Photochemical Reactions of Substituted Cyclopropenium Salts

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Received August 22, 2001

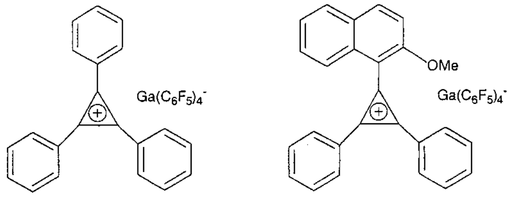
Photochemical reactions of triphenylcyclopropenium tetrakis(pentafluorophenyl)gallate (TPCPGa) and diphenyl-(2-methoxy-1-naphthyl)-cyclopropenium tetrakis(pentafluorophenyl)gallate (DPMNCPGa) (Chart 1) have been investigated in acetonitrile. Traces of water were required for the photochemical reactions to proceed. The disappearance of both TPCPGa and DPMNCPGa obeys zero-order kinetics with rate constants (*k*) having a linear dependence on the concentration of water. Electron-transfer from water to the cyclopropenium cation is proposed as the primary process in the formation of the cyclopropenyl radical. The latter dimerizes leading to the photoproducts.

Introduction

Cyclopropenium salts have attracted considerable attention in that they are representatives of the smallest two-π-electron Hückel aromatic systems. Since triphenylcyclopropenium (TPCP) ion, the first cyclopropenium salt, was synthesized by Breslow and co-workers,[2] numerous others have been studied.[3−8] In a study of the photochemistry of stable carbenium ions, Van Tamelen[9] reported that TPCP bromide, when irradiated in sulfuric acid, produced hexaphenylbenzene. He also proposed that charge transfer, followed by radical coupling, lead to product formation. Though it was not said, we surmise that bromide ion was the reducing agent.

Recently we reported that TPCPGa in the presence of cyclohexanone catalyzed the cationic polymerization of glycidyl phenyl ether.[10] Since the reduction potential of TPCP cation, measured in acetonitrile, is −0.75 V vs SCE,[11] there is significant thermodynamic stability of the ground state. However, we thought cyclopropenium might be a potentially interesting cation with which a cascade of nonnucleophilic anions might be paired for investigation as photochemical superacid sources. As a result, we have synthesized series of triarylcyclopropenium tetrakis(pentafluorophenyl)gallates and found that these compounds release acid when irradiated.[12] In view of the fact that the photochemistry of cyclopropenium salts has seen little recent attention, herein we report the results of photoreactions of triphenylcyclopropenium tetrakis(pentafluorophenyl)gallate (TPCPGa) and diphenyl-(2-methoxy-1-naphthyl)-cyclopropenium tetrakis(pentafluorophenyl)gallate (DPMNCPGa) (Chart 1) and discuss the kinetics of their reactions in acetonitrile.

Chart 1



1 : TPCPGa **2 : DPMNCPGa**

Results and Discussion

UV−Vis Spectra of TPCPGa and DPMNCPGa. The spectra of TPCPGa (2×10^{-5} M) and DPMNCPGa (7.5×10^{-5} M) in acetonitrile are shown in Figures 1 and 2. The peaks arising from TPCPGa at 306 and 320 nm, respectively, are bleached by 80% in 20 min with UV-irradiation (300 nm), Figure 1a. Degassing significantly increases the rate of disappearance of the salt, and bleaching was complete in 5 min in the absence of air. Similar results were obtained with DPMNCPGa (Figure

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(1) Contribution no. 455 of the Center for Photochemical Sciences.

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10.1021/jo0108562 CCC: $20.00 © 2001 American Chemical Society
Published on Web 11/15/2001

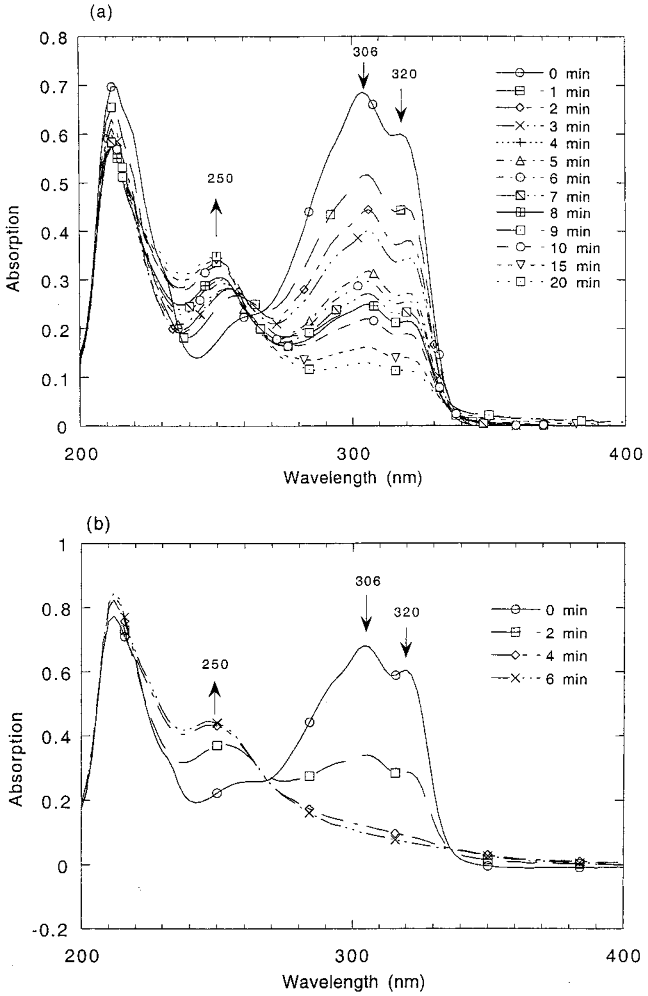


Figure 1. UV–vis spectra of TPCPGa in acetonitrile (2.0 × 10^{-5} M) following irradiation at 300 nm. (a) In the presence of trace water, without degassing; (b) with degassing.

