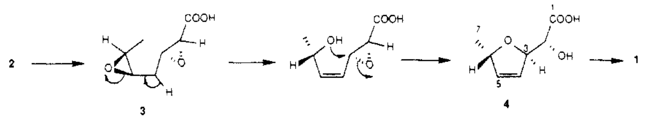
Table II. Incorporation of ($^{18}O_2$) into Furanomycin[a]

C	^{13}C shift (ppm)	% enrchmnt	$\Delta\delta^b$ (ppm)
3	86.46	25	0.024
6	86.39	25	0.031

[a] Carbon spectra were measured in D_2O at 75.47 mHz with Gaussian multiplication with LB = −1.0 Hz, GB = 0.40, SW = 20 000, 64 K data points. [b] $^{13}C^{18}O$ isotope shift.

Scheme II



system. When both the base and acid traps were present, and when the fermentation was carried out for 72 h under normal conditions before connection to the closed system, then significant production of furanomycin was observed. Administration of ^{18}O-labeled molecular oxygen (52.8 atom % ^{18}O) under these conditions yielded furanomycin whose ^{13}C NMR spectrum exhibited ^{18}O-induced shifts for both C-3 and C-6 (Table II). It can therefore be concluded that the oxygen atom comprising the ether linkage of furanomycin is derived from molecular oxygen.

On the basis of the findings described above, two mechanisms can be considered for the formation of the ether linkage of furanomycin. On the one hand, an oxygen atom could be introduced by hydroxylation of C-2 of the propionic acid moiety after its incorporation into the growing polyketide chain. Ether formation could then take place by attack of the oxygen-derived hydroxyl group upon the carbonyl carbon of the adjacent acetate unit. The plausibility of this mechanism is limited by the fact that hydroxylations at a saturated carbon atom generally take place with retention of configuration.[9] Alternatively, an oxygen could be introduced by epoxidation of a double-bond generated between C-5 and C-6 of the furanomycin skeleton as the result of a "processive" polyketide assembly process.[10] A likely substrate for this epoxidation would be *trans,cis*-2,3,5,6-heptadienoic acid (**2**) which could undergo epoxidation to give the diepoxide **3**. Ring-opening of the 5,6-epoxide followed by attack of the resulting hydroxyl group on the adjacent epoxide would then yield the α-hydroxy acid **4** that could be readily converted into furanomycin (Scheme II). This second mechanism for the formation of the ether linkage of furanomycin is of particular interest since it bears a close resemblance to that suggested for the formation of the ether linkages in the polyether antibiotics.[7] Support for the second mechanism is provided by studies of the allylic rearrangements catalyzed by β-hydroxydecanoylthioester dehydrase,[11] an enzyme involved in the anaerobic synthesis of unsaturated fatty acids. These studies suggest that the 5,6-double bond of **2** could arise by isomerization of a *trans*-2,3-pentenoate thiol ester intermediate to a *cis*-3,4-pentenoate thiol ester with loss of the 4 *pro*-R hydrogen. Since the 2 *pro*-R hydrogen of propionate corresponds to the 4 *pro*-R hydrogen atom of the putative 2,3-pentenoate thiol ester, the observed loss of the 2 *pro*-R hydrogen atom of propionate during furanomycin biosynthesis is consistent with such an isomerization and with the cyclization mechanism shown in Scheme II.

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Registry No. 1, 18455-25-9; O_2, 7782-44-7; propionic acid, 79-09-4; *trans,cis*-2,3,5,6-heptadienoic acid, 85110-95-8.

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Evolution of Electronically Excited Triphenylmethyl Radical. Picosecond Preparation-Pump-Probe Spectroscopic Experiments

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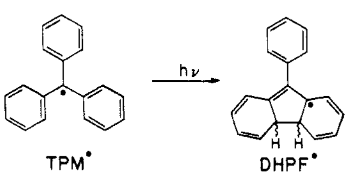
Investigations of the photochemistry and photophysics of excited states of short-lived organic species in solution are increasing in number as experimental methods are developed which permit the study of these intermediates.[1] Recent ns-resolved fluorescence and absorption studies of arylmethyl radicals revealed that the lifetime of the excited-state diphenylmethyl (DPM) radical in solution at room temperature is ~250 ns.[10-13,16] Itoh and coworkers[17] published the emission spectrum of benzyl radical (Bz•) in room temperature hexane solution and reported a fluorescence lifetime of ~1 ns. Meisel and co-workers[10,12,16] reported that excitation of the triphenylmethyl (TPM) radical in solution resulted in no detectable emission on the ns time scale at room temperature. For excitation of TPM• (eq 1),[10,12] an absorption band at 490 nm that appeared within the 10-ns excitation pulse was assigned to the 4a,4b-dihydro-9-phenylfluorenyl (DHPF) radical which persisted with a lifetime greater than 100 μs.



