the superscript indicates the λ (a = 323.5 nm; b = 309.0 nm; c = 269.6 nm; d = 257.2 nm). λ^a, λ^c, and λ^d are the wavelengths of maximum absorbance of **3**, **4**, and **1** in aqueous solutions, respectively. At λ^a and λ^b, only **3** and **2** absorb, and at λ^c and λ^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 α-naphthol as internal standard after finishing the irradiation. The results obtained by both methods are in good agreement.

Acknowledgment. This research was supported in part by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina, and the Consejo Provincial de Investigaciones Científicas y Tecnológicas (CONICOR), Córdoba, Argentina.

Registry No. 1, 122-79-2; 1-CD, 122710-04-7; CD, 7585-39-9.

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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Received January 24, 1990

10-Methylphenothiazine cation radical perchlorate ($MP^{•+}ClO_4^-$) 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 $MP^{•+}ClO_4^-$ to the alkyne were formed. In contrast, irradiation of such solutions with visible light (λ > 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 $MP^{•+}ClO_4^-$ 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 ($MP^{•+}$-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. $MP^{•+}ClO_4^-$ has, however, strong absorption across a range of wavelengths (300–600 nm) with λ_{max} 513 nm and $\epsilon = 9 \times 10^3$ in acetonitrile. The spectra of freshly prepared solutions of mixtures of each of these alkynes with $MP^{•+}ClO_4^-$ in acetonitrile showed no evidences of complexation between the alkyne and $MP^{•+}ClO_4^-$. Quenching a freshly prepared solution of $MP^{•+}ClO_4^-$ 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 $MP^{•+}ClO_4^-$ 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 $MP^{•+}ClO_4^-$ to 1 mol of PTA. Our

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Table I. Products of Irradiation of Solutions of 10-Methylphenothiazine Cation Radical Perchlorate ($MP^{\bullet+}ClO_4^-$) in Acetonitrile Containing *p*-Tolylacetylene (PTA)[a] at 0 °C

run	$[MP^{\bullet+}ClO_4^-]_0$, mmol × 10^2	$[PTA]_0$, mmol	time, min	products, mmol × 10^2					acct of $MP^{\bullet+}$, %
				MP	MPO	**1a**	**2a**	**3a**	
1	2.62	1.36	200	1.83	0.491	0.131	0.023	0.182	102
2	2.62	1.36	200[b]	1.63	0.853	0	0	0.135	105
3	2.62	1.36	260	1.81	0.454	0.159	0.038	0.202	102
4	2.62	1.36	260[b]	1.62	0.719	0	0	0.189	104
5	5.81	0	1[c]	2.94	2.90	0	0	0	101
6	2.56	1.36	150[d]	1.87	0.064	0.241	0.062	0.200	91
7	2.57	1.36	300[e,f]	1.78	0.497	0.119	0.063	0.169	102
8	2.57	1.36	300[e]	1.71	0.575	0.106	0.024	0.162	101

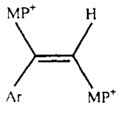
[a] A 2.0-mL solution of reactants was used. Unless otherwise stated a freshly prepared light-filter solution, and the mercury arc lamp were used. [b] No irradiation; solution was kept in the dark. [c] Control experiment. [d] Lamps were Rayonet 350-nm U tubes. [e] The light-filter solution had been used previously, and its transmittance at 400 nm was lower than that of a fresh solution. [f] The solution was saturated with O_2.

Table II. Irradiation of Solutions of $MP^{\bullet+}ClO_4^-$ and PTA.[a] Effect of PTA Concentration and Irradiation Time on Yields of 1a and 2a

run	$[PTA]_0$, mmol	*t*, h	products,[b] mmol × 10^4				$[(\mathbf{1a} + \mathbf{2a}) \times 10^4]/2t$
			MP	MPO	**1a**	**2a**	
9	1.63	3	167	22.5	6.08	4.65	1.79
10	0.816	6	168	17.2	6.00	4.11	0.843
11	0.408	6	156	54.2	3.63	1.30	0.411
12	0.204	9	170	52.4	2.27	1.25	0.196

[a] Each Pyrex irradiation tube contained 3.12 × 10^{-2} mmol of $MP^{\bullet+}ClO_4^-$ in 1.2 mL of acetonitrile and was degassed. Irradiation was carried out with 350-nm lamps in the Rayonet reactor. [b] **3a** was formed but not assayed.

assumption is supported by the accounting of products from the $MP^{\bullet+}$ that was used (Table I, last column).