2) in that each of the bands at 260, 288, 342, 386, and 400 nm was bleached by 40% (calculated using 400 nm) in 60 min, and the bleaching rate increased dramatically after degassing (Figure 2b). The addition of water also greatly influenced the photodecomposition rate (Figure 2c).

Water accelerated photoreactions of both TPCPGa and DPMNCPGa. In a typical experiment, varying quantities of water were added to an acetonitrile solution of TPCPGa (5.85 × 10^{-5} M), the solution stirred, degassed for 5–10 min and then irradiated at 300 nm through a glass filter. The absorption at 315 nm was monitored to measure conversion of the salt. Reactions were carried to greater than 50% completion and zero-order kinetic rate constants (k) calculated using eq 1:

$$A[\mathrm{TPCP}^+]_0 - A[\mathrm{TPCP}^+]_t = kt \qquad (1)$$

$$[\mathrm{TPCP}^+] = A/l\epsilon,\ l = 1\ \mathrm{cm},\qquad \epsilon_{315} = 4.32 \times 10^4\ \mathrm{cm}^{-1}\ \mathrm{M}^{-1}$$

k was obtained from the slopes of eq 1 (Figure 3), Table 1.

In the case of DPMNCPGa (1.5 × 10^{-4} M), the absorption at 400 nm (ϵ_{400} = 1.92 × 10^4 M^{-1} cm^{-1}) was monitored, and zero-order kinetic rate constants are shown in Figure 4 and the results listed in Table 2.

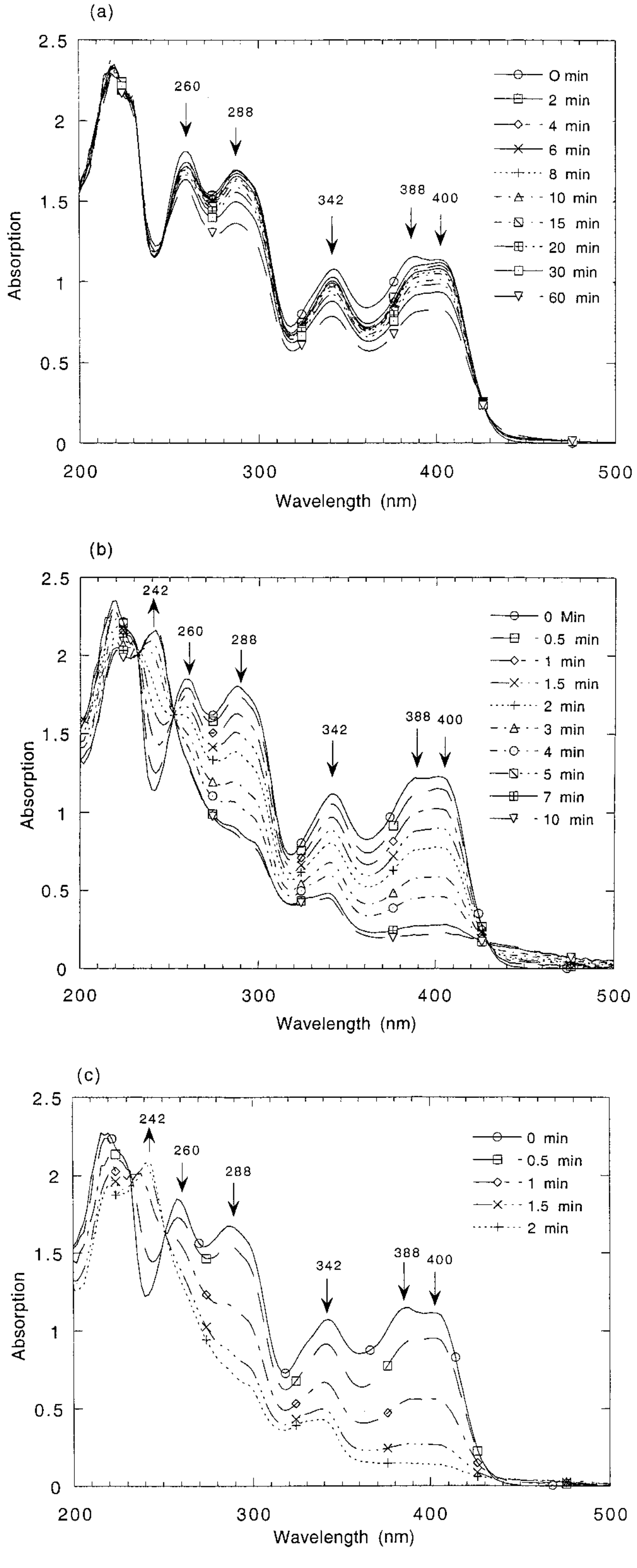


Figure 2. UV–vis spectra of DPMNCPGa in acetonitrile (7.5 × 10^{-5} M) following irradiation at 300 nm. (a) In the presence of trace water, without degassing; (b) with degassing. (c) In the presence of water (1.2 M), with degassing.

Both TPCPGa and DPMNCPGa obey zero-order kinetics, the rate constants of which have a linear relationship to the concentration of water (Figure 5).

We propose the following mechanism (Scheme 1). In the presence of water, an excited state of the triarylcyclopropenium cation–water complex (B) serves to the

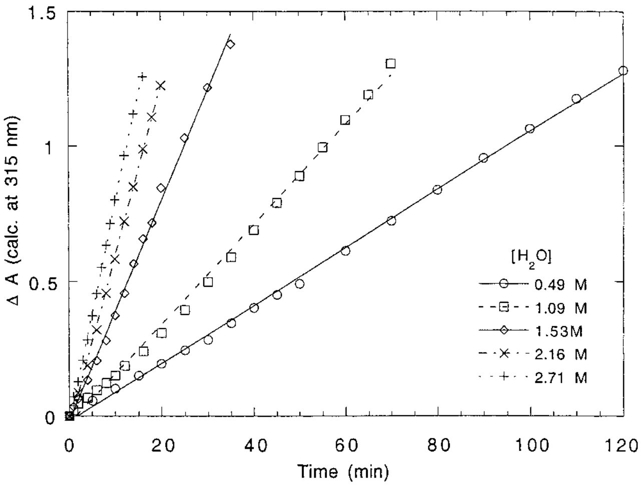


Figure 3. Zero−order kinetic rate constant fittings for the photolysis of TPCPGa: in acetonitrile. Initiation concentration of TPCPGa: 5.85 × 10^{-5} M, measured at 315 nm