(1)

We have performed a series of novel three-pulse ps-resolved absorption experiments which provide information about the excited-state TPM radical prior to the formation of DHPF•. For these experiments, three 30-ps pulses of light are generated from a single 1064-nm pulse emitted from an actively-passively mode-locked Nd:YAG laser.[21] The time of arrival of each of

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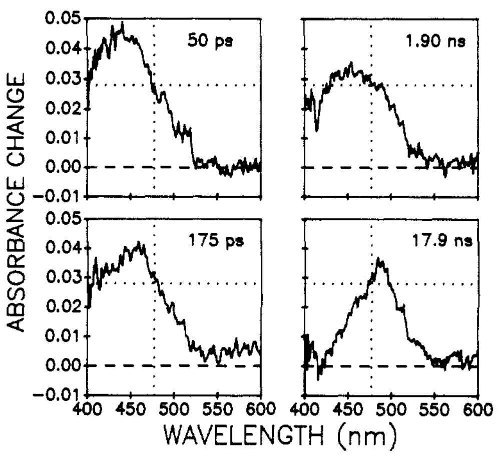

Figure 1. Selected transient absorption spectra recorded for p1, p2, and p3 arriving 0 ps, 75 ps, and *x* + 75 ps, respectively, at a sample of 3 mM TPMCl in C_6H_{12}; *x* is indicated for each spectrum. The crossed dotted lines emphasize the existence of an isosbestic point at 477 nm.

these pulses at the sample can be adjusted independently. The first laser pulse, p1, is used to prepare photochemically a short-lived species from a stable precursor. The second pulse, p2, is used to pump the prepared species to an electronically excited state. The third pulse, p3, is a white-light pulse used to probe the evolution of the excited species so that, in conjunction with multichannel optical detection, a 240-nm portion of the absorption spectrum can be recorded at a selected time relative to p1 and p2 for a single original laser pulse. With this laser system, species whose lifetimes are as short as ~10 ps can be monitored. When excitation with p1 produces two fragments, it is possible that interfragment and solvent-cage dynamics can be studied if p2 can stimulate a distance-dependent interaction between the two fragments, such as exciplex formation, electron transfer, or excitation energy transfer.

We made use of the results of Manring and Peters[22] who observed that TPM$^{\bullet}$ was generated within 50 ps after excitation of triphenylmethyl chloride (TPMCl) in cyclohexane with a 266-nm, 25-ps laser pulse. In our experiments which were conducted at ~22 °C, 3 mM TPMCl in C_6H_{12}, flowed through a 2-mm pathlength optical cell, was excited with p1, a 266-nm, 30-ps laser pulse (0.2–0.3 mJ). The pulse, p1, which prepared the TPM$^{\bullet}$–Cl$^{\bullet}$ pair was followed by p2, a 355-nm, 30-ps laser pulse (0.2–0.3 mJ), which excited TPM$^{\bullet}$ without exciting ground-state TPMCl or Cl$^{\bullet}$.[23] The transient absorption spectrum over the range of wavelengths from 400–640 nm at a selected time after p1 and p2 was recorded as a result of probing the sample with an independently timed, weak, 30-ps, white-light pulse (p3).

In the first series of experiments that we performed, the time of arrival of p2 at the sample was set at 75 ps after p1. The arrival time of p3 was continuously variable with respect to the preparation-pump pair of pulses. This sequence of pulses permits the recording of the evolving absorption spectrum of the excited sample. Figure 1 illustrates several of the transient absorption spectra that were recorded. The absorption band at 440 nm that is present at 50 ps after p2 is completely replaced within ~10 ns by the 490-nm band of DHPF$^{\bullet}$ that remains unchanged for as long as 18 ns after p2. When the spectrum of unreacted TPM$^{\bullet}$ was subtracted from the spectrum recorded for p1, p2, and p3 at 0 ps, 75 ps, and 10.0 ns, respectively, the resulting spectrum is superimposable with the one recorded by Meisel and coworkers[12] after excitation of TPM$^{\bullet}$. Analyses of our spectra reveal that ~25% of the ground-state TPM radicals are excited and removed with p2.

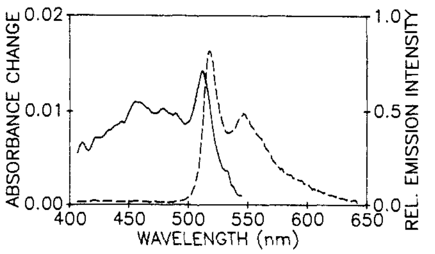

Figure 2. The transient absorption spectrum (—) of TPM$^{\bullet}$ recorded in the visible region at 100 ps after 266-nm excitation of TPMCl in pentane. This spectrum is the result of smoothing (25-point, ~1 nm/point)[29] the initially recorded spectrum. The emission spectrum (---) recorded during ~100 ms following 355-nm excitation of TPM$^{\bullet}$; the 355-nm excitation followed 100 ps after 266-nm excitation of 3 mM TPMCl in pentane.