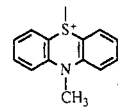


3

3a, Ar = $CH_3C_6H_4$

3b, Ar = C_6H_5

MP^+ =



Irradiation of a solution of $MP^{\bullet+}ClO_4^-$ and PTA with filtered light (λ > 400 nm) for 200 min gave not only MP, MPO, and **3a**, but also two other products, 2-methyl-3,6-di-*p*-tolylpyridine (**1a**) and the cyclic peroxide, 1,4-di-*p*-tolyl-5,6-dioxa-1,3-cyclohexadiene (**2a**) (run 1). Irradiation of a similar solution for a longer time (260 min, run 3) gave more of these last two products.

Product **1a**, mp 93–94 °C, was isolated and identified by ^{1}H NMR spectroscopy and high-resolution mass spectrometry,[10] *m/e* 273.1517 as compared with the required *m/e* 273.1513. Product **2a** was isolated and identified by ^{1}H NMR spectroscopy and low-resolution mass spectrometry. Attempts to recrystallize **2a** for high-resolution mass spectrometry caused its deterioration. It was found that the relative yield of **2a** could be increased by irradiating a solution under an oxygen atmosphere (run 7 compared to run 8).

The yields of **1a** and **2a** were increased by longer irradiation time (runs 1 and 3) and by increasing the concentration of PTA. The effect of concentration of PTA is seen in Table II. In that table the effects of changing both concentration of PTA and time of irradiation with unfiltered light in a Rayonet reactor are recorded. Although the relative amounts of **1a** and **2a** show no trend, the sum of the amounts of **1a** and **2a** formed per unit time can be seen to decrease with decreasing initial concentration of PTA. By coincidence, when the unit time is 30 min the yields of products per unit time are numerically almost a replica of the initial concentrations of PTA.

Table III. Products of Irradiation of a Solution of $MP^{\bullet+}ClO_4^-$ and Phenylacetylene in Acetonitrile at 0 °C[a]

run	products,[b] mmol × 10^4				acct of $MP^{\bullet+}$, %
	MP	MPO	**1b**	**4b**	
13	95.3	70.9	1.6	1.0	97
14	89.1	76.2	0	0	97

[a] Each tube contained 1.71 × 10^{-2} mmol of $MP^{\bullet+}ClO_4^-$ and 0.24 mmol of phenylacetylene in 2.0 mL of acetonitrile and was either irradiated (run 13) or kept in the dark (run 14) for 13 h. Traces of **3b** were found in each run but were not assayed.

Somewhat similar reactions between $MP^{\bullet+}ClO_4^-$ and PA occurred but were not investigated in as much detail (Table III). That is, a dark reaction led to a perchlorate salt, again assumed to be the bis-adduct **3b**. Irradiation led to the formation of 2-methyl-3,6-diphenylpyridine (**1b**), and 1-phenylnaphthalene (**4b**), each of which was identified by GC–MS. The formation of the cyclic peroxide **2b** was not observed.

Irradiation of solutions containing $MP^{\bullet+}ClO_4^-$ and 1-pentyne with filtered light gave traces of 2-methyl-3,6-dibutylpyridine (**1c**), detected only by GC–MS.

Discussion

The polarographic half-wave oxidation potential of PA has been reported to be 2.25 V.[11] We found the cyclic voltammograms of PA and PTA in acetonitrile to be irreversible and to have anodic peak potentials (E_p) of 2.2 and 2.0 V vs SCE, respectively.[12] In comparison, the half-wave potential of MP is 0.70 V.[6] Consequently, SET from the alkynes to $MP^{\bullet+}$ is highly unlikely; instead, addition of $MP^{\bullet+}$ to the alkynes occurs slowly in the dark. We have assumed that bis-adducts were formed, based on analogous reactions between thianthrene and phenoxathiin

