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A Photochemical Probe for Single Electron Transfer in Nucleophilic Aliphatic Substitution: Evidence for Geminate Radical Coupling in the Solvent Cage

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Abstract: A major effort to establish single electron transfer (SET) as an important pathway in nucleophilic aliphatic subsitution reactions has involved the use of cyclizable probes, e.g., 6-iodo-5,5-dimethyl-1-hexene. In order to examine the partition between cyclization and direct radical–radical recombination, we have investigated the ground-state and excited-state chemistry of the 9-phenylfluorenyl anion (**9PF**$^-$) with neopentyl-type iodides. It has been shown that **9PF**$^-$ does not react with Me_3CCH_2I, but it does undergo efficient reaction upon irradiation ($\Phi = 1.0$) to yield nucleophilic aliphatic substitution products. With the sterically analogous cyclizable probe 6-iodo-5,5-dimethyl-1-hexene, no ground-state reaction is observed. However, both cyclized and uncyclized products of substitution, **9PFR**$_c$ and **9PFR**$_u$, are produced upon irradiation. Thus photoproducts clearly involving electron-transfer-induced radical intermediates can result without acommpanying free-radical cyclization. These results suggest that, although the observation of cyclized products in the reaction of a cyclizable radical probe with a nucleophile is evidence of a radical intermediate, the absence of such cyclized products does not require the absence of radical intermediates.

Introduction

About ten years ago, one of us proposed that certain nucleophilic aliphatic substitution reactions, particularly involving hindered primary alkyl iodides, proceed through free radical intermediates formed by a single electron transfer (SET) initiation step.[1,2] Although the evidence in favor of this process was based upon a diversity of evidence, including the presence of hydrogen atom abstraction from the solvent, deuterium labeling, and trapping of intermediates, a significant part of the evidence involved the observation of cyclized intermediate radicals.[2] For instance, we observed that 6-iodo-5,5-dimethyl-1-hexene yielded cyclized products upon reaction with nucleophiles such as lithiopropiophenone, lithium thiolates, lithium diisopropylamide (LDA), $NaSnMe_3$, lithium diphenylphosphide, and $LiAlH_4$.[2,3] A difficulty in such studies is that, while the cyclized product is associated with radical intermediates, the presence of noncyclized products is generally associated with two-electron pathways. We have reported, however, that optically active secondary alkyl iodides lose optical activity upon substitution with nucleophiles which are plausible one-electron donors, suggesting that such reactions may involve radical intermediates that cause the loss of stereochemical integrity in the products.[4] Similarly, protium incorporation in $LiAlD_4$ reduction of a cyclizable alkyl iodide has been used as evidence

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for the intervention of free radical intermediates.[5] Although these observations regarding free radicals have been reinterpreted by Newcomb and Curran,[6] we reemphasize that the formation of noncyclized products, in the reaction of a cyclizable alkyl iodide probe as the dominant reaction product, does not necessarily rule out a single electron transfer pathway, but may simply reflect the relative efficiency of cyclization vs cage radical–radical recombination. We note that cyclization of the 2,2-dimethyl-5-hexenyl radical has a rate constant[7] of 3.6×10^6 s^{-1}, so that radical–radical recombination within a cage (rate constant $\sim 10^{11}$ s^{-1}) would certainly preclude the observation of cyclized products even when electron transfer is the dominant pathway, but would not preclude the formation of products in the solvent cage via radical–radical coupling.