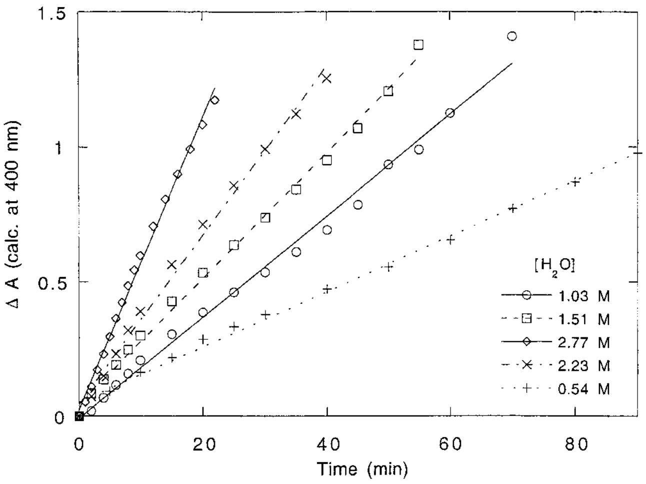


Figure 4. Zero−order kinetic rate constant fittings for the photolysis of DPMNCPGa: in acetonitrile. Initiation concentration of DPMNCPGa: 1.5 × 10^{-4} M, measured at 400 nm.

Table 1. Zero-Order Kinetic Rate Constants for the Photoreaction of TPCPGa

$[H_2O]$ (M)	0.49	1.09	1.53	2.16	2.71
k_{ob} (10^6 M/min)[a]	0.25	0.43	0.95	1.46	1.88
R	0.999 41	0.998 32	0.998 73	0.999 11	0.999 42

[a] $k_{ob} = k/l\epsilon$.

Table 2. Zero-Order Kinetic Rate Constants for the Photoreaction of DPMNCPGa

$[H_2O]$ (M)	0.54	1.03	1.51	2.24	2.77
k $_{ob}$ (10^6 M/min)[a]	0.54	0.98	1.22	1.63	2.82
R	0.997 67	0.996 20	0.998 37	0.996 86	0.997 81

[a] $k_{ob} = k/l\epsilon$.

proximate water forming the radical−radical cation pair (C). Cage escape releases the cyclopropenyl radical which dimerizes to give products. This is followed by photorearrangement of the dimer (discussed in the following sections).

In Scheme 1, we assume that a rapid equilibrium is established between cation A and complex B and that B is a loose complex; i.e., a hydrated cation:

$$K_1 = k_{f1}/k_{r1} = [B]/\{[A][H_2O]\}$$

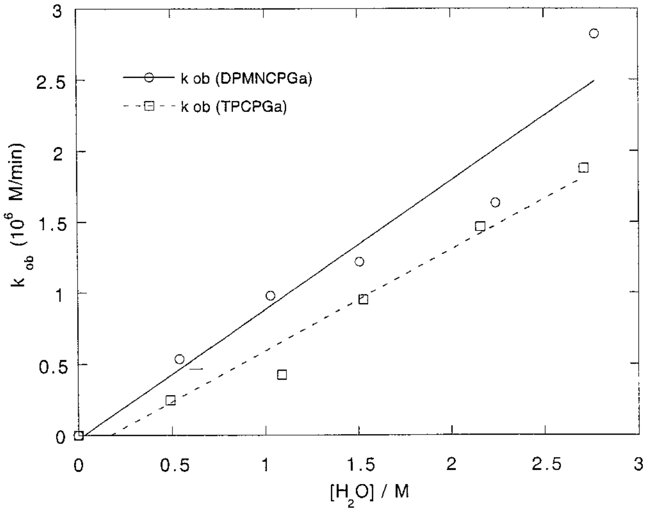
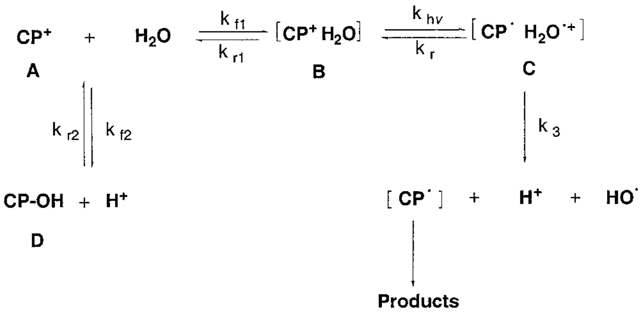


Figure 5. Zero−order kinetic rate constants varied with concentration of water: for the photolysis of TPCPGa and DPMNCPGa.

Scheme 1. Mechanism for Water Involvement in the Photoreaction of TPCPGa and DPMNCPGa



The rate of formation of C, the product of electron transfer, is then

$$d[C]/dt = I_{abs(B)}$$

where $I_{abs(B)}$ is the rate of light absorption by the complex B. The rate of formation CP•, the rate of reaction, is the rate of formation of B times the fraction of the excited complex C, which goes on to CP•:

$$a = k_3/\{k_3 + k_r\}$$

The formation of CP• becomes

$$I_{abs(B)} \times k_3/\{k_3 + k_r\}$$

Thus the rate of reaction depends only on the rate of light absorbed by B and the fraction that decays.

