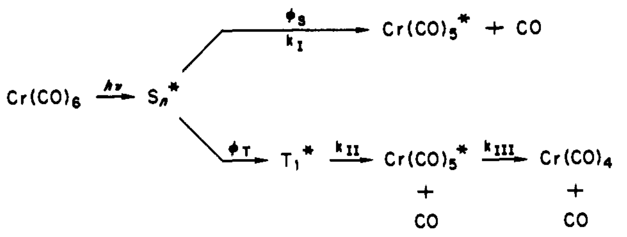
Scheme I



to ca. 36% of the total absorption amplitude at low pressure; III, a region where the rise time is more strongly pressure dependent than in II with a CO appearance rate[9] $k_{\rm III} \simeq 2 \times 10^6$ s^{-1} at 26 mtorr, corresponding to ca. 35% of the total absorption amplitude at low pressure; IV, a region where CO($v = 0$) is produced by collisional relaxation of CO($v \geq 1$) as determined by control experiments and pressure-dependence studies using argon buffer gas. The contribution from IV represents $\lesssim 9\%$ of the total absorption amplitude. In Figure 2, the slope for I is pressure independent while the slopes for II–IV each have a *different* pressure dependence. This provides good evidence that CO formation is occurring as a result of at least four processes. Neither II or III can be due to rotational relaxation of nascent CO, since in both cases, the observed rate constants decrease with increasing pressure. The processes associated with I–III can occur in the absence of collisions since they are observed even at p[Cr(CO)$_6$] < 5 mtorr where the time between collisions is ≥ 10 μs.

If photoexcitation of Cr(CO)$_6$ at 249 nm were followed by rapid internal conversion to yield the vibrationally hot ground state with unit efficiency, then the yield of CO must remain constant or decrease over the sequence I–III (Figure 2). This is clearly not the case. Moreover, RRKM estimates of the decomposition rates[10,11] for Cr(CO)$_n$* (n = 5,6) in the ground state are too fast (by ca. 10^4) to be consistent with the observed decarbonylation rates in regions II and III. Thus, most of the CO formed in our experiments must come from a relatively long-lived excited electronic state (or states) of Cr(CO)$_6$, e.g., a low-lying triplet state.[12] By contrast, the CO in region I is formed from a state whose lifetime is <100 ns. Pressure-dependence studies using pure Cr(CO)$_6$ and Cr(CO)$_6$/argon mixtures demonstrate that under all conditions $k_{\rm III} < k_{\rm II}$ and that the yield (absorption amplitude) associated with region III is less than or equal to that for II. This suggests the sequential nature of the associated decarbonylation steps, i.e.,

$$\mathrm{Cr(CO)_6^*} \xrightarrow{k_{\rm II}} \mathrm{Cr(CO)_5^*} + \mathrm{CO} \qquad (1)$$

$$\mathrm{Cr(CO)_5^*} \xrightarrow{k_{\rm III}} \mathrm{Cr(CO)_4} + \mathrm{CO} \qquad (2)$$

Thus, the yield for II is a measure of the efficiency, ϕ_T, with which the Cr(CO)$_6$ state initially prepared at 249 nm, S_n*, decays to the long-lived triplet state, T_1*. Similarly, the yield for I is a measure of the efficiency, ϕ_S, of the detector-limited decarbonylation, which likely results from the rapid predissociation of S_n* (or its internal conversion to the ground electronic state). Our data demonstrate that $\phi_S \leq 0.36$ and $\phi_T \leq 0.64$. With increasing pressure, vibrational energy is removed from T_1* via collisions, so that the decarbonylation rates of this species and the subsequently generated fragments decrease. The model proposed is summarized in Scheme I. It is possible that the process k_I forms Cr(CO)$_5$* with sufficient internal energy to decarbonylate further within our 100-ns detector rise time. In this case, the value determined for ϕ_S is an upper limit and that for ϕ_T is a lower limit. The mechanistic model suggested here is not unique and will undoubtedly be refined as further data become available. It is, nevertheless, the simplest model consistent with our observations and the findings of Yardley and co-workers,[4] who report that Cr(CO)$_4$ is the species formed in greatest abundance upon the 249-nm photolysis of Cr(CO)$_6$ vapor.