Since sorting out the difference between two-electron and one-electron pathways is difficult when both processes can occur simultaneously, we sought conditions under which the two-electron pathway could be excluded and for which the SET pathway would be the exclusive route to product. Tolbert and co-workers observed previously that the 9-phenylfluorenyl anion (**9PF⁻**), while a modest electron donor in the ground state ($E_{1/2}$ = −0.55 V vs SCE),[8] has an excited state potential more negative than −2.64 V vs SCE.[9] Since, under the proper conditions, **9PF⁻** might resist alkylation by either ground-state single electron transfer or two-electron nucleophilic pathways, we elected to investigate this nucleophile as a possible substrate for further mechanistic investigations, using the cyclizable probe 6-iodo-5,5-dimethyl-1-hexene as the alkylating agent. We expected that the presence of a neopentyl moiety would minimize the intervention of ground-state reactions. In anticipation of the intervention of a radical-chain mechanism for formation of cyclized products via atom transfer, we chose to independently investigate the reaction of the cyclized alkyl iodide, 1-(iodomethyl)-3,3-dimethylcyclopentane, with **9PF⁻**. Finally, the efficient fluorescence quenching of **9PF⁻** by electron-acceptors made additional photophysical studies feasible.

Results

Synthesis of Reactants. The compounds 6-iodo-5,5-dimethyl-1-hexene and 1-(iodomethyl)-3,3-dimethyl-cyclopentane were prepared according to published methods[3a] and purified by preparatory gas–liquid chromatography. 1-Iodo-2,2-dimethylhexane was prepared by a method similar to that employed for the unsaturated compound.[3b] 9-Phenylfluorene (**9PF**) was synthesized by treatment of 9-fluorenone with phenyllithium or phenylmagnesium bromide followed by reduction of the resulting carbinol with formic acid.[10]

Table 1. Products of Irradiation of **9PF⁻** with Alkyl Iodides[a]

RI	yields, %[b]				
	9PFR$_c$	9PFR$_u$	R$_c$I	RH	R–R
6-iodo-5,5-dimethyl-1-hexene (**R$_u$I**)	41.7	16.5	trace	23.9[c]	2.3[c]
1-iodo-2,2-dimethylhexane		54.0		29.2	5.0
1-iodo-2,2-dimethylpropane		83.6			
1-iodomethyl-3,3-dimethyl-cyclopentane (**R$_c$I**)[d]	70.0		21.7		

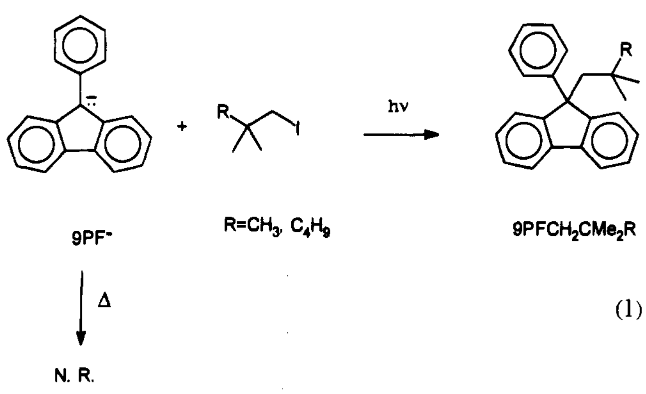
[a] Reactions conducted at −25° C, 0.32 M **9PF⁻** in THF for 2 h with 1.1 equiv of alkyl iodide. [b] Yields determined by GC analysis using internal standard. [c] Reduction products are cyclized in the case of R$_u$I. [d] Dark reaction at O °C for 3 h.

Table 2. Products of Irradiation of **9PF⁻** with 5,5-Dimethyl-6-iodo-1-hexene (**R$_u$I**)[a]

R$_u$I, M/L	yields, %[b]				
	9PFR$_c$	9PFR$_u$	R$_c$I	R$_c$H	R$_c$–R$_c$
0.47	57.4	12.8	0.0	21.6	1.7
0.67	54.5	15.7	0.0	26.7	2.0
0.90	43.4	14.5	0.0	22.1	4.5
1.10	41.7	16.5	trace	23.9	2.3
2.00	36.5	19.0	trace	17.3	2.9
3.00	31.0	17.5	2.4	13.0	2.5

[a] Reactions conducted at −25 °C in THF for 2 h using 0.032 M solutions of **9PF⁻**. [b] Yields determined by GC analysis using internal standard.