Because B is the hydrated ion of A, we assume that A and B have similar extinction coefficients. If this is the case, the fraction of the light absorbed by B is

$$[B]/\{[A] + [B]\}$$

We assume that the equilibrium for the reaction A + H_2O = B lays toward starting material. Therefore, [A] is always much larger than [B], and the total ion concentration that absorbs light is

$$\text{Total}\{[A] + [B]\} \cong [A]$$

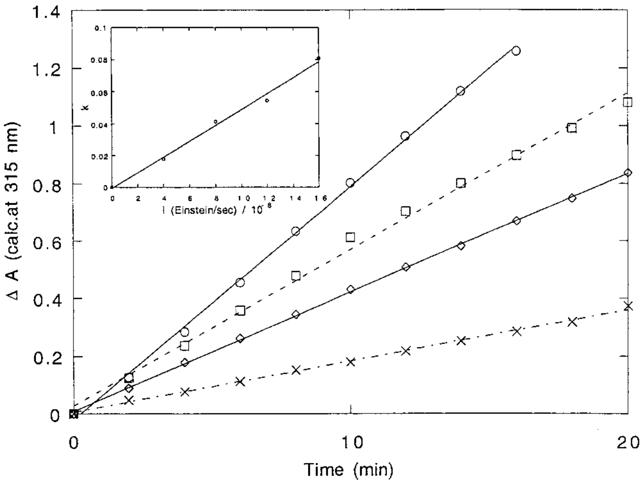


Figure 6. Effects of light intensity on the photolysis of TPCPGa: in acetonitrile, [TPCPGa] = 5.85 × 10^{-5} M, [H_2O] = 2.7 M (light intensity (*I*) in Einstein/s: (×) 4 × 10^{-8}; (◇) 8 × 10^{-8}; (□) 12 × 10^{-8}; (○) 16 × 10^{-8}]. Inset: kinetic rate constants variation with light intensity.

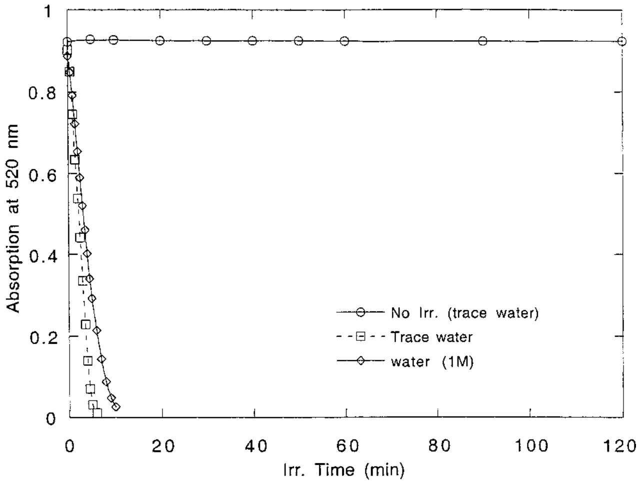


Figure 7. Photoacid release measurement of TPCPGa. Aceonitrile, [TPCPGa] = 1 × 10^{-3} M, [QR] = 10 ppm, monitored at 520 nm.

Thus, the light absorbed by B is

$$I_{\mathrm{abs(B)}} = I_{\mathrm{total}}[\mathrm{B}]/\{[\mathrm{A}] + [\mathrm{B}]\} \cong I_{\mathrm{total}}[\mathrm{B}]/[\mathrm{A}] = I_{\mathrm{total}}\, K_1[\mathrm{H_2O}]$$

So the rate of reaction is proportional to the H_2O concentration:

$$\mathrm{d}[\mathrm{CP}^\bullet]/\mathrm{d}t = I_{\mathrm{abs(B)}}k_3/\{k_3 + k_\mathrm{r}\} = I_{\mathrm{total}}k_{\mathrm{f1}}k_3[\mathrm{H_2O}]/k_\mathrm{r}(k_3 + k_\mathrm{r})$$

This fits the results.

From the equations above, the reaction rate should be light intensity dependent. The rate constants of the photochemical reaction of TPCPGa show a linear dependency on light intensity, Figure 6.

Additional evidence in support of the proposed mechanism comes from trapping protons produced using the base quinaldine red (QR) as an indicator (Figure 7). TPCPGa itself does not react with QR in that there is no change in the UV−vis spectrum, even after 24 h, when it is added to a QR solution. However, the sharp visible band of QR at 520 nm is completely bleached in 5 min with UV irradiation (300 nm). We also found that there is no change in the sharp visible band when water (1 M) is added to a solution of TPCPGa (1.0 × 10^{-3} M) containing ~10 ppm QR. This indicates that few protons are produced without irradiation and that the equilibrium (eq 2) lays toward starting material.

$$\mathrm{TPCP^+ + H_2O \rightleftarrows TPCPOH + H^+} \qquad (2)$$

The rate of acid release was slowed by the addition of water since the produced proton is first trapped by water and then transferred to QR (since the amount of water was much higher than QR):

$$\mathrm{TPCP^+ + 2H_2O} \xrightarrow[h\nu]{} \mathrm{H_3O^+} \xrightarrow[\mathrm{QR}]{} \mathrm{QRH^+ + H_2O}$$

The feasibility of electron-transfer from water to the triarylcyclopropenium salt may be estimated by comparing the standard electrode potentials E_p for the redox reactions involved. From the spectrum of TPCPGa, $E_\mathrm{s} \approx$ 84 kcal/mol (335 nm). The measured $E_{\mathrm{red}} = -0.75$ V (vs SCE) [10] for the reaction

$$\mathrm{TPCP^+ + e \rightleftharpoons TPCP^\bullet}$$

while $E_{\mathrm{ox}} = 2.85$ V (vs SCE)[13] for the reaction

$$\mathrm{HO^\bullet + H_3O^+ + e \rightleftharpoons 2H_2O}$$

From the Relm−Weller equation,[14]

$$\Delta G_{\mathrm{ET}} = 23.06[E_{\mathrm{ox}} - E_{\mathrm{red}} - \mathrm{e}^2/\alpha\epsilon] - E_\mathrm{s}$$

$$\Delta G_{\mathrm{ET}} = 23.06(2.85 + 0.75 - 0.06) - 84 = -\ 2.37\ (\mathrm{kcal/mol})$$

The singlet state energy of DPMNCPGa, was $E_\mathrm{s} \approx 81$ kcal/mol (350 nm). Though we did not determine E_{red} for

$$\mathrm{DPMNCP^+ + e \rightleftharpoons DPMNCP^\bullet}$$

reaction, it should be less negative than that for the reduction TPCPGa, because of the methoxy groups on the naphthalene ring.