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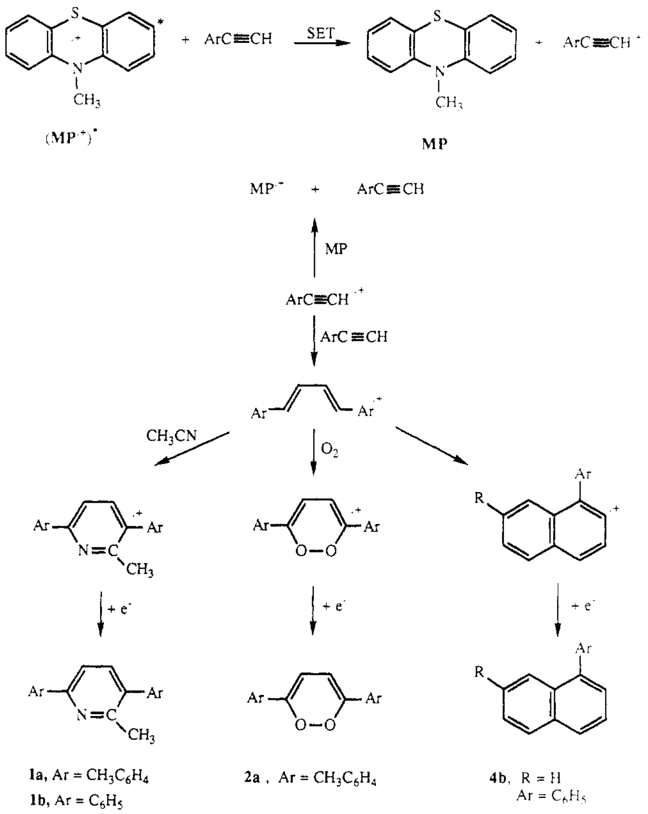
(10) Midwest Center for Mass Spectrometry, a regional NSF Center.

(11) Katz, M.; Wendt, H. *Electrochim. Acta* **1976**, *21*, 215–218, at a platinum anode, vs SCE.

(12) We thank Donald T. Robertson for these measurements.

Scheme I



cation radical perchlorates with alkynes.[9] Attempts to characterize the adducts by ^{1}H NMR spectroscopy failed because dissociation occurred in solution, and the MP$^{\bullet+}$ that was released broadened the NMR signals. Similar behavior was observed in some cases earlier.[9]

Irradiation of solutions of MP$^{\bullet+}$ClO$_4^-$ containing PTA led to the formation of **1a** and **2a**. The filtered light (λ > 400 nm) could not have excited the PTA. It is evident, therefore, that oxidation of PTA occurred by SET to excited state MP$^{\bullet+}$ (MP$^{\bullet+}$)*, that the dimer cation radical (PTA)$_2^{\bullet+}$ was formed and added to solvent acetonitrile (Scheme I). The energy gap between the highest doubly occupied MO (HDOMO) and the SOMO of M$^{\bullet+}$ was found from the fluorescence emission spectrum (λ_{max} 600 nm) to be 2.0 eV, analogous to the gap of 2.13 eV in the thianthrene cation radical.[13] Thus, what would be an endothermic electron transfer between ground-state reactants has been turned into an exothermic transfer by excitation of MP$^{\bullet+}$.

Scheme I shows the formation of the cyclic peroxide **2a**. This occurred even though the solutions of reactants were degassed and indicates that (PAT)$_2^{\bullet+}$ was able to scavenge the small amounts of oxygen left by mechanical-pump degassing.

It is evident that the relative amounts of **1a** and **2a** that are likely to be formed will depend on the amount of oxygen that is available. On the other hand, once PAT$^{\bullet+}$ is formed by SET to (MP$^{\bullet+}$)*, the likelihood of its forming the dimer cation radical (PAT)$_2^{\bullet+}$ depends on the concentration of PAT. Therefore, the sum of the yields of products **1a** and **2a** should be increased with increasing initial concentration of PAT, and this is observed (Table II).

The quantum yields of formation of **1a** (4.6×10^{-3}) and **2a** (1.2×10^{-3}) were very low. The quantum yield of fluorescence of (MP$^{\bullet+}$)* was also very low (3×10^{-4}). Therefore, deactivation of (MP$^{\bullet+}$)* must occur rapidly in a nonradiative way.

Irradiation of solutions of PA and MP$^{\bullet+}$ClO$_4^-$ caused the formation of the analogous **1b**. Formation of products from PA appeared to be less efficient than of products from PTA. Comparison of the results of run 1 (Table I) with those of run 13 (Table III) shows, for example, that the sum of the yields of **1a** and **2a** (1.54×10^{-3} mmol) was about 6 times greater than the sum (0.26×10^{-3} mmol) of the yields of **1b** and **4b**. This might be expected since the initial concentration of PTA was about 6 times greater than that of PA. But, **1b** and **4b** were formed by irradiating 13 h for PA as compared with irradiation of 3.3 h for PTA.