Initial Product Studies. We first investigated whether the presence of a neopentyl group would efficiently inhibit ground-state reactions. The 9-phenylfluorenyl anion (9PF⁻) was formed by deprotonation of 9-phenylfluorene (9PFH) in THF with *n*-butyllithium. The orange solution was treated with 1.1 equiv of 2,2-dimethyl-1-iodopropane and allowed to stand in the dark for 24 h. No detectable amounts of alkylation products were observed. Similarly, 6-iodo-5,5-dimethyl-1-hexene did not react with 9PF⁻ in the dark, nor did the saturated analog, 1-iodo-2,2-dimethylhexane. In contrast, upon irradiation of identical solutions with a tungsten flood lamp, efficient formation of new products was observed, and the compounds were identified by nuclear magnetic resonance and high-resolution mass spectroscopy. In the case of 2,2-dimethyl-1-iodopropane, a single product was observed in 83.6% yield. This product exhibited a parent ion in the mass spectrum at *m/e* 312.1881 (calculated for $C_{24}H_{24}$, 312.1878) and a base peak at 241.1, corresponding to the 9-phenylfluorenyl cation. The NMR spectrum consisted of singlets at δ 0.50 (9H), 2.70 (2H), and 7.1–7.9 (13H). Thus the structure of the product of alkylation at the formal site of negative charge was assigned to be 9-(2,2-dimethylpropyl)-9-phenylfluorene (eq 1). Similarly, on the basis of the mass spectrum, including a parent ion peak at 354.2352 (calculated for $C_{27}H_{30}$, 354.2348) and a base peak at 241.1, the reaction product from 1-iodo-2,2-dimethylhexane was assigned as 9-(2,2-dimethylhexyl)-9-phenylfluorene (see eq 1).



(1)

In the case of 6-iodo-5,5-dimethyl-1-hexene (**R$_u$I**), two products were produced in 16.5% and 41.7% yield. Both products exhibited parent ions at 352.2192 (calculated for $C_{27}H_{28}$, 352.2191) and base peaks at 241.1, indicating the formation of alkylation products at C-9. The 16.5% product was assigned to be 9-(2,2-dimethyl-5-hexenyl)-9-phenylfluorene (**9PFR$_u$**) on the basis of its NMR spectrum (see Experimental

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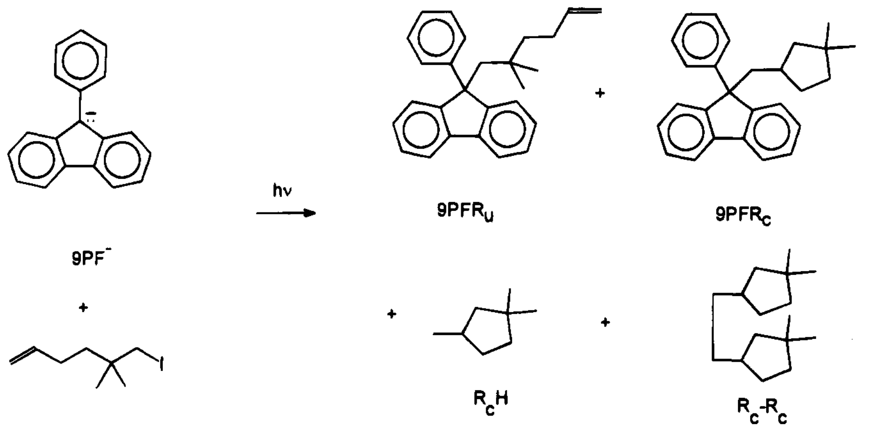

(2)

Section). The product formed in 41.7% yield was confirmed to be 9-((3,3-dimethylcyclopentyl)methyl)-9-phenylfluorene (**9PFR$_c$**) on the basis of its NMR spectrum and independent synthesis (eq 2). Additionally, products of hydrogen atom abstraction and radical dimerization were obtained, namely, 1,1,3-trimethylcyclopentane (23.9%) and 1,2-bis(3,3-dimethylcyclopentyl)ethane (2.35%). The products and yields are summarized in Table 1.