When DPMNCP tetrafluoroborate was refluxed with zinc in anhydrous benzene,[15] similar products as observed in the photoreaction were isolated.[16] This is further evidence for a single electron-transfer reaction to the cyclopropenium cation in the photochemical process.

Photochemical Reactions of TPCPGa and DPMNCPGa Monitored by ^{1}H NMR. In a typical experiment, 10 mg of TPCPGa and DPMNCPGa was irradiated (λ_{rr} = 300 nm) in CD_3CN (0.75 mL). The disappearance of TPCPGa signals at δ 7.87−8.42 ppm was accompanied by a new signal at δ 6.84 ppm that could be assigned to hexaphenylbenzene. The disappearance of methoxy groups of DPMNCPGa at δ 4.18 ppm was accompanied by four new signals due to the photoproducts at δ 3.22 (a), 3.67 (b), 3.74 (c), and 3.85 (d) ppm (Figure 8). No intermediate(s) were detected implying the intermediate bicyclopro-

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(16) The structures of the products were confirmed by ^{1}H NMR and MS spectroscopies.

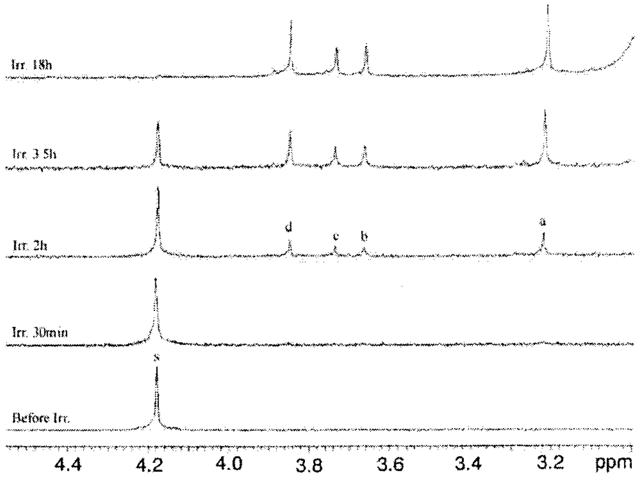
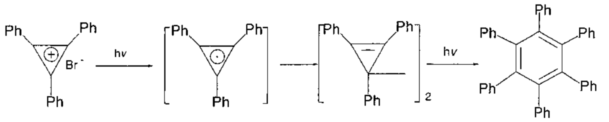
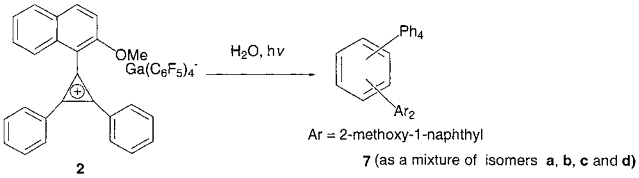


Figure 8. ^{1}H NMR monitored photolysis of DPMNCPGa in CD_3CN (10 mg/0.75 mL). Changes of 2-methoxy group during irradiation.

Scheme 2. Photochemical Reaction of TPCP Salt



Scheme 3. Photochemical Reaction of DPMNCPGa



penyl undergoes secondary photorearrangement under the irradiation conditions as soon as it is formed.

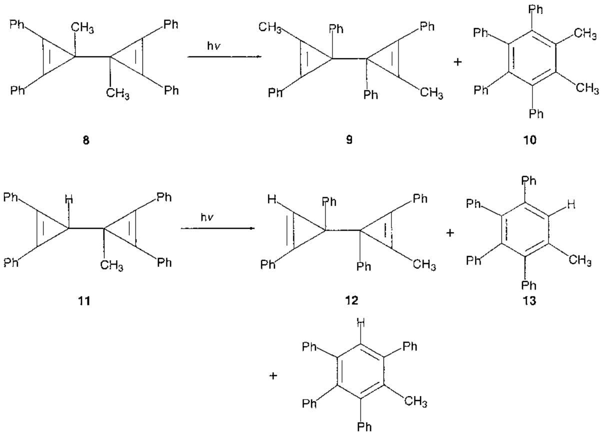
Mechanism for the Formation of the Photoproducts. The only report on the photolysis of a TPCP salt was published in 1968[9] where it reported that photolysis of TPCP bromide (**3**) in 10% aqueous sulfuric acid gave primarily hexaphenylbenzene (**6**). The authors proposed that "charge transfer" formed the cyclopropenyl radical (4) from the cation, which couples to the bicyclopropenyl (5), the precursor of final product (Scheme 2). Though the electron source was not mentioned, we surmise it to be bromide ion.

Though hexaphenylbenzene is the main photoproduct formed from TPCPGa,[17] four isomers of bis(2-methoxy-1-naphthyl)-tetraphenylbenzene (7) were isolated in the DPMNCP case (see Scheme 3).

