$CDCl_3$) $\delta$ 0.51 (d, 3 H, $J$ = 6.9 Hz), 2.05–2.15 (m, 1 H), 2.60–3.40 (br s, 2 H), 3.79 (s, 6 H), 4.44 (d, 2 H, $J$ = 9.8 Hz), 6.85–7.20 (m, 8 H).

Hydrogenolyses of **3b,c** were carried out in a manner similar to that described above for **3a**, except that **3d,e** were hydrogenated in dry benzene.[11]

**Supplementary Material Available:** Spectral data ($^1$H NMR, $^{13}$C NMR, IR, MS), elemental analyses, and melting points for **1a–e, 2a, 3b–e, 4b–e,** and **6b–e** and NOSEY spectra of **3d** and **6d** (7 pages). Ordering information is given on any current masthead page.

# Change of Selectivity in the Photo-Fries Rearrangement of Phenyl Acetate Induced by β-Cyclodextrin

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The photolysis of phenyl acetate (1) in water and in solutions containing β-cyclodextrin (CD) leads to *p*-hydroxyacetophenone (2), *o*-hydroxyacetophenone (3), and phenol (4). There is a decrease in the total amount of rearrangement products when the reactions are carried out in the presence of oxygen, but the inhibition is less marked in the presence of CD. The [3]/[2] and [4]/([3] + [2]) ratios increase from 2.4 to 3.7 and from 0.21 to 0.76 respectively when the CD concentration changes from 0 to 10 mM. These changes are due to the increase in the quantum yield for the formation of 3 and 4 in solutions containing CD. Under the conditions of this study, the substrate reacted in the bulk solution and in the cavity of CD. The quantum yields for the formation of 3 and 4, $\Phi_{CD}^3$ and $\Phi_{CD}^4$, are higher for the included substrate than the corresponding values for the free substrate. This effect is attributed to the fact that the reaction is taking place in a less polar microenvironment. Besides, $\Phi_{CD}^4$ also increases due to the availability of hydrogens bonded to secondary carbons in the cavity of cyclodextrin.

## Introduction

During the last few years, we have been concerned with the study of several aspects of the chemistry of cyclodextrins, which are doughnut-shaped molecules formed by six, seven, or eight glucose units ($\alpha$, $\beta$, or $\gamma$) and are able to form inclusion complexes with a great variety of compounds.[1] This property of cyclodextrins is responsible for changes in the reactivity and selectivity of organic reactions. In this respect, we have reported some examples.[2,3]

Recently, it was reported that cyclodextrin induces ortho selectivity in the photorearrangement of phenyl esters and anilides in solution and in the solid state.[4] These results are in disagreement with those presented in a short communication for phenyl acetate (1) in the presence of β-cyclodextrin (CD)[5] in aqueous media, which show that the para-substituted product is formed predominantly. Results from our laboratory for the photo-Fries rearrangement of acetanilide are consistent with the increase in the ortho product.[6]

We have undertaken the study of the photolysis of 1 in water solutions in the presence of CD in order to determine the effect of inclusion complex formation on the quantum yield for the ortho- and para-rearrangement products.
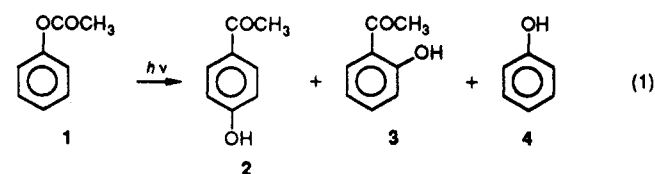
## Results

**Photolysis.** The photolysis of 1 in water solution and in solutions containing CD leads to *p*-hydroxyaceto

**Table I. Effects of Oxygen and β-Cyclodextrin on the Photolysis of Phenyl Acetate in Aqueous Solution**[a]

| conditn | $[CD]_0$[b], mM | yields,[c] % 3 | yields,[c] % 2 | $[3]/[2]$[d] |
|---------|-----------------|----------------|----------------|--------------|
| $N_2$ | | 28.4 | 24.1 | 1.3 ± 0.1 |
| $O_2$ | | 9.7 | 5.5 | 1.8 ± 0.1 |
| $N_2$ | 15 | 35.4 | 15.8 | 2.4 ± 0.2 |
| $O_2$ | 15 | 23.0 | 7.0 | 3.3 ± 0.1 |

[a] [1] = 2 mM. $T$ = 25 °C. Irradiation time = 4 h. [b] Initial concentration. [c] Absolute yields based on the initial substrate concentation as determined spectrophotometrically by 1/10 dilution of a reaction aliquot. Because of the small absorbance of 1 and 4, these concentrations cannot be determined. [d] Average ratio of *o*-hydroxyacetophenone and *p*-hydroxyacetophenone from four determinations carried out every hour during the irradiation time.

phenone (2), *o*-hydroxyacetophenone (3), and phenol (4) (eq 1).