The yields of alkylation, reduction, and dimerization products were dependent upon the initial concentration of the alkyl iodide; the yield of cyclized product *decreased* with increasing iodide concentration, and the uncyclized product *increased.* The results of varying the iodide concentration are shown in Table 2. The ratio of cyclized product **9PFR$_c$** to uncyclized product **9PFR$_u$** was linear with the reciprocal of the alkyl iodide concentration (see Figure 1).

In contrast to the results with neopentyl iodide, reaction with the cyclized iodide 1-(iodomethyl)-3,3-dimethylcyclopentane (**R$_c$I**), a secondary iodide, occurred in the dark over a period of 3 h to give **9PFR$_c$** as the exclusive product in 70% yield in addition to 21.7% recovery of the unreacted iodide. Finally, in order to examine the possibility of a halogen atom radical chain pathway, reaction of **9PF**$^-$ in the presence of a 1:1 mixture of uncyclized and cyclized alkyl iodides **R$_u$I** and **R$_c$I** totaling 1 equiv was allowed to proceed to completion. An 85% yield of **9PFR$_c$** was obtained in addition to 11% recovery of unreacted cyclized iodide **R$_c$I**. No uncyclized alkylation product was obtained, and the acyclic alkyl iodide **R$_u$I** was recovered unchanged. In the absence of **9PF**$^-$, **R$_u$I** was also inert to the photochemical conditions employed.

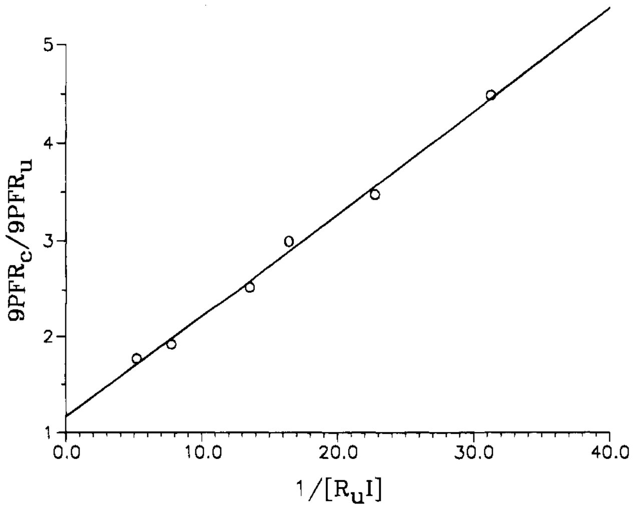

Figure 1. Dependence of cyclized/uncyclized ratio of products on **R$_u$I** concentration.

Photophysical Measurements. The fluorescence of **9PF**$^-$ was investigated as a function of alkyl iodide concentration and subjected to the Stern–Volmer kinetic treatment. Thus a plot of Φ_0/Φ vs [RI] was linear with excellent statistics except for the ground-state-active alkyl iodide. However, in all cases the slope of the Stern-Volmer plot ($k_q\tau$) was, within experimental error, the same regardless of the identity of the alkyl iodide (see Table 3). The value of k_{dt} for **9PF**$^-$ in THF was also determined by time-resolved single-photon counting and found to be 2.28×10^7 s^{-1}, which is within experimental error of the previously determined value in dimethyl sulfoxide (2.27×10^7 s^{-1}).[6b]

The absolute quantum yields for disappearance of **9PF**$^-$ in the presence of the two acyclic probes 6-iodo-5,5-dimethyl-1-hexene (**R$_u$I**) and 1-iodo-2,2-dimethylhexane were determined using ferrioxalate actinometry according to the procedure of Hatchard and Parker.[11] The quantum yields for both alkyl iodides were, within experimental error, 1.0 (see Table 3).