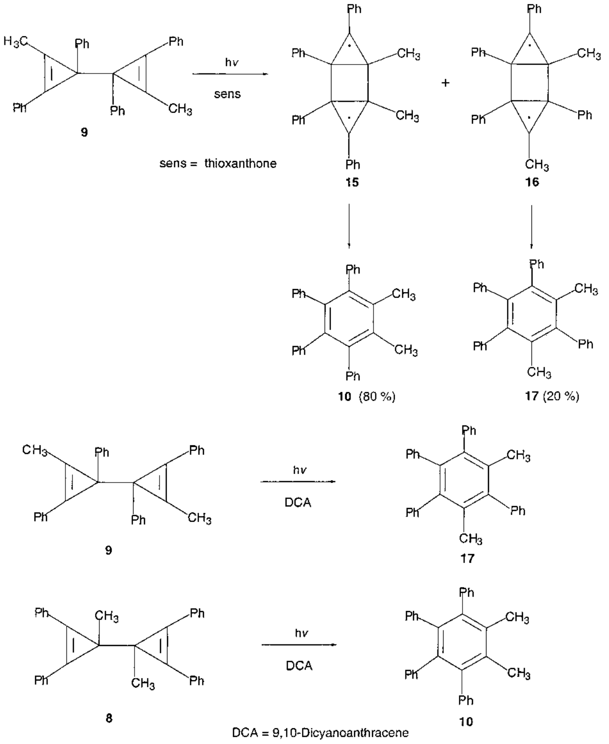
Weiss et al.[18] had studied the photorearrangement of bicyclopropenyl derivatives to benzene analogues finding that dimethyl compound (**8**) produced only 1,2-dimethyltetraphenylbenzene (**10**), while monomethyl compound (**11**) gave two benzene derivatives (**13**) and (**14**), along with their bicyclopropenyl isomers (**9**) and (**12**) (see Scheme 4).

Subsequently, Padwa et al. reported the sensitized photolysis of bicyclopropenyls 8 and 9.[19] Triplet (thioxanthone) sensitized photolysis of **9** produces a 4:1 mixture of ortho (**10**) and meta (**17**) isomers, while 9,10-dicyanoanthracene (DCA)-sensitized photolysis produces only the meta isomer (see Scheme 5).

Scheme 4. Photorearrangement of Bicyclopropenyl to Benzene



Scheme 5. Sensitized Photolysis of Bicyclopropenyl Compounds



Both reports imply that photolysis of bicyclopropenyls give ortho- and meta-substituted benzene isomers in either the direct irradiation or the sensitized process.

We propose a similar radical coupling process for formation of bis(2-methoxy-1-naphthyl)tetraphenylbenzenes (**7**). Electron transfer from water to the excited cyclopropenium salts, followed by cage escape of the radical−radical cation pair, gives cyclopropenyl radical (**18**) which dimerized to bicyclopropenyls **19** or **20**. Secondary photorearrangement of **19** or **20** gives the photoproducts 1,2-bis(2-methoxy-1-naphthyl)tetraphenyl-

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[17] The structure of hexaphenylbenzene was confirmed by comparison with a commercial sample.

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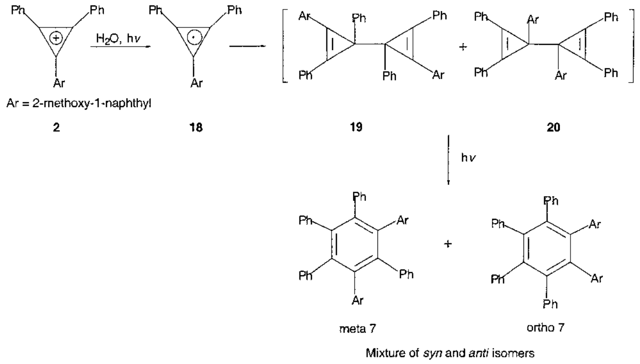
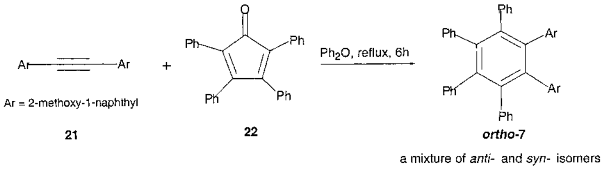
[19] Padwa, A.; Goldstein, S. I.; Rossenthal, R. J. *J. Org. Chem.* **1987**, *52*, 3278.

Scheme 6. Formation of Bis(2-methoxy-1-naphthyl)Tetraphenylbenzenes (7)



Scheme 7. Synthesis of the Photoproducts 1,2-Bis(2-methoxy-1-naphthyl)-tetraphenylbenzene (*ortho*-7)



benzene (*ortho*-**7**) and 1,3-bis(2-methoxy-1-naphthyl)-tetraphenylbenzene (*meta*-**7**) (see Scheme 6).

Assignment of the structure of the two *ortho*-**7** isomers can be made by comparison with independently synthesized samples (Scheme 7). The synthesis of *meta*-**7** has been attempted but has so far been unsuccessful.

Conclusions

Photochemical reactions of triarylcyclopropenium tetrakis(pentafluorophenyl)gallates TPCPGa and DPMNCPGa have been studied. Traces of water were found necessary for the reactions to proceed. The kinetics of these reactions found both salts obey zero-order kinetic laws with the rate constants (k) showing a linear dependence on the concentration of water. Four isomers of bis(2-methoxy-1-naphthyl)tetraphenylbenzene (**7**) were isolated in the DPMNCPGa case. *syn*-/*anti*-Isomers were formed along with *ortho*/*meta*-isomers during the irradiation. An electron-transfer from water to the cyclopropenium cation is proposed as the primary process in the formation of the cyclopropenyl radical which dimerizes leading to the photoproducts.

Experimental Section

Materials and Solvents. All chemicals and solvents (anhydrous grade) were used as received from Aldrich unless otherwise noted. Quinaldine Red (QR) was purchased from Acros Organics. Lithium tetrakis(pentafluorophenyl)gallate and triphenylcyclopropenium hexafluoroantimonate were prepared as previously reported.[10,20]

General Methods. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 200 or 400 MHz. $CFCl_3$ was used as an external standard for ^{19}F NMR. Irradiations were carried out in a Rayonet photochemical reactor (16 300 nm lamps) equipped with a jacketed beaker (Pyrex). Thin-layer chromatography was performed with Whatman silica gel coated TLC plates. Elemental analysis was performed by Atlantic Microlab, Inc.

