel} *vs.* $\Sigma\sigma^\bullet$.

The $\sigma^{\bullet}$ values of the *ortho*- and *meta*-methyl groups are not available in the literature. Therefore, we take the $\sigma^{\bullet}$ value of the *para*-methyl group as that of the *ortho*-methyl group based on the reasonable assumption that the *ortho*-methyl group has almost the same electronic influence on the phosphorus as the *para*-methyl substituent.[19] The Q_{rel} value for the reaction of tris(*o*-tolyl)phosphine **1e** was plotted *versus* the $\Sigma\sigma^{\bullet}$ of **1f**. The point was significantly deviated downward from the line. Such an inhibitory effect by the *ortho*-methyl groups on Q_{rel} could be attributed to a steric factor. **1h** having six *ortho*-methyl groups produced much smaller Q_{rel} values than those expected from the electronic effects of the substituents as shown in Table 2 (not plotted in Fig. 3).

Reaction mechanism

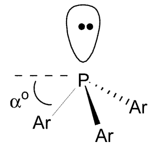
The previous study based on LFP and product analysis has shown that the photoreaction is initiated by the ET from **1** to DCA in the singlet excited state, ^{1}DCA*.[11] The ET generates the radical cation **1**$^{\bullet+}$, which decays through the reaction of **1**$^{\bullet+}$ with O_2 to give the intermediate peroxy radical cation **3** (Scheme 2). Our next task is to determine the fate of **3** leading to the final product **2**.

It is highly unlikely that **3** undergoes radical coupling with **1**$^{\bullet+}$, because the concentrations of **3** and **1**$^{\bullet+}$ are so low that there is very little possibility for both species to encounter each other. Much more likely, **3** attacks the phosphorus in **1** under our experimental conditions where **1** exists in a high concentration.[20–22] This reaction affords the dimeric radical cation **4** in which one of the phosphorus atoms has an unpaired electron on it. The observed substituent effect supports the participation of **4** in the present photoreaction. Thus, the positive value of $\rho^{\bullet}$ given in Fig. 3 shows clearly that the present photoreaction takes place *via* an intermediate in which the phosphorus atom has an unpaired electron. The step from **3** to **4** *does* determine Q_{rel}. On the other hand, the reaction of **1**$^{\bullet+}$ with O_2 cannot be the Q_{rel}-determining step because the results from the LFP reveal no correlation between k_{O2} and Q_{rel}.

The ET from **1** to **3**, instead of the radical attack by **3** on **1**, has been reported for the O_2-mediated oxidation of **1** to **2** in CH_2Cl_2.[12b] The ET mechanism is unlikely at least under our experimental conditions where the solvent is MeCN. The ET would promote a chain reaction, which is against our observations in the present study. Thus, the quantum yields of the formation of **2** from **1** were smaller than 0.1, indicating no chain reaction was involved. The phosphonium center in **3** is thought to be more stabilized by solvation in MeCN than in CH_2Cl_2, whereas the radical center on the oxygen atom is not very solvated. If this is true, **3** could accept an electron more easily in CH_2Cl_2 than in MeCN.

In the present photoreaction, a steric effect has been observed in the step where **3** attacks **1**. Importantly, the LFP for **1h** in the O_2 atmosphere produced a spectrum that strongly suggests the formation of **3h** (Fig. 2). This finding further supports the significance of the steric effect on the radical attack by **3** on **1**. The two *ortho*-methyl groups of **1h** prevent the radical attack by **3h** on **1h**, making **3h** long-lived enough for the spectroscopic observation. This is also the reason for the lower Q_{rel} in the photo-oxidation of **1h**.

Tris(*o*-tolyl)phosphine **1e**, which has *ortho*-methyl groups, produced a low Q_{rel} value. This finding is also in line with the steric inhibition by the *ortho*-methyl groups on the radical attack. Tordo *et al.* performed an X-ray analysis on several triarylphosphines and obtained the degree of pyramidalization of these phosphines (α°; see Scheme 3).[23] The α°-values are almost unchanged upon introduction of the *para*- or *meta*-methyl substituents on the aryl groups. Meanwhile, the introduction of one *ortho*-methyl on each aryl group results in a small but explicit change in α° (27.2° for **1a** and 25.7° for **1e**). That is, the C–P–C angle is flattened, increasing the p-character of the lone pair on the phosphorus atom. As a result, **1e** becomes less reactive toward the radical attack by **3**. This may be the reason why the reaction of **1e** produces the lower Q_{rel} value than expected from the electronic effect of the methyl substituents (Fig. 3). Such a steric effect is much more significant with the phosphine having two *ortho*-methyl groups on each aryl group; thus, 18.8° for **1h**. In fact, the Q_{rel} value for the reaction of **1h** is much smaller than expected based on the electronic effect of the methyl substituents.



Scheme 3

We are now convinced that the DCA-photosensitized oxidation of **1** proceeds according to the mechanism shown in Scheme 2. The intermediate **4** affords the product **2** along with the radical cation **5**. Yet, how **5** yields the final product **2** remains unsolved in the present study, and will be clarified in due course.

Experimental

Instruments

The instruments used in the present study were described in a previous article.[11]

Materials

Phosphines **1**, biphenyl (BP) and 9,10-dicyanoanthracene (DCA) were commercially available and purified through recrystallization as described.[11]

Laser flash photolysis

A solution of **1** (1.00×10^{-2} M), BP (1.00×10^{-1} M) and DCA (5.00×10^{-5} M) in MeCN was photolyzed. The decrease in the resulting absorption was monitored at the appropriate wavelengths (Table 1).

General procedure

A 5 ml solution containing BP (1.00×10^{-1}M) and DCA (5.00×10^{-5} M) in MeCN was prepared in air. 2 ml portions from the solution were separately added to two square quartz cells (1 cm × 1 cm), one containing 2.00 mmol of **1a** (as a standard) and the other containing 2.00 mmol of the particular phosphine **1**. These solutions were subjected to the photoreaction as described below. Each cell was irradiated with light from a xenon arc short lamp through a sharp-cut filter (irradiation at $\lambda > 390$ nm). At specific intervals, a 50 µl aliquot was taken and diluted with 25 µl of MeCN with benzyl ether (for **1a**, **b**, **e** and **f**) or hydroquinone dibenzyl ether (for **1c**, **d** and **g–j**) as the external standard, and the resulting mixture was analyzed by GC.

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