Even greater inefficiency was experienced with the use of 1-pentyne, when only traces of an adduct (2-methyl-3,6-dibutylpyridine, **1c**) could be detected by GC–MS. On the basis of these results it was felt that *p*-anisylacetylene (E_p 1.65 V[12]) would readily undergo electron transfer to (MP$^{\bullet+}$)*. Unfortunately, the dark reaction between MP$^{\bullet+}$ and *p*-anisylacetylene also took place readily, and the photoexcitation experiments had to be abandoned.

Products **1b** and **4b** were obtained earlier by photosensitized electron transfer from PA to 9,10-dicyanoanthracene (DCA) and 2,4,6-triphenylpyrylium tetrafluoroborate.[14] We have not been able to find the formation of **1a** or **2a** in the literature. Formation of a saturated cyclic peroxide, analogous to **2a**, occurred in DCA-photosensitized oxydations of 1,1-diphenylethene.[15]

Scheme I shows the formation of **1**$^{\bullet+}$, **2**$^{\bullet+}$, and **4**$^{\bullet+}$. These must in some way be reduced to products **1**, **2**, and **4**. In principle the necessary electron for each product could be supplied by MP, and product formation could thus be catalytic in MP$^{\bullet+}$. In that case the amount of [MP$^{\bullet+}$ClO$_4^-$]$_0$, as compared with the yields of products (Table I), seems unnecessarily large (i.e., about 10-fold). We did not pursue this point, that is, as to whether or not truly catalytic conversion could be achieved. It is apparent, however, from the long times of irradiation that were needed that the electron-transfer process must be very inefficient and that an excessive amount of MP$^{\bullet+}$ is therefore useful. Table I shows also, however, that reduction of MP$^{\bullet+}$ to MP, in a way or ways unconnected with product formation, occurred during the relatively long times of usage. That is, the control reaction (run 5) gave, as expected from workup of MP$^{\bullet+}$ with water, equal amounts of MP and MPO. In contrast, all of the other runs, whether irradiated or not, gave larger amounts of MP than MPO. Consequently, the amount of [MP$^{\bullet+}$ClO$_4^-$]$_0$, seemingly unnecessarily large for a catalytic electron-transfer reaction, may have been fortuitously useful. In the overall view, one can appreciate, here, the limitations inherent in using excited doublet states as reagents in bimolecular reactions.

Experimental Section

Phenylacetylene, *p*-tolylacetylene, and 1-pentyne were from Farchan Laboratories and were distilled at atmospheric pressure and stored under argon. *p*-Anisylacetylene was prepared as described[16] and was obtained as an oil: bp 50–52 °C (5 Torr); ^{1}H NMR (CDCl$_3$) δ, 2.94 (s, 1 H), 3.81 (s, 3 H), 6.84 (d, 2 H, J = 8.6 Hz), 7.42 (d, 2 H, J = 8.6 Hz). 10-Methylphenothiazine cation radical perchlorate (MP$^{\bullet+}$ClO$_4^-$) was prepared as described.[17]

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(14) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 126–128.

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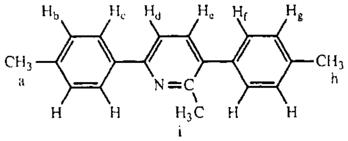
Warning: although we have had no problems in work with this salt, it should be considered as potentially explosive. Filtration through and removal by scraping from sintered-glass funnels should be avoided. Rhodamine-590 was used as received from Exiton. Acetonitrile (Kodak 488) was dried over calcium chloride and distilled over phosphorus pentoxide. Visible, IR, NMR, and emission spectra were recorded with Perkin-Elmer Lambda 5, Beckman AccuLab 8, Bruker NR-300, and Shimadzu RF-540 instruments, respectively. GC analyses were carried out with a Varian Model 3700 FID instrument and an SE30 capillary column, 25 m × 0.25 mm, over the range 100–250 °C. The cyclic voltammograms of phenyl-, *p*-tolyl- and *p*-anisylacetylene were completely irreversible. Anodic peak potentials were measured in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate, against a reference electrode of $Ag/AgNO_3$ (0.01 M), and have been converted to an SCE standard by adding 0.30 V.[12] Preparative-scale thin-layer chromatography (TLC) was carried out with Analtech silica gel Uniplates-T (No. 81013).