A second series of experiments was performed in which the separation between p2 and p3 was fixed at 75 or 100 ps, and the time of arrival of this pump-probe pair of pulses was continuously variable relative to the 266-nm preparation pulse. This sequence of pulses potentially allows us to monitor the dynamics associated with the TPM$^{\bullet}$–Cl$^{\bullet}$ pairs in cyclohexane and possibly to elucidate the role of Cl$^{\bullet}$ in the photoinduced phenomena observed for the first pulse sequence described above. When p1, p2, and p3 arrived at 0 ps, *x* ps, and (*x* + *y*) ps, respectively, the spectra recorded for *y* = 100 ps and *x* = 75, 150, and 250 ps and for *y* = 75 ps and *x* = 1.00, 2.00, 3.00, 4.00, and 10.00 ns were the same within experimental error.

Any of several species can be assigned to the 440-nm absorption band observed at early times after p2. A possible assignment for this absorption band includes a $D_n \leftarrow D_1$ transition of TPM$^{\bullet}$,[24] an electronic transition associated with a TPM$^{\bullet}$–Cl$^{\bullet}$ complex, or an $S_n \leftarrow S_0$ transition[25] of TPM^{+} which is generated as a result of electron transfer from TPM$^{\bullet *}$ to Cl$^{\bullet}$ or from TPM$^{\bullet *}$ to solvent. Although it seems unlikely that 355-nm excitation of TPM$^{\bullet}$ results in electron ejection to C_6H_{12}, it cannot be rigorously excluded at this time. Without knowledge of the rates of separation of TPM$^{\bullet}$ and Cl$^{\bullet}$ and of the spin multiplicity of the first-formed radical pair, the results of the time-resolved absorption experiments for TPMCl described above are ambiguous with respect to the involvement of Cl$^{\bullet}$. If the Cl$^{\bullet}$ formed by photodissociation of TPMCl reacts via hydrogen-atom abstraction from the solvent with a rate constant that is comparable to that of "free" Cl$^{\bullet}$ ($k = 4.7 \times 10^9$ M^{-1} s^{-1} for cyclopentane[28]), effects of the presence of Cl$^{\bullet}$ can go undetected because the lifetime of Cl$^{\bullet}$ under our experimental conditions is too short.

Additional experiments have provided information concerning the identity of the 440-nm band. When p2 arrived at the sample of TPMCl in C_6H_{12} or pentane after p1, a yellow-green emission was visible that was not present when either p1 or p2 alone impinged upon the sample. The emission spectrum (Figure 2), whose intensity is linearly dependent on the 355-nm pulse energy, is the result of collecting light from the sample during ~100 ms

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(24) The similarity between the 440-nm band and the TPM^{+} absorption spectrum[25] or the DPM^{+} absorption spectrum[26] is noteworthy. A polar state ($Ar_2C^{+}{-}Ar^{\bullet -}$; Ar = aryl) has been proposed[27] as an intermediate generated after electronic excitation of the perchlorotriphenylmethyl radical.

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following p2 and, as a result, does not provide information about the lifetime of the emitting species. This emission spectrum compares well with those reported for TPM$^\bullet$ in frozen solutions at 90 K[30] and at 77 K[11] and therefore represents the first such measurement for TPM$^\bullet$ in room temperature solution.

Preliminary results of time-resolved absorption experiments, obtained for TPM$^\bullet$ generated from *tert*-butyl triphenylperacetate, which utilized the two sets of pulse sequences described for TPMCl revealed that the spectral evolution of this system is analogous to that recorded for TPM$^\bullet$ generated from TPMCl. These results indicate that the presence of Cl$^\bullet$ is not necessary for the generation of the 440-nm band.

Our current tentative assignment of the species responsible for the 440-nm absorption band observed at early times after 355-nm excitation of TPM$^\bullet$ is a $D_n \leftarrow D_1$ transition of TPM$^\bullet$. A firm assignment awaits the results of experiments that are in progress. Among these experiments is the measurement of the emission lifetime associated with the spectrum depicted in Figure 2, so that a comparison can be made with the decay time of the 440-nm absorption band. Also underway are attempts to probe the behavior of TPM$^\bullet$–Cl$^\bullet$ pairs in solvents that react less rapidly with Cl$^\bullet$.

Acknowledgment. This research was supported by National Science Foundation Grants CHE-8605560 and CHE-8602678, by a Bristol-Myers Company Grant of Research Corporation, and by a grant of the Florida State University Council on Research and Creativity. We thank Professor Marye Anne Fox for a preprint of the paper describing the mechanism of the photolysis of the perchlorotriphenylmethyl radical.