In summary, CO laser absorption spectroscopy has been used to study the dissociation dynamics of Cr(CO)$_6$ following photoactivation. Our results suggest that the excited state prepared at 249 nm yields CO both by rapid predissociation, with an efficiency $\phi_S \leq 0.36$, and by intersystem crossing to a long-lived triplet, with an efficiency $\phi_T \geq 0.64$. The triplet state thus formed undergoes serial decarbonylation yielding Cr(CO)$_5$ and Cr(CO)$_4$.

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Registry No. Cr(CO)$_6$, 13007-92-6; Cr(CO)$_5$, 26319-33-5; Cr(CO)$_4$, 56110-59-9; CO, 630-08-0.

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Evidence for Rapid Pseudorotation in Triphenylcyclopropenyl Anion

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The Jahn–Teller theorem[1] predicts that the lowest singlet state (^{1}E′) of a symmetrically substituted cyclopropenyl anion will show first-order instability to C–C bond-length distortions that lower the symmetry from D_{3h}. Nevertheless, time-averaged equivalence of the three ring carbon atoms can be restored by pseudorotation.[2] Ab initio calculations have been used to locate the stationary points on the lowest energy pseudorotation pathway for the planar cyclopropenyl anion[3] and for the isoelectronic (NH)$_3^{2+}$.[4] In this Communication we present evidence that pseudorotation in triphenylcyclopropenyl anion is faster than proton capture.

Previous attempts to probe the symmetry of cyclopropenyl anions with three identical substituents[5] have been frustrated by the high pK_a of even triphenylcyclopropene.[6,7] When, in order to increase the acidity, the cyclopropene ring is substituted with groups that are more electron withdrawing than phenyl, Michael addition of the base to the strained-ring double bond occurs.[8] We sought to overcome these problems by using fluorodesilylation for carbanion generation.[9,10]

1,2,3-Triphenyl-3-(trimethylsilyl)cyclopropene (**2a**) was prepared by the photolysis of phenyl(trimethylsilyl)diazomethane

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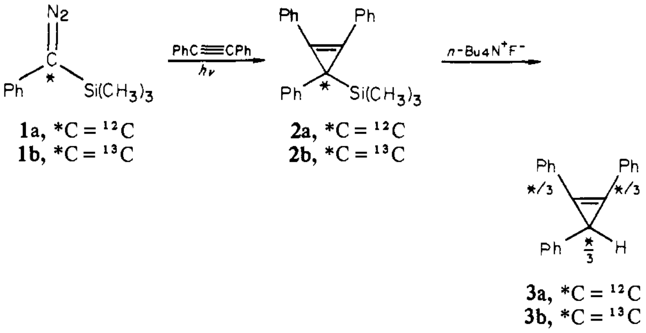
(**1a**)[11] in molten diphenylacetylene. After chromatography on silica gel and recrystallization from pentane at −20 °C, **2a**, mp 106.0–107.0 °C, was obtained in 78% yield.[12] Fluorodesilylation was carried out by heating 100 mg of **2a** in 3 mL of THF at 65 °C for 2 days with 0.6 mL (2.0 equiv) of 1 M tetra-*n*-butylammonium fluoride (Aldrich). An ^{1}H NMR spectrum of the crude reaction mixture after workup showed 1,2,3-triphenylcyclopropene (**3a**) to be the only detectable product. After recrystallization from pentane, **3a**, mp 111.0–112.0 °C (lit.[6] 112–113 °C), was isolated in 74% yield.



1a, *C = ^{12}C
1b, *C = ^{13}C

2a, *C = ^{12}C
2b, *C = ^{13}C

3a, *C = ^{12}C
3b, *C = ^{13}C

Proton abstraction by the putative triphenylcyclopropenyl anion formed in this reaction presumably occurred from the 5% H_2O present in the tetra-*n*-butylammonium fluoride solution. In order to verify that this was the case and to show that hydrogen atoms were not being abstracted from the THF solvent by a radical or diradical species, 0.6 mL of the tetra-*n*-butylammonium fluoride solution was evaporated and dried for 30 min at 0.1 torr. Then 1 mL of D_2O was added, the solution evaporated, and the salt dried again in the same way. The residue was dissolved in 3 mL of THF, and the fluorodesilylation reaction was carried out as before. The ^{1}H NMR and mass spectrum of the triphenylcyclopropene that was isolated showed the incorporation of 0.8 atoms of deuterium at C-3.