We determined the product distribution spectrophotometrically (see Experimental Section). The results for experiments with more than 10% conversion are summarized in Table I, where it can be seen that the yield of rearrangement products decreases when oxygen is present in the solution, and there is a slight increase in the [3]/[2] ratio. The oxygen inhibition in aqueous solution contrasts with the results reported in other solvents.[7,8] On the other hand, the addition of CD increases the [3]/[2] ratio from

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**Table II. Effects of β-Cyclodextrin on the Quantum Yields (Φ) of the Products Formed in the Photolysis of Phenyl Acetate in Aqueous Solutions[a]**

| [CD],[f] mM | f[b] | 3 | | 2 | | 4 | | [3]/[2][e] |
|---|---|---|---|---|---|---|---|---|
| | | $\Phi_{exp}$ | $\Phi_{CD}$[d] | $\Phi_{exp}$[c] | $\Phi_{CD}$[d] | $\Phi_{exp}$[c] | $\Phi_{CD}$[d] | |
| | | 0.16 | | 0.067 | | 0.048 | | 2.4 |
| 2, 1.53 | 0.23 | 0.18 | 0.23 | 0.072 | | 0.097 | 0.24 | 2.8 |
| 4, 3.22 | 0.39 | 0.19 | 0.24 | 0.068 | | 0.12 | 0.23 | 2.8 |
| 6, 5.00 | 0.50 | 0.20 | 0.22 | 0.063 | 0.055 | 0.15 | 0.24 | 3.2 |
| 8, 6.84 | 0.58 | 0.19 | 0.20 | 0.062 | 0.054 | 0.17 | 0.25 | 3.1 |
| 10, 8.73 | 0.64 | 0.21 | 0.23 | 0.058 | 0.050 | 0.21 | 0.28 | 3.7 |
| | Average | | 0.22 | | 0.053 | | 0.25 | |

[a] [1] = 2 mM. $T$ = 25 °C. Maximum time of irradiation = 1 h, nondegassed solutions. [b] Fractions of 1⁻CD complex calculated as $f = K_S[CD]/(1 + K_S[CD])$, with $K_S \approx (2 \pm 1) \times 10^2$ M⁻¹ determined spectrometrically. [c] Observed quantum yield for the formation of the product above. [d] Calculated from eq 2 by using $K_S = 2 \times 10^{-2}$ and $\epsilon_c/\epsilon_w = 1.074$. The estimated error in each calculated value is about 10%. [e] Ratio of yield of o-hydroxyacetophenone and p-hydroxyacetophenone. [f] Initial concentration of CD, followed by equilibrium concentration of CD.

1.3 to 2.4 in deoxygenated solutions and from 1.8 to 3.3 in oxygenated solutions. It should be noted that the $O_2$ inhibition is less marked in the presence of CD.

**Inclusion Complex Formation.** The addition of CD to a water solution of the substrate (2 mM) produced a small bathochromic shift (1 nm) in the absorption band of 1 centered at 257.2 nm and also an increase in absorbance, indicating that an inclusion complex is being formed. The change in optical density (ΔOD) of the difference spectrum was measured at the wavelength that shows the maximum value (265.8 nm). From these values at various CD concentrations (0–15 mM), the equilibrium constant for the 1:1 association, $K_S = (2 \pm 1) \times 10^2$ M⁻¹, was determined.[9] The high error is produced by the small change in ΔOD (ΔOD$_{max}$ = 0.073). The value of $K_S$ is in good agreement with the one reported by other authors,[4b] namely, $K_S = 107$ M⁻¹, but they worked at much lower concentrations of 1 and CD. Although the change in optical density fits an equation that considers only a 1:1 complex, the fact that there is not an isosbestic point indicates that there is more than one type of complex. Similar results were obtained with other substrates.[3]

**Quantum Yield Determinations.** The addition of increasing amounts of CD results in an increase in the quantum yield (Φ) of 3 (≈35%), but the change in the quantum yield of 2 is barely outside experimental error. In these experiments, we observed an important increase in the quantum yield of 4. These results are summarized in Table II. The [3]/[2] ratio increases steadily with the CD concentration.