Gas-Phase Reactions of Bis(η^5-cyclopentadienyl)methylzirconium(1+) with Dihydrogen, Ethylene, and Propylene

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Electron deficient d^0 transition-metal and d^{0}f^n lanthanide complexes have shown a wide range of reactivities including the catalysis of alkene polymerization[1–6] and the metatheses of both saturated and unsaturated hydrocarbons.[7,8] The synthetic utility of these reactions has generated considerable interest in this area of C–C bond-forming and C–H bond-activating processes. Our interest in directly comparing solution-phase and gas-phase reactions at metal centers[9] led us to investigate the ion/molecule reactions of a cationic d^0 zirconium(IV) alkyl complex, $[Cp_2ZrCH_3]^+$ (**1**; Cp = cyclopentadienyl), which has also been studied in solution by Jordan and co-workers.[4] To our knowledge this is the first direct comparison of an isolated cationic homogeneous mononuclear ethylene polymerization catalyst to its gas-phase analogue.

We applied Fourier transform ion cyclotron resonance mass spectrometry[10] to study the gas-phase reactions of $[Cp_2ZrCH_3]^+$. Electron impact (11 eV) on $Cp_2Zr(CH_3)_2$ ($P \approx 10^{-8}$–10^{-7} Torr) yields predominantly $[Cp_2ZrCH_3]^+$ and $[Cp_2Zr]^+$. A RF pulse is used to eject $[Cp_2Zr]^+$ from the ICR cell, thereby isolating $[Cp_2ZrCH_3]^+$ for ion/molecule reaction studies with substrates ($P \approx 10^{-6}$ Torr). Collision-induced dissociation[11,12] (CID) experiments on **1** show the loss of CH$_3$, strongly implying a metal–methyl structure. Binuclear zirconium ion formation limits the study of ion/molecule reactions to those with rate constants in the 3×10^9–5×10^{11} M^{-1} s^{-1} (2×10^{-12}–8×10^{-10} cm^3 s^{-1} $\approx k_{\text{collision}}$)[13] range. No evidence was found for the involvement of the Cp rings in the reactions examined; therefore, the transformations below are assumed to retain the Cp$_2$Zr unit.

Reaction of **1** with D$_2$ is observed with formation of a deuteride complex exclusively, proceeding at ~375 K with a second-order rate constant $k = 3.7 \times 10^9$ M^{-1} s^{-1} (6.1×10^{-12} cm^3 s^{-1}, efficiency $= k/k_{\text{collision}} \approx 0.006$) (eq 1). This result is consistent with a

$$[Cp_2ZrCH_3]^+ + D_2 \rightarrow [Cp_2ZrD]^+ + CH_3D \tag{1}$$

four-membered transition state used to describe the metathesis reactions of other d^{0}f^n metal complexes.[6,7,14] The reverse of eq 1 is not observed, and, unlike the bond strengths determined in the gas phase for most bare metal–methyl and metal–hydride ions,[15] eq 1 indicates $D[Cp_2Zr–CH_3]^+ < D[Cp_2Zr–H]^+$. Clearly, addition of ligands to the zirconium ion leads to a gas-phase bond strength order typical for condensed-phase-ligated transition-metal complexes.[16]

Jordan et al.[4] have observed ethylene polymerization by $[Cp_2ZrCH_3(THF)]^+$ in CH$_2$Cl$_2$ solution, but polymerization of ethylene by the solvent-free ion **1** is not observed in the gas phase. Instead, interaction of ethylene with **1** is followed by an intramolecular decomposition of the apparent insertion product, producing a metal–allyl complex, $[Cp_2ZrC_3H_5]^+$ (**2**), and H$_2$ (eq 2).

$$Cp_2ZrCH_3{}^+ + C_2H_4 \rightarrow Cp_2ZrC_3H_5{}^{\bullet +} + H_2 \tag{2}$$

Reactions of **1** with ethylene and propylene follow the stoichiometry $\mathbf{1} + C_nH_m \rightarrow [Cp_2ZrC_{n+1}H_{m+1}]^+ + H_2$. CID experiments performed on **2** are consistent with allyl formation, as fragments corresponding only to the loss of one and two molecules of H$_2$ as well as C$_3$H$_5$ are produced. The absence of further reaction of **2** with ethylene is also consistent with an η^3-allyl structure. Ballard and co-workers[21] reported the absence of activity toward polymerization of ethylene for the closely related complex Cp$_2$ZrCl(C$_3$H$_5$).

Reaction of **1** with ethylene does not produce $[Cp_2ZrH]^+$; thus, β-hydride abstraction followed by alkene elimination[1,17] is not observed in the gas phase. Insufficient information is available on the polymer formed in the Jordan system to determine the significance of reaction 2 in the solution polymerization of ethylene by **1**.[18]

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