In order to probe the symmetry of the putative triphenylcyclopropenyl anion intermediate, ^{13}C-labeled 1,2,3-triphenyl-1-(trimethylsilyl)cyclopropene (**2b**) was prepared by addition of labeled phenyl(trimethylsilyl)diazomethane (**1b**) to diphenylacetylene. The diazo compound was synthesized starting with $^{13}CO_2$ (90% ^{13}C), which was allowed to react with phenylmagnesium bromide. The labeled benzoic acid was reduced to benzyl alcohol, which was converted to benzyl chloride. Formation of the Grignard reagent, reaction with trimethylsilyl chloride,[13] oxidation of the benzyltrimethylsilane product to benzyl trimethylsilyl ketone in two steps,[14] and pyrolysis of the lithium salt of the tosylhydrazone[11] resulted in the production of **1b** in an overall yield of 10% for the eight steps.

When Pyrex-filtered light from a 550-W Hanovia high-pressure mercury arc or from a 300-W General Electric quartz slide projector lamp was used to decompose the diazo compound **1b** in molten diphenylacetylene, the ^{13}C label in the resulting triphenyl(trimethylsilyl)cyclopropene was found by ^{13}C NMR to be totally scrambled. Although thermally induced 1,2 shifts of trimethylsilyl groups in cyclopropenes are known,[15] the modest temperature (65 °C) at which the addition reaction was conducted made such a rearrangement in **2b** unlikely under these conditions. Instead, it seemed probable that photoexcitation of **2b**, whose UV absorption extends out to 400 nm, was responsible for the observed scrambling of the ^{13}C label. Indeed, when a KV 470-nm filter was used with the quartz lamp, decomposition of the diazo compound (λ_{max} = 450 nm) again occurred; but **2b** was obtained with all of the ^{13}C label at C-3.

The **2b** thus prepared was subjected to the fluorodesilylation reaction described above. The upfield portion of the ^{1}H NMR spectrum of the product consisted of two doublets centered at δ 3.23, one with J = 168 Hz and the other with J = 2 Hz. The former corresponds to **3b** with the ^{13}C label at C-3 and the latter to **3b** with the ^{13}C label at C-1 and C-2. Correcting the integral of the central peak for the 10% of unlabeled **3a** hidden under it, gave a ratio of 1:1.8 ± 0.1 for the two integrals. Integration of the ^{13}C NMR spectrum in the presence of $Cr(acac)_3$, a paramagnetic relaxation reagent, gave essentially the same result.

The distribution of ^{13}C label in **3b** is close to the statistical ratio of 1:2.0. Substantial scrambling of the label thus occurs in the transformation of **2b** into **3b** by fluorodesilylation, although the scrambling does not appear to be quite complete. When the fluorodesilylation reaction of **2b** was interrupted after 75% completion and the unreacted **2b** examined by ^{13}C NMR, no scrambling of the label in **2b** was detected. Therefore, scrambling does not take place in the starting material under the reaction conditions. Since trimethylsilyl groups are known to undergo sigmatropic migrations with considerably greater facility than do protons,[16] the absence of detectable scrambling in **2b** renders it highly unlikely that the labeling pattern that is observed in **3b** is the result of scrambling that occurs after proton capture.

The nearly statistical distribution of ^{13}C in **3b** argues against proton capture occurring in an intermediate in which a pentavalent silicon remains bonded to C-3 of the three-membered ring. It would be quite surprising if this type of intermediate reacted with water in such a nonregioselective fashion. Moreover, we have found that 1,2-dimethyl-3-phenyl-3-(trimethylsilyl)cyclopropene[15] fails to undergo fluorodesilylation under the above reaction conditions. This provides further evidence against the rate-determining step involving a transition state that is not substantially stabilized by phenyl substituents on the double bond of the reactant.

We believe that the most economical interpretation of our data is in terms of the formation of a singlet triphenylcyclopropenyl carbanion. Although such a carbanion could conceivably undergo intersystem crossing to the triplet, the fact that proton capture rather than hydrogen atom abstraction apparently occurs suggests that singlet–triplet crossing is not competitive with protonation under our reaction conditions. If a singlet cyclopropenyl anion is, in fact, the reactive species, the nearly statistical distribution of the label in **3b** indicates that pseudorotation must occur faster than protonation. This in turn implies that the barriers to pseudorotation in the anion are small and/or that tunneling[17] makes an important contribution to the pseudorotation process.

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Formation of Photoactive Charge-Transfer Complexes between Methylviologen and Sacrificial Electron Donors. EDTA and Triethanolamine

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In recent years, model systems have been extensively studied that promote the photoreduction of H_2O to H_2 through the use