Discussion

The 9-phenylfluorenyl anion (**9PF**$^-$) undergoes electron-transfer-mediated alkylation reactions.[12] Moreover, picosecond absorption spectroscopy in the presence of electron scavengers, such as biphenyl, indicates the intervention of radical and radical–anion mediated pathways. These observations, together with the formation of cyclized alkylation, reduction, and dimerization products from the reaction of **9PF**$^-$ with the 6-iodo-5,5-dimethyl-1-hexene, require that the photomediated alkylation of **9PF**$^-$ by neopentyl iodides proceeds via a single electron transfer pathway. However, the dependence of product yields upon alkyl iodide concentration requires a more complicated mechanistic scheme. The proposed mechanism is described in Scheme 1. Based upon our observations, we have come to the following conclusions:

1. Quantum yield experiments show that photochemically promoted alkylations of **9PF**$^-$ with neopentyl iodides occur by a single electron transfer mechanism. Thus acyclic products from the cyclizable probe 6-iodo-5,5-dimethyl-1-hexene must also occur by single electron transfer. Clearly the formation of **9PFR$_u$** under conditions where SET is the only conceivable pathway establishes that cyclization is not an *a priori* condition for electron transfer. The absence of cyclized products in reactions with potential single-electron-transfer pathways, while

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Table 3. Photophysical Data for Reaction of 9PF$^{\cdot}$ with Alkyl Iodides in THF

RI	$k_q\tau$, M^{-1}	k_q, 10^{10} s^{-1}	Φ_{dis}
6-iodo-5,5-dimethyl-1-hexene (**R$_u$I**)	480	1.09 ± 0.16	1.01
1-iodo-2,2-dimethylhexane	484	1.10 ± 0.17	0.98
1-iodo-2,2-dimethylpropane	547	1.24 ± 0.15	
1-iodomethyl-3,3-dimethyl-cyclopentane (**R$_c$I**)	654	1.49 ± 0.36	

suggestive, is not *prima facie* evidence against such pathways, but represents a problem in relative rates.[13]

2. Our results support the notion that the radical anions of alkyl iodides, if they exist in potential energy minima, must have exceedingly short lifetimes.[14] To the extent that such radical anions exist, back electron transfer to the 9-phenylfluorenyl radical becomes a method for quenching the excited state and should lead to quantum yields considerably less than the observed value of 1.0. Although the possibility of dissociative electron transfer to alkyl iodides is not unprecedented, use of photoexcited carbanions as electron sources presents new experimental techniques for measuring such lifetimes.

3. Alkyl iodides undergo electron-transfer from photoexcited **9PF**$^-$ at diffusion controlled rates. Combination of the Stern–Volmer slopes (k_q/k_{dt}) with the measured value of k_{dt} allows us to calculate k_q for the alkyl iodides (Table 2). These values of k_q are the same, within experimental error, as the calculated value of the diffusion-controlled rate constant k_{diff} (1.06×10^{10} M^{-1} s^{-1}) in THF using the Debye equation[15] and the reported viscosity of THF (0.55 cp).[16]

4. 6-Iodo-5,5-dimethyl-1-hexene does not rearrange to 1-(iodomethyl)-3,3-dimethylcyclopentane under the conditions involved in these photochemical reactions. The ground-state reaction of 1-(iodomethyl)-3,3-dimethylcyclopentane with **9PF**$^{\cdot}$ does *not* proceed via single electron transfer or a chain transfer mechanism. To the extent that SET were involved, reaction of **9PF**$^-$ with 1-(iodomethyl)-3,3-dimethylcyclopentane in the presence of 6-iodo-5,5-dimethyl-1-hexene would lead to consumption of the latter, an observation which is not observed. Thus, at least for *sterically hindered* iodides, which are represented here by the acyclic iodides, but not by the cyclic iodides, electron transfer dominates the nucleophilic pathway.