**Cyclodextrin Complex Photolysis.** The solid 1–CD complex, prepared as described in the literature,[10] was irradiated during 4 h with a continuous flow of nitrogen. There was about 20% reaction, and the [3]/[2] ratio was 2.8, which is similar to the value obtained in solution at 15 mM CD concentration (see Table I). These results contrast with the highest ortho selectivity reported in the literature[4] in analogous systems analyzed by other experimental procedures. This discrepancy may be due to the fact that in the previous work[4] 4 was not quantified. Coincidentally, the ratio ([3] + [4])/[2] ≈ 7 reported here is similar to the value reported in the literature as the [3]/[2] ratio.

### Discussion

The photo-Fries rearrangement of 1 has been extensively studied in protic[11] as well as in nonprotic solvents[7] and in the vapor phase,[12] but there have not been detailed studies in aqueous solutions.[7] The general mechanism accepted for the reaction[8,13] is shown in Scheme I.

**Scheme I**



**Scheme II**
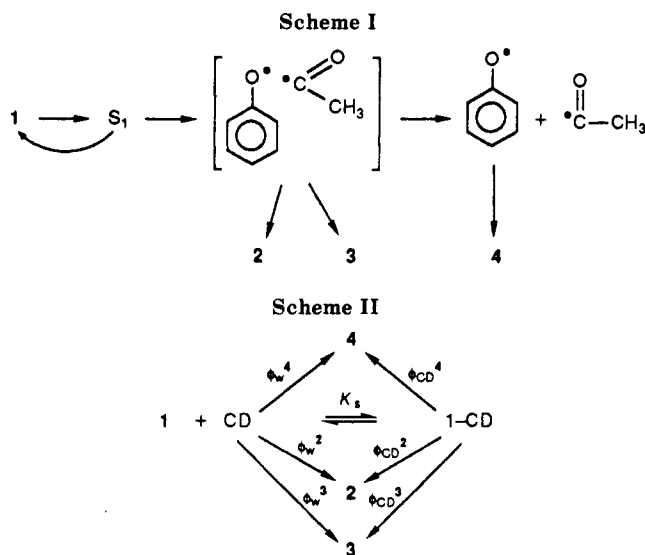


The primary photochemical process produces a pair of radicals, which upon recombination leads to the rearranged products **2** and **3**. The formation of the phenol is strongly dependent on the viscosity of the reaction medium and arises from the escape of the phenoxyl radical from the solvent cage.[8,13]

The ratio of quantum yield for ortho to para product changes from 1.4 in ethanol to 9 in hexane. This change is mainly due to a decrease in the quantum yield for the para product while the ortho product does not change. The effect is attributed to the "solvent caging" effect. Ethanol would produce the strongest solvent cage because of the relatively high degree of molecular association.[8]

In the presence of cyclodextrin at the maximum concentration used, only 64% of the substrate is complexed; therefore the photochemical reaction must be taking place in both environments.[14] The kinetic scheme must be represented as in Scheme II, where $\Phi_w^i$ and $\Phi_{CD}^i$ are the quantum yields for each product ($i$ = 2–4) in water and in CD, respectively.

The quantum yield observed for each product, $\Phi_{exp}$, may be described by eq 2,

$$\Phi_{exp}^i = \Phi_w^i(1 - f) + \Phi_{CD}^i(\epsilon_c/\epsilon_w)f \qquad (2)$$

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(14) We assume that the photophysical and photochemical primary processes of phenyl acetate are not appreciably altered by association with CD. A referee has suggested the possibility of diffusion out of cyclodextrin during the singlet-state lifetime of the complexed molecule of phenyl acetate. Although it appears as an attractive explanation for the small changes in the experimental quantum yields, we think that this is unlikely because singlet-state lifetimes are in the range of 10⁻⁹ s, whereas the rate of diffusion of organic species out of the cavity of CD is on the order of 10⁴–10⁶ s⁻¹ (see, for instance: Schiller, R. L.; Lincoln, S. F.; Coates, J. H. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2123).

where $f = K_S[CD]/(1 + K_S[CD])$ is the fraction of complexed substrate (1–CD) and $\epsilon_c/\epsilon_w$ is an approximate correction factor for the differences in light absorption by 1–CD and 1. This value is $\epsilon_c/\epsilon_w = 1.074$ and was determined from the absorbance at 254 nm of known initial concentration of 1 and CD solutions and from the equilibrium concentration determined from $K_S$.