Synthesis of Triphenylcyclopropenium Tetrakis(pentafluorophenyl)gallate (TPCPGa). To a solution of TPCP hexafluoroantimonate (0.503 g, 1 mmol) in acetonitrile (5 mL) was added a solution of lithium tetrakis(pentafluorophenyl)gallate (1.072 g, 1.2 mmol) in acetonitrile (5 mL). The mixture was stirred for 1.5 h at room temperature, and solvent was removed in vacuo. The residue was dissolved in dichloromethane (30 mL) and washed with water. After drying over $MgSO_4$, the filtrate was concentrated to give a white solid that was recrystallized from CH_2Cl_2-pentane to afford white crystals (0.8454 g) (84.1%), mp: 208−209 °C. ^1H NMR ($CDCl_3$): δ 7.87 (dd, $^3J_{H-H} = 7.9$ Hz, 6H, 3,5-H on phenyl), 8.04 (dd, $^3J_{H-H} = 7.8$ Hz, 3H, 4-H on phenyl), 8.42 (d, $^3J_{H-H} = 7.4$ Hz, 6H, 2,6-H on phenyl). ^{13}C NMR (CD_3CN): δ 120.98 (1-C on phenyl), 131.46, 136.90 (2,3,5,6-C on phenyl), 139.53 (4-C on phenyl), 156.80 (C on cyclopropenyl). ^{19}F NMR ($CDCl_3$): δ −123.63 (d, 2,6-F on C_6F_5), −158.96 (sm, 4-F on C_6F_5), −164.18 (s, 3,5-F on C_6F_5). Anal. Calcd for $C_{45}H_{15}F_{20}Ga$: C, 53.76; H, 1.50. Found: C, 54.01; H, 1.59. MS: m/z 570.30 [4.32, $Ga(C_6F_5)_3$]; 434.35 (30.97, $C_{21}H_{15}$-C_6F_5); 267.25 (100.00, $C_{21}H_{15}$).

Synthesis of Diphenyl-(2-methoxy-1-naphthyl)cyclopropenium tetrakis(pentafluorophenyl)gallate (DPMNCPGa). DPMNCP tetrafluoroborate was prepared in 78.7% overall yield following a modified literature procedure.[21] Thionyl chloride was used in place of phosgene and allowed to react with diphenylcyclopropenone at 50 °C for 30 min. Removal of the excess thionyl chloride gave 3,3-dichloro-1,2-diphenylcyclopropene which was used for the next step without purification. mp 178−180 °C (lit. 177 °C).

To a solution of DPMNCP tetrafluoroborate (0.0868 g, 0.2 mmol) in CH_2Cl_2 (1.5 mL) was added a solution of lithium tetrakis(pentafluorophenyl)gallate (0.196 g, 0.22 mmol) in CH_2Cl_2 (1.5 mL). The mixture was stirred for 2 h at room temperature, and the solid removed by filtration. To the mother liquid was added hexane to precipitate the product as a yellow solid (0.175 g,) with yield of 80.7%, mp: 182−184 °C. The product was further purified by a silicon gel column using CH_2Cl_2−pentane as eluent. ^1H NMR (CD_3CN): δ 4.19 (s, 3H, OCH_3), 7.63−7.81 (m, 3H, 4,5,6-H on naphthyl), 7.85−7.92 (m, 5H, 3,5-H on phenyl and 7-H on naphthyl), 8.00−8.08 (m, 2H, 4-H on phenyl), 8.14 (d, d, $^3J_{HH} = 8.4$ Hz, 1H, 3-H on naphthyl), 8.41−8.45 (m, 4H, 2,6-H on phenyl), 8.58 (d, $^3J_{HH} = 9.2$ Hz, 1H, 8-H on naphthyl). ^{19}F NMR (CD_3CN): δ −119.61 (d, 2,6-F on C_6F_5), −154.37 (sm, 4-F on C_6F_5), −160.30 (s, 3,5-F on C_6F_5). Anal. Calcd for $C_{50}H_{19}F_{20}OGa$; C, 55.33; H, 1.76. Found: C, 55.26; H, 1.95. MS (Dip): m/z 570.40 [20.83, $Ga(C_6F_5)_3$]; 514.45 (100.00, $C_{26}H_{19}O$-C_6F_5); 347.15 (4.32, $C_{26}H_{19}O$).

Synthesis of 1,2-bis(2-methoxy-1-naphthyl)tetraphenylbenzene (*ortho*-7). A solution of bis(2-methoxy-1-naphthyl-1)acetylene (**21**)[22] (0.338 g, 1 mmol) and tetraphenylcyclopentadienone (0.384 g, 1 mmol) in diphenyl ether (2 mL) was degassed with dry argon for 5−10 min. The mixture was then heated to reflux for 7 h and subsequently cooled to room temperature. Solvent was removed by washing with hexane, and the crude product was purified by recrystallization from CH_2Cl_2-cyclohexane to give a white solid (0.20 g, a mixture of *anti*- and *syn*-isomers), mp: >320 °C. ^1H NMR ($CDCl_3$): δ 3.08 (s, 1.5H, OMe), 3.55 (s, 1.5H, OMe), 6.47−6.52 (m, 1.5H), 6.58−6.74 (m, 3.5H), 6.85−6.95 (m 5.5H), 7.00−7.10 (m, 1.5H), 7.22−7.26 (m, 2.5H), 7.38 (d, 0.5H), 7.60−7.80 (m 0.5H), 7.88 (d, 0.5H). MS (dip): m/z 694.75 (100.00), 347.25 (12.43). A crystal (0.28 g, one isomer) was obtained from the mother liquid after standing for several days. ^1H NMR ($CDCl_3$): δ 3.08 (s, 3H, OMe), 6.49 (d, $J = 9.2$ Hz, 2H), 6.58−6.75 (m, 3H), 6.85−6.97 (m, 5H), 7.02−7.09 (d, d, $J = 6.6$ Hz, $J = 8.0$ Hz, 2H), 7.22−7.29 (m, 2H), 7.37 (d, $J = 8.8$ Hz, 1H), 7.87 (d, $J = 8.6$ Hz, 1H). MS (dip): m/z 694.75 (100.00), 347.25 (13.92).

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(20) Ren, K.; Mejiritski, A.; Malpert, J. H.; Grinevich, O.; Gu, H.; Neckers, D. C. *Tetrahedron Lett.* **2000**, *41*, 8669.