5. The excited-state reaction of 6-iodo-5,5-dimethyl-1-hexene does proceed via single electron transfer, but does *not* proceed via a chain mechanism of the S$_{RN}$1 or halogen atom transfer type. The presence of a chain mechanism would clearly multiply the quantum yield, producing quantum yields greater than 1, since the resulting cyclized iodide would react via a ground-state mechanism. The fact that the quantum yield is 1 means that one photon consumes one molecule of product.

6. The dependence of product yields upon alkyl iodide concentration suggests that two different quenching mechanisms are operative. The fact that low alkyl iodide concentrations favor the cyclization pathway suggests that (a) the high-concentration regime involves a cage process in which radical–radical recombination occurs in competition with cyclization of the intermediate 2,2-dimethyl-5-hexenyl radical and that (b) the low-concentration regime favors the non-cage process in which radical–radical recombination does not compete with cyclization. Several plausible mechanisms would produce this observation. First, a minor pathway involving the formation of solvated electrons which are scavenged by alkyl iodide could dominate in the low alkyl iodide regime. This pathway is consistent with other spectroscopic observations that suggest the formation of solvated electrons[17] in the photoexcited triphenylmethyl anion. However, it is not compatible with the observation of diffusion-controlled fluoresence quenching. Second, both long-range (diffusional) and short-range (static) electron-transfer pathways, analogous to outer-sphere and inner-sphere electron transfer, may be operative. Thus irradiation of **9PF**$^-$, within a solvent cage containing alkyl iodide, could lead to prompt dissociative electron transfer and radical–radical recombination, while normal diffusion of the alkyl iodide to photoexcited **9PF**$^-$ could lead to long-range electron transfer outside the solvent cage. A third explanation was suggested by a referee, and involves the formation of a higher concentration of fluorenyl radicals at high alkyl iodide concentration. Under these conditions, the concentration of **9PF**$^{\bullet}$ may build up and exceed the concentration of the alkyl radicals. The acyclic product **9PFR$_u$** could be formed by a cage mechanism and the varying ratio of acyclic to acyclic products would depend upon the relative concentration of the persistent radical **9PF**$^{\bullet}$,[18] which at higher concentration would lead to increased trapping of **R$_u$** before cyclization. In all these mechanisms, radical reduction by tetrahydrofuran solvent is presumed to provide the source of protium. Although we lack sufficient evidence to prove this pathway or other pathways, the increased yields of reductive and dimeric products at low alkyl iodide concenrations are certainly evocative of the competition between cage and non-cage products.

Conclusions

Determining the limits to the intervention of single electron transfer in nucleophilic aliphatic substitution reactions remains a daunting task. Clearly, however, the upper limit to SET processes is *not* set by the yield of cyclized products in the reaction of hindered cyclizable alkyl iodides with nucleophiles, since uncyclized products can still be formed via SET pathways. The use of 9-phenylfluorenyl anion **9PF**$^-$ as a nucleophile, unreactive in the ground state, but reactive in the excited state, suggests that more quantitative methods based upon time-resolved spectroscopy may provide further insight into this challenging issue.

Experimental Section

Materials. Tetrahydrofuran (THF) was purchased from Aldrich and distilled from sodium benzophenone ketyl prior to use. *n*-Butyllithium, 9-fluorenone, and phenyllithium were purchased from Aldrich and used as received.