After replacement of $f$ in eq 2, the equation can be rearranged to eq 3.

$$\frac{1}{\Phi_w^{\ i} - \Phi_{exp}^{\ \ i}} = $$
$$\frac{1}{\Phi_w^{\ i} - (\epsilon_c/\epsilon_w)\Phi_{CD}^{\ \ i}} + \frac{1}{[\Phi_w^{\ i} - (\epsilon_c/\epsilon_w)\Phi_{CD}^{\ \ i}]K_S[CD]} \quad (3)$$

Table II shows that $\Phi_{exp}^{\ \ 3}$ and $\Phi_{exp}^{\ \ 4}$ increase when the CD concentration increases, while $\Phi_{exp}^{\ \ 2}$ remains almost constant. A plot (not shown) of the left-hand side of eq 3 vs $[CD]^{-1}$ for *o*-hydroxyacetophenone yields a straight line. From the intercept of this plot, $\Phi_{CD}^{\ \ 3} = 0.23 \pm 0.01$ is calculated. The ratio of intercept over slope yields $K_S = (2.1 \pm 0.6) \times 10^2$ M$^{-1}$, in good agreement with the spectrophotometric value. A similar plot for $\Phi_{exp}^{\ \ 4}$ yields $\Phi_{CD}^{\ \ 4} = 0.27 \pm 0.03$ and $K_S = (1.7 \pm 0.4) \times 10^2$ M$^{-1}$, also in fair agreement with the spectrophotometric value.

Since there is not a marked trend in the values of $\Phi_{exp}^{\ \ 2}$, we estimated $\Phi_{CD}^{\ \ 2}$ using eq 2 for each experimental point. The average value is $0.053 \pm 0.002$.

The changes in the quantum yield for the para product and the ortho product are similar to the results obtained with acetanilide in the presence of the same host,[6] as expected, considering the similarities in the mechanism of both reactions.[15]

Studies regarding the penetration of substituted benzene rings in the cavity of cyclodextrin indicate that the ortho position is not sterically hindered.[16] The substrate included is in a less polar microenvironment than that in the bulk solution, as indicated by the observed bathochromic shift in the absorption band; therefore the increase in $\Phi_{CD}^{\ \ 3}$ can be attributed to a microsolvent effect since it is known that $\Phi_{CD}^{\ \ 3}$ increases in nonpolar solvents. The change in polarity may also be responsible in part for the increase observed in $\Phi_{CD}^{\ \ 4}$ since it was reported that the quantum yield for the formation of 4 is higher in hexane (h) than in ethanol (e) $(\Phi_h^{\ 4}/\Phi_e^{\ 4} = 2.6)$.[8] Since the formation of phenol is attributed to the escape of radicals from the solvent cage, we suggest that an important part of the products is formed from the recombination of radicals which are not in the solvent cage but are trapped in the cavity of the cyclodextrin. Under this condition, the competition with hydrogen abstraction becomes more important than in water solution since in the interior of the cavity of cyclodextrin there are 14 available hydrogen atoms bonded to secondary carbons and close to the radical center.

## Experimental Section

**Reagents.** The water used was obtained from a Millipore apparatus. Compounds 1–3, prepared as reported in the literature,[17,18] or the commercial reagents (Aldrich), as received, were used; 4 (Merck, analytical grade) was used without further purification. The purity of compounds 1–4 was checked by high-performance liquid chromatography (HPLC). β-Cyclodextrin (FDS Publications, Wilts, Enland) was used as received. Its purity was determined by ultraviolet–visible spectrophotometry (UV).

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Methanol was HPLC grade (Sintorgan).

**Apparatus.** The gas chromatographic analyses were done in a Shimadzu GC 8 A instrument equipped with a Shimadzu CR 1A processor. The column was 1.5 m × $^1/_8$ in. packed with 5% OV 17 on Chromosorb HP. The spectrophotometric determinations were carried out in a Shimadzu UV 260 instrument. A Varian Vista 5500 liquid chromatograph equipped with a Varian 2550 UV–visible detector and a Varian 4290 integrator was used for the HPLC analysis. The column was a 15 cm × 4 mm 4929 Micro Pack MCH-5-n-cap instrument.