Light Sources and Irradiation Apparatus. Two irradiation systems were used. In one, from Ace Glass, Inc., a 450-W Hanovia medium-pressure lamp was housed in a jacketed Pyrex immersion well that was cooled with running water. The well was placed in a beaker containing a solution of sodium nitrite and sodium hydrogen phthalate that had been made as described earlier[18] and adjusted to pH 12 with sodium hydroxide. The whole assembly was placed in an ice bath. The tube to be irradiated was placed 1 cm away from the wall of the immersion well and 5 cm away from the lamp. In this circumstance irradiation by light of wavelength <400 nm was prevented. In the second system, sample tubes were placed in the rotating "merry-go-round" compartment of a Rayonet RPR-208 photochemical reactor and irradiated with eight lamps (RUL-3500 Å) with principal output at 350 nm. In each system, all irradiation tubes were made of Pyrex.

General Procedure. A solution of $MP^{\bullet+}ClO_4^-$ and alkyne in acetonitrile was placed in a Pyrex tube (10 × 150 mm) equipped with a Teflon stopcock. The solution was degassed by three freeze–thaw (dry ice/acetone) cycles with a mechanical pump and irradiated. When irradiation was finished, 1 Ml of water containing 30 mg of sodium bicarbonate was added to the tube, and the mixture was shaken until the brown color of $MP^{\bullet+}ClO_4^-$ had disappeared. To this mixture was added 4 mL of dichloromethane. The yellow organic layer was removed, and the aqueous layer was extracted with 3 × 1.5 mL of dichloromethane. The combined extract was washed with water and dried over magnesium sulfate. The dried solution was evaporated under reduced pressure and finally under vacuum to remove unused alkyne. The residue was weighed, and to it was added a known amount of thianthrene to serve as an internal standard for GC analysis, carried out in dichloromethane solution.

Preparation and Separation of Products 1a and 2a. A 30-mL tube containing a solution of 4 mL of PTA in 17 mL of acetonitrile under air was irradiated continuously in the Ace apparatus for 2 days. During that period 230 mg (0.735 mmol) of $MP^{\bullet+}ClO_4^-$ was added in portions. Workup gave 380 mg of residue. TLC with ethyl acetate/hexane (1:19) gave 5.9 mg of **1a** (R_f 0.45) as a yellow solid, 90% pure by GC integration, and 6.0 mg of **2a** (R_f 0.30), 62% pure by GC integration. Repetitive TLC gave 2.3 mg of **1a** and 1.1 mg of **2a**, each 95% pure by GC integration. Compound **1a**: ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H, H_a or H_h), 2.41 (s, 3 H, H_h or H_a), 2.57 (s, 3 H, H, H_i), 7.25 (br s, 4 H, H_f and H_g), 7.27 (d, 2 H, H_b, J = 8.2 Hz), 7.55 (AB q, 2 H, H_d and H_e, J = 8.2 Hz), 7.92 (d, 2 H, H_c, J = 8.2 Hz); IR (Nujol) (cm^{-1}) 1542 (m), 1445 (s), 1430 (s), 1183 (m), 1000 (s), and 810 (s). A 12-mg sample of **1a**, obtained by repetitions of the irradiation, was crystallized repeatedly from cyclohexane to give 4 mg, mp 93–94 °C, m/e 273.1517. $C_{20}H_{19}N$ requires 273.1513. Compound **2a**: ^1H NMR ($CDCl_3$) δ 2.43 (s, 6 H, CH_3), 7.31 (d, 4 H, J = 8.1 Hz), 7.96 (d, 4 H, J = 8.1 Hz), 7.99 (s, 2 H); m/e (relative intensity) 264 (M^+, 80), 145 (11), 119 (100), 91 (100), and 65 (95); IR (Nujol) (cm^{-1}) 1650 (m), 1610 (s), 1330 (s), 1300 (s), and 750 (s). Attempts to recrystallize **2a** caused its further deterioration.