General Procedures and Apparatus. All glassware and syringes with stainless steel needles were flame dried under vacuum and cooled under argon before use. Liquids were transferred under argon using stainless steel cannulas and gas-tight syringes. Proton NMR spectra were recorded on a Varian Gemini 300 spectrometer with chemical shifts reported relative to tetramethylsilane. Mass spectra were obtained on a Varian MAT-112S mass spectrometer equipped with a gas chromatograph and electron-impact ionization. Analytical gas chromatography was performed on a Varian Model 3700 equipped with a FID detector and a 30 m DB-5 capillary column. Preparatory gas–liquid chromatography was carried out on a Hewlett Packard F&M Model 720 equipped with a thermal conductivity detector and a 6 ft

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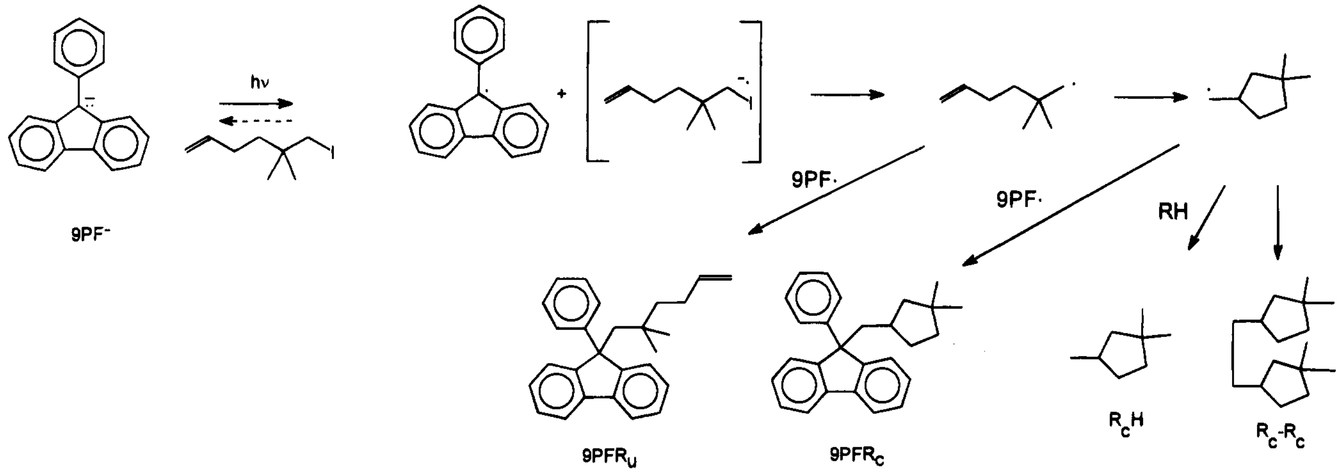
Scheme 1. Mechanism of Formation of Alkylation Products from **9PF⁻**



by 0.25 in. column of 10% Apiezon on Chromosorb P. Fluorescence spectra were recorded on a SPEX Model F112X spectrofluorometer. UV–visible spectra were obtained on a Gilford Response spectrophotometer.

General Procedure for Reactions of the 9-Phenylfluorenyl Anion with Alkyl Iodides. A 25-mL round-bottomed flask, equipped with a three-way stopcock and stirrer, containing 45 mg (0.18 mmol) of 9-phenylfluorene was dried under vacuum and filled with argon. After addition of 5 mL of anhydrous THF the flask was cooled to −25 °C, and 0.1 mL (0.16 mmol) of 1.6 M *n*-butyllithium in hexane was added. The mixture was allowed to react for 30 min, and the flask was allowed to reach the appropriate temperature (dark reaction at 0 °C, photoreaction at −25 °C). Then 35 mg (0.15 mmol) of 6-iodo-5,5-dimethyl-1-hexene in 2 mL of THF was added. For the photochemical reactions, the light from a 275W GE sunlamp was focused on the reaction flask. After 1 h, the mixture was quenched by a drop of MeOH, and the mixture was subjected to gas chromatographic analysis. For preparative purposes, the reaction amounts were increased by a factor of 10. The products were separated by flash chromatography via silica gel column chromatography (200−400 mesh) using pentane as eluent. 2,2-Dimethyl-1-hexane and 1,1,3-trimethylcyclopentane were identified by comparison with their known spectra. 1,2-Bis(3,3-dimethylcyclopentyl)ethane was identified by mass spectrometry. Starting materials and products obtained in each case are listed in Table 1. The following compounds were identified using ^{1}H NMR and mass spectral analysis.