**Photolysis Method.** The reactions were carried out in a quartz reactor up to 10% conversion. Solutions of 1 (2 mM) with or without CD were irradiated at 254 nm with an immersion type low-pressure mercury lamp of 6 W either with or without bubbling nitrogen. The solid complex 1–CD was irradiated in the same reactor but in a horizontal position at the same height of the filament lamp. In all cases, the reactor was covered with aluminum foil. To check the photostability of the products, solutions containing the compound 2, 3, or 4 (0.7 mM) in pure water and in water and 15 mM CD were irradiated for 4 h. No change in the UV spectrum was observed, indicating that the products are stable under these conditions.

**Quantum Yield Determinations.** Aqueous solutions of phenyl acetate (2 mM) and the required amount of CD contained in square quartz cuvettes were placed in a merry-go-round apparatus. They were irradiated with a low-pressure mercury lamp (254 nm, 6 W), and every 15 min, the lamp was covered to stop irradiation and the spectra of the solutions were taken to determine the yield of the photoproducts, as indicated in the next section. The irradiation was stopped when about 5% conversion was obtained, and the solutions were analyzed by HPLC to check the concentration of the product calculated by the spectrophotometric method. The results of both analytical methods agreed within experimental error. The concentrations of 2–4 were plotted vs time, and the slopes were used to calculate the quantum yields and the values of the [3]/[2] ratios reported in Table II. The quantum yields were determined by using a solution of acetanilide in water as actinometer. The quantum yield for acetanilide was reported previously.[6]

We found no differences between the quantum yields of solutions bubbled with nitrogen for 15 min before irradiation and those used without this treatment, which might be indicating that oxygen was not efficiently eliminated by our procedure.

**Analytical Methods.** Attempts to quantify the photolysis products by gas chromatography were unsuccessful because we could not extract quantitatively all products either doing it five times with 30 mL or 15 times with 5 mL of ether, benzene, or Cl$_2$CH$_2$. With the last two solvents, an additional complication was that CD precipitated when they were added to water solutions. Besides, the retention time of 4 changes with the concentration (50 mg/mL, $t_R$ = 7; 5 mg/mL, $t_R$ = 15 min). Under the best conditions, only 90% of 2, 40% of 3, and 25% of 4 were recovered from a solution containing known amounts of the substrate and products. Since the analyses in previously published work[4,5] were based on gas chromatographic analyses of the products, this may be the reason for the discrepancies with our results.

**UV–Visible Spectophotometry.** The analysis of the products by spectophotometry was carried out by the multicomponents-multilambda method using eqs 4–11.

$$[3] = (\epsilon_2^b/D)A^a - (\epsilon_2^a/D)A^b \quad (4)$$

$$[2] = -(\epsilon_3^b/D)A^a + (\epsilon_3^a/D)A^b \quad (5)$$

$$D = \epsilon_3^a\epsilon_2^b - \epsilon_3^b\epsilon_2^a \quad (6)$$

$$A_{(1+4)}^{\ \ c} = A^c - \{\epsilon_2^c[3] + \epsilon_2^c[2]\} \quad (7)$$

$$A_{(1+4)}^{\ \ d} = A^d - \{\epsilon_3^d[3] + \epsilon_2^d[2]\} \quad (8)$$

$$[4] = (\epsilon_1^d/F)A_{(1+4)}^{\ \ c} - (\epsilon_1^c/F)A_{(1+4)}^{\ \ d} \quad (9)$$

$$[1] = -(\epsilon_4^d/F)A_{(1+4)}^{\ \ c} + (\epsilon_4^c/F)A_{(1+4)}^{\ \ d} \quad (10)$$

$$F = \epsilon_4^c\epsilon_1^d - \epsilon_4^d\epsilon_1^c \quad (11)$$

In these equations, $A$ is the observed absorbance, $\epsilon$ is the extinction coefficient, the subscript indicates the compound, and

the superscript indicates the $\lambda$ ($a$ = 323.5 nm; $b$ = 309.0 nm; $c$ = 269.6 nm; $d$ = 257.2 nm). $\lambda^a$, $\lambda^c$, and $\lambda^d$ are the wavelengths of maximum absorbance of **3**, **4**, and **1** in aqueous solutions, respectively. At $\lambda^a$ and $\lambda^b$, only **3** and **2** absorb, and at $\lambda^c$ and $\lambda^d$, the four compounds absorb. In all cases, the reference cell contains CD at the appropriate concentration. Since the spectrum of all compounds changes in the presence of CD, solutions of known concentrations of the 1–4 compounds and CD were prepared and analyzed by UV spectrophotometry in order to correct the values measured in the quantum yield determinations. In the cases where the percentage of **2** + **3** formed was higher than 10%, as in photolysis experiments, we quantified 1/10 dilutions. Under these conditions, the difference in absorbance due to inclusion complex formation is barely outside experimental error. However, **1** and **4** cannot be determined since their absorbances (eqs 7 and 8) are in the range of the experimental error ($\epsilon_4{}^c$, $\epsilon_1{}^c$

and $\epsilon_4{}^d$, $\epsilon_1{}^d$ are smaller than $\epsilon_3{}^c$, $\epsilon_2{}^c$ and $\epsilon_3{}^d$, $\epsilon_2{}^d$).