(21) Föhlisch, B.; Bürgle, P. *Liebigs Ann. Chem.* **1967**, *701*, 67. ^1H NMR (CD_3CN): δ 4.19 (s, 3H, OCH_3), 7.63−7.81 (m, 3H, 4,5,6-H on naphthyl), 7.85−7.93 (m, 5H, 3,5-H phenyl and 7-H naphthyl), 8.14 (d, $3J_{HH} = 8.4$ Hz, 1H, 3-H naphthyl), 8.00−8.08 (m, 2H, 4-H phenyl), 8.41−8.45 (m, 4H, 2,6-H phenyl), 8.58 (d, $3J_{HH} = 9.6$ Hz, 1H, 8-H naphthyl). MS: m/z 366 ($C_{26}H_{19}$-F); 347 ($C_{26}H_{19}O$), 694 ($C_{26}H_{19}O$-$C_{26}H_{19}O$).

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General Procedure for ^{1}H NMR Monitored Photolysis of TPCPGa and DPMNCPGa and Isolation of the Photoproducts. TPCPGa (10 mg) or DPMNCPGa (10 mg) was dissolved in CD_3CN (0.75 mL) in an NMR tube. The solution was degassed with dry argon for 5−10 min and then irradiated in a Rayonet photoreactor (16 300 nm lamps) equipped with a jacketed beaker (Pyrex). ^{1}H NMR spectra were followed during irradiation.

The photoproduct from TPCPGa precipitated during irradiation and was collected by filtration. ^{1}H NMR ($CDCl_3$): δ 6.84 (m). MS (dip): *m*/*z* 534 (100.00).

The photoproducts derived from DPMNCPGa were isolated by preparative TLC using hexane/CH_2Cl_2 as eluent. Four isomers, **a**, **b**, **c**, and **d,** were isolated as white solids. **a** (yield[23] 30.2%), ^{1}H NMR ($CDCl_3$): δ 3.08(s, 3H, OMe), 6.49 (d, $J = 8.6$ Hz, 2H), 6.58−6.75 (m, 3H), 6.85−6.97 (m, 5H), 7.02−7.09 (d, d, $J = 7.00$ Hz, $J = 7.00$ Hz, 2H), 7.22−7.29 (m, 2H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 9.0$ Hz, 1H). MS (dip): *m*/*z* 694.40/695.40 (100.00/55.74), 347.30 (21.39). **b** (yield[24] 14.4%), ^{1}H NMR ($CDCl_3$): δ 3.69 (s, 3H, OMe), 6.38−6.54 (m, 2H), 6.62−6.86 (m, 6H), 6.94 (m, 1H), 7.06−7.20 (m, 2H), 7.24−7.37 (m, 2H), 7.45 (d, d, $J = 8.4$ Hz, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz 1H). MS (dip): *m*/*z* 694.40/695.45 (100.00/52.60), 347.10 (17.34). **c** (yield[23] 14.1%), ^{1}H NMR ($CDCl_3$): δ 3.55 (s, 3H, OMe), 6.49 (m, 2H), 6.58−6.70 (m, 1H), 6.72 (d, 2H), 6.84−6.94 (m, 7H), 6.99−7.04 (m, 1H), 7.18−7.26 (m, 2H), 7.64 (m, 1H). MS (dip): *m*/*z* 694.40/695.45 (100.00/57.18), 347.25 (21.94). **d** (yield[23] 41.4%), ^{1}H NMR ($CDCl_3$): δ 3.61 (s, 3H, OMe), 6.51 (m, 2H), 6.65 (d, $J = 6.6$ Hz, 1H), 6.73−7.00 (m, 6H), 7.03−7.20 (m, 3H), 7.27−7.52 (m, 3H), 7.69 (d, $J = 8.0$ Hz, 1H). MS (dip): *m*/*z* 694.40/695.45 (100.00/59.13), 347.00 (16.86).

Reaction of DPMNCP Tetrafluoroborate with Zinc. A suspension of DPMNCP tetrafluoroborate (0.217 g, 0.5 mmol) and zinc (1.0 g, 15 mmol) in dry benzene (25 mL) was refluxed for 3 h. The solid was filtered to recover the starting material (0.17 g), the filtrate was concentrated, and the residue purified by preparative TLC. Four fractions **a**, **b**, **c**, and **d** found to be identical with **a**, **b**, **c**, and **d** isolated above were obtained as white solids. The structures of the products were confirmed from their ^{1}HNMR and mass spectra.

Kinetics for the Photolysis of TPCPGa and DPMNCPGa. A solution of TPCPGa (5.85×10^{-5} M) in acetonitrile to which water was added was degassed by bubbling with dry argon for 5−10 min, sealed in a quartz cuvette and then irradiated for 20−120 min in a Rayonet photoreactor (16 300 nm lamps) equipped with a jacketed beaker (Pyrex). Conversion of TPCPGa was followed to over 50% using UV−vis spectroscopy through the monitoring of the absorption at 315 nm. In the case of DPMNCPGa, the concentration of DPMNCPGa was 1.5×10^{-4} M and the absorption at 400 nm was monitored.

Measurement of Acid Produced. Solutions of TPCPGa (1×10^{-3} M) in acetonitrile containing ~10 ppm Quinaldine red were prepared such that the initial absorption of the solution at 520 nm was ~0.9. This solution was irradiated in a Rayonet photochemical reactor and the absorption of QR at 520 nm measured.

Measurement of Light Intensity. Light intensity was determined using 2-hexanone in cyclohexane.[24] Acetone was monitored by GC analysis to determine the progress of the reaction and dodecane was used as an internal standard in GC calibration.

Acknowledgment. The authors gratefully acknowledge financial support from NSF. We sincerely appreciate Dr. George Hammond for his helpful suggestion and discussion for the kinetic study. We also would like to thank Dr. Ling Zang, Ms. Haiyan Gu, and Ms. Fei Wang for helpful discussions.

JO0108562

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[23] The yields were calculated based on ^{1}H NMR spectroscopy.

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