9-((3,3-Dimethylcyclopentyl)methyl)-9-phenylfluorene (9PFR$_c$): ^{1}H NMR (CDCl$_3$) δ 7.1−7.8 (13H, m), 2.65 (2H, d), 0.6−1.3 (13H, m). MS *m/z* (rel intensity) 354.3 (0.5), 353.3 (4.0), 352.3 (13.3), 241.1 (100.0), 111.1 (10.4). Anal. Calcd for $C_{27}H_{28}$ 352.2191, found 352.2192.

9-(2,2-Dimethyl-5-hexenyl)-9-phenylfluorene (9PFR$_u$): ^{1}H NMR (CDCl$_3$) δ 7.0−7.8 (13H, m), 5.0−5.9 (3H, m), 2.60 (2H, s), 0.8−1.4 (10H, m). MS *m/z* (rel intensity) 353.3 (2.2), 352.3 (7.7), 241.1 (100.0), 111.1 (3.5), 69.1 (11.0), 55.1 (8.7). Anal. Calcd for $C_{27}H_{28}$ 352.2191, found 352.2192.

9-(2,2-Dimethylhexyl)-9-phenylfluorene: ^{1}H NMR (CDCl$_3$) δ 7.0−7.8 (13H, m), 2.70 (2H, s), 0.6−1.4 (15H, m). MS *m/z* (rel intensity) 355.2 (2.6), 354.2 (9.4), 241.1 (100.0), 113.1 (3.3), 71.1 (10.2), 57.1 (12.6). Anal. Calcd for $C_{27}H_{30}$ 354.2348, found, 354.2352.

9-(2,2-Dimethylpropyl)-9-phenylfluorene: ^{1}H NMR (CDCl$_3$) δ 7.1−7.9 (13H, m), 2.70 (2H, s), 0.50 (9H, s). MS *m/z* (rel intensity) 312.2 (17.6), 241.1 (100.0). Anal. Calcd for $C_{24}H_{24}$ 312.1878, found, 312.1881.

1,2-Bis(3,3-Dimethylcyclopentyl)ethane: The ^{1}H NMR exhibited multiplets from δ 0.8−1.6, but no peaks from δ 5−6. MS *m/z* (rel intensity) 222.3 (1.8), 207.2 (84.1), 151.2 (35.6), 97.1 (90.0), 55.1 (100.0), 41.0 (58.7).

Procedure for Fluorescence Quenching. A solution of 9-phenylfluorenyl anion (**9PF⁻**) in THF was prepared from 5 mg of 9-phenylfluorene in 100 mL of THF to which was added 13 μL of 1.6 M *n*-butyllithium in hexane. This solution had a molarity of 2×10^{-4} M and exhibited an absorbance of 0.7−0.8 at λ_{max} = 489 nm.[19] Aliquots of 5 mL were placed in six flame/vacuum dried anaerobic fluorescence cells via gas tight syringe. The fluorescence spectrum from 510−700 nm (λ_{ex} = 489 nm) was recorded, then 1, 2, 3, 4, and 5 μL of alkyl iodide were added to each cell. The fluorescence spectrum was again recorded and the ratio of integrated fluorescence intensity, with and without alkyl iodide, was calculated and plotted vs [RI]. The slope of the line, from linear regression analysis, is reported in Table 2 as k_q/k_{d1}.

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[19] Although absorbances below 0.05 are optimum for quantitative studies, concentrations below 10^{-4} M were difficult to control. Zimmerman and Tolbert have demonstrated that absorbances below 0.9 will not lead to serious errors due to self-absorption or concentration quenching: Zimmerman, H. E.; Tolbert, L. M. *J. Am. Chem. Soc.* **1975**, *97*, 4397.