**High-Performance Liquid Chromatography.** In order to check the concentration of products obtained from the spectrophotometric analysis, the samples of each reaction were analyzed by HPLC with $\alpha$-naphthol as internal standard after finishing the irradiation. The results obtained by both methods are in good agreement.

# Electron Transfer to Excited Doublet States. Photoirradiation of 10-Methylphenothiazine Cation Radical Perchlorate in Solutions of Phenylacetylene and *p*-Tolylacetylene in Acetonitrile

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10-Methylphenothiazine cation radical perchlorate (MP$^{\bullet+}$ClO$_4^-$) underwent slow reaction with *p*-tolylacetylene (PTA) and phenylacetylene (PA) in solution in acetonitrile in the dark. Perchlorate salts (**3a** and **3b**) assumed to be bis-adducts of MP$^{\bullet+}$ClO$_4^-$ to the alkyne were formed. In contrast, irradiation of such solutions with visible light ($\lambda$ > 400 nm) caused oxidation of the alkyne. 2-Methyl-3,6-di-*p*-tolylpyridine (**1a**) and 1,4-di-*p*-tolyl-5,6-dioxa-1,3-cyclohexadiene (**2a**) were formed from PTA, whereas 2-methyl-3,6-diphenylpyridine (**1b**) and 1-phenylnaphthalene (**4b**) were formed from PA. Irradiation of a solution of MP$^{\bullet+}$ClO$_4^-$ and 1-pentyne gave only a trace of 2-methyl-3,6-dibutylpyridine (**1c**).

## Introduction

Irradiation of a cation radical, an electronic ground-state doublet, ordinarily causes the excitation of an electron from a lower lying doubly occupied MO to the frontier, singly occupied one.[1,2] Examples of photoexcitation of cation radicals in solid matrices at low temperatures, and of the rearrangements that may ensue, are now reasonably well documented.[1,3] An excited doublet state is a stronger oxidant than the ground-state cation radical[1,2] and can cause single electron transfer (SET) to occur from a donor that otherwise might not be oxidized. Examples of this type of photoinduced oxidation in solution are not at all common, and, in fact, have been reported for the most part from the laboratories of Reverdy and of Moutet with 1,1-diarylethenes and aryl carbinols.[4-8] We report here the reactions of the cation radicals of phenyl- and *p*-

tolylacetylene formed by SET to photoexcited 10-methylphenothiazine cation radical perchlorate (MP$^{\bullet+}$ClO$_4^-$) in acetonitrile solution at 0 °C.

## Results

Phenylacetylene (PA) and *p*-tolylacetylene (PTA), each 1 M in acetonitrile, did not absorb substantially (absorbance approximately 0.10) at 340 nm, and their absorbances diminished almost to zero at 360 nm. MP$^{\bullet+}$ClO$_4^-$ has, however, strong absorption across a range of wavelengths (300–600 nm) with $\lambda_{max}$ 513 nm and $\epsilon$ = 9 × 10$^3$ in acetonitrile. The spectra of freshly prepared solutions of mixtures of each of these alkynes with MP$^{\bullet+}$ClO$_4^-$ in acetonitrile showed no evidences of complexation between the alkyne and MP$^{\bullet+}$ClO$_4^-$. Quenching a freshly prepared solution of MP$^{\bullet+}$ClO$_4^-$ in acetonitrile with aqueous NaHCO$_3$ produced 10-methylphenothiazine (MP) and its 5-oxide (MPO) in equal amounts, as expected (Table I, run 5). When a solution of MP$^{\bullet+}$ClO$_4^-$ and PTA was quenched after storage in the dark for approximately 4 h, MP and MPO were formed along with a small amount of a perchlorate salt (Table I, runs 2 and 4). We have assumed from analogy with earlier work with organosulfur cation radical perchlorates and alkynes[9] that this salt is the adduct (**3a**) of 2 mol of MP$^{\bullet+}$ClO$_4^-$ to 1 mol of PTA. Our

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