1a

Irradiation of $MP^{\bullet+}ClO_4^-$ in a Solution Containing *p*-Tolylacetylene (PTA). Runs 1 and 2. A 2-mL solution containing 8.2 mg (0.0262 mmol) of $MP^{\bullet+}ClO_4^-$ and 0.20 mL (1.36 mmol) of PTA was irradiated at 0 °C for 200 min. No change in the color ($MP^{\bullet+}$) of the solution was seen. Workup and GC analysis gave MP, MPO, **1a**, and **2a** (Table I) with retention times 13.5, 17.0, 17.3, and 17.2 min respectively. The bulk of the solution was transferred to a 15-mL centrifuge tube and evaporated. The residue was dissolved in 0.2 mL of dichloromethane, and to the solution was added 5 mL of ether, causing precipitation of a yellow solid. The supernatant solution was decanted, and the residue was washed with ether and dried under vacuum to give 1.35 mg of **3a** (assumed), having IR (Nujol) 1085 cm^{-1} (s, ClO_4^-). A similar 2-mL solution of $MP^{\bullet+}ClO_4^-$ and PAT was kept in the dark at 0 °C for 200 min. Workup gave MP, MPO, and (assumed) **3a**; no **1a** and **2a** were found.

Quantum Yield Measurements for Formation of 1a and 2a. Two tubes (A and B) were prepared, each containing 2.0 mL of a benzene solution that was 0.05 M in benzophenone and 0.10 M in benzhydrol. A third tube (C) contained 0.0256 mmol of $MP^{\bullet+}ClO_4^-$ and 1.36 mmol of PTA. The tubes were irradiated in the "merry-go-round" for 20 min (tubes A and B) and 150 min (tube C). The light intensity of the 350-nm lamps was calculated to be 3.5 × 10^6 einstein/min with the use of the molar extinction coefficient of benzophenone and quantum yield (0.74) for its disappearance at 342 nm.[19] The photolysate in tube C was worked up in the usual way to give MP, MPO, **3a**, **1a** (24.1 × 10^{-4} mmol), and **2a** (6.19 × 10^{-4} mmol). The quantum yields of formation were thus 4.6 × 10^{-3} (**1a**) and 1.2 × 10^{-3} (**2a**).

Irradiation of $MP^{\bullet+}ClO_4^-$ in a Solution Containing Phenylacetylene (PA). Irradiation was carried out in the same way as described for PTA. Workup followed by GC–MS and GC analysis gave MP, MPO, **1b**, and 1-phenylnaphthalene (**4b**, assumed) (Table III). The presence of **2b** could not be detected. A perchlorate salt, IR (Nujol) 1085 cm^{-1}, assumed to be **3b**, was precipitated from both the irradiation and dark experiment solutions.

Irradiation of $MP^{\bullet+}ClO_4^-$ in a Solution Containing 1-Pentyne. A 2.0-mL solution of $MP^{\bullet+}ClO_4^-$ (0.038 mmol) and 1-pentyne (4.0 mmol) was irradiated in the Ace equipment for 11.5 h. Workup gave 0.0227 mmol of MP and 0.0186 mmol of MPO. The formation of 2-methyl-3,6-dibutylpyridine (**1c**) was detected by GC, retention time 8.7 min, and identified by GC–MS, m/e (relative intensity) 205 (M^+, 40), 162 (100). Its yield (<10^{-5} mmol) was too low for assay.

Fluorescence Quantum Yield of $MP^{\bullet+}ClO_4^-$. A 10^{-5} M solution of $MP^{\bullet+}ClO_4^-$ in acetonitrile was sparged with argon for 10 min after which its absorption and emission spectra were recorded. The emission band was centered on λ_{max} 600 nm and was obtained by excitation at λ_{ex} 496 nm. The emission band (λ_{max} 554 nm) of a 10^{-4} M solution of rhodamine-590 in ethanol was recorded similarly. The quantum yield of fluorescence (Φ_1 = 3 × 10^{-4}) of $MP^{\bullet+}ClO_4^-$ was calculated from eq 1,[20] in which Φ_2 is

$$\Phi_1 = \Phi_2\,[(1 - 10^{x})/(1 - 10^{y})](D_1/D_2)(n_1^2/n_2^2) \qquad (1)$$

the emission yield (0.95[21]) of rhodamine-590, x and y are the absorbances of rhodamine-590 and $MP^{\bullet+}ClO_4^-$ at 496 nm, respectively, D_1 and D_2 are the integrated areas of the emission bands of $MP^{\bullet+}$ and rhodamine-590, respectively, and n_1 and n_2 are the refractive indices of acetonitrile and ethanol, respectively.

Acknowledgment. We thank the National Science Foundation for support under Grant CHE 8612031.

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