

Communications to the Editor

Spectral Evidence for Single Electron Transfer in Nucleophilic Aliphatic Substitution of a Carbanion by Methyl Iodide

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Introduction

Despite the simmering debate within the community of physical organic chemists over the scope and importance of electron transfer in nucleophilic aliphatic substitution,¹ evidence continues to accumulate that electron transfer may play a role in some mechanisms for this substitution,² particularly when the electrophiles are sterically hindered alkyl iodides. In a recent paper, we described the ground state and excited state chemistry of 9-phenylfluorenyl anion (9PF⁻) with neopentyl-type iodides.³ Reaction with Me₃CCH₂I only occurred upon irradiation ($\Phi = 1.0$), whereas reaction with the sine qua non of alkyl iodides, methyl iodide, occurred rapidly in the dark. Thus, we contemplated the mechanistic consequences of using a sterically hindered nucleophile, 9-mesitylfluorenyl anion (9MsF⁻) with methyl iodide. We now report the first evidence that this reaction unequivocally produces radicals by direct and nearly quantitative observation of radical intermediates.

9-Mesitylfluorenyl anion (9MsF⁻) was prepared in tetrahydrofuran by deprotonation of 9-mesitylfluorene with butyllithium at -78 °C.⁴ Solutions of the anion were stable at room temperature and exhibited the characteristic three-peak absorbance at 460, 496, and 532 nm associated with the poorly allowed $\pi-\pi^*$ absorptions of fluorenyl anion.⁵ When MeI was added at 0 °C, the orange solution turned yellow, and gas chromatography/mass spectroscopic analysis indicated the formation of the methylated product, 9-methyl-9-mesitylfluorene, in ca. 60% yield. Methylation of 9-mesitylfluorene in Me₂SO/KOH produced the same product in >70% yield and allowed isolation of the methylated product.⁶ The color changes associated with the reaction in tetrahydrofuran could be monitored in the absorption spectrophotometer at low temperatures. Upon warming the sample from -78 to -40 °C, the characteristic absorption of the anion was replaced by the known

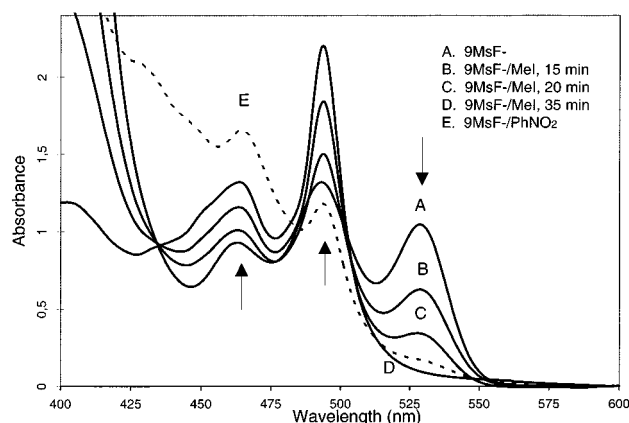


Figure 1. Evolution of 9-mesitylfluorenyllithium absorption spectrum at -40 °C: (A) after addition of butyllithium; (B) 15 min after addition of MeI; (C) 20 min after addition of MeI; (D) 35 min after addition of MeI; (E) after addition of PhNO₂.

absorption spectrum of 9-mesitylfluorenyl radical,² consisting of a peak at 495 nm and a broader peak at 465 nm. When the carbanion was oxidized with nitrobenzene, the same absorptions, superimposed on benzenenitronate absorptions, could be produced in equivalent amounts (Figure 1).

The spectroscopic observations are consistent with an electron transfer pathway in this alkylation reaction. Above -40 °C, 9MsF⁻ undergoes dissociative electron transfer to methyl iodide to yield methyl radical. Methyl radical can recombine with mesitylfluorenyl radical 9MsF• in the solvent cage to yield methylated product. Alternatively, radical pair separation leads to irreversible methyl radical dimerization or hydrogen atom abstraction, leaving the persistent mesitylfluorenyl radical.

From the unreactivity of 9PF⁻ toward neopentyl iodides, its strong reactivity toward sterically unhindered iodides, and the sluggish reactivity of 9MsF⁻ toward methyl iodide, a coherent picture begins to emerge. All of these alkyl iodides undergo dissociative electron transfer on the polarographic time scale, making direct electrochemical comparisons difficult. However, there is little electronic distinction between the sterically hindered and unhindered alkyl iodides, and thus, these would be expected to exhibit similar reduction potentials. Although the reduction potential of alkyl iodides cannot be measured due to their irreversibility, their reduction potential is below ca. -2 V vs SCE.^{2b} Similarly, 9-arylfluorenyl anions show little distinction between oxidation potentials⁷ and at ca. -0.5 V vs SCE⁵ provide a roughly constant but insufficient driving force for "outersphere" electron transfer. Hence, the mechanism must involve approach of the donor carbanion to the alkyl iodide at a near bonding distance which allows the electron transfer to occur at lower potentials (i.e., an "innersphere" electron transfer). What distinguishes the three cases mentioned here is the ease of steric approach, bearing in mind that, regardless of mechanism, the frontier orbital of the electrophile will be the $\sigma^* \text{C-I}$ orbital associated with Walden inversion (Scheme 1). Although S_N2 mechanisms are known to exhibit significant steric constraints, of which Walden inversion is the most profound, evidence has been presented that electron transfer processes may have steric components as well.^{2c} For methyl iodide and 9-phenylfluorenyl anion, backside approach is sterically feasible; whereas, with the same nucleophile and neopentyl iodide, it is not, and photoactivation is required. Conversely, for 9MsF⁻

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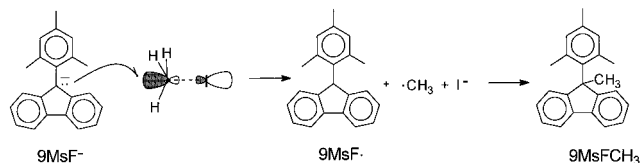
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(6) Spectral data: ¹H NMR (CDCl₃) δ 7.77 (d, $J = 7.5$, 2H), 7.33 (m, 2H), 7.22 (m, 4H), 6.93 (s, 1H), 6.58 (s, 1H), 2.90 (s, 3H), 2.23 (s, 3H), 1.88 (s, 3H), 1.01 (s, 3H); MS m/z (intensity) 298 (88), 203 (100), 268 (19), 253 (12), 252 (11), 179 (29), 178 (28). The gas chromatographic retention times of the two products were also identical.

(7) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979.

Scheme 1

reported here, backside approach is possible but not to within an $\text{S}_{\text{N}}2$ bonding distance. Rather, "innersphere" single electron transfer (SET) occurs.^{2d} Thus, the potential energy surface for the electron transfer mechanism is probably shallower but at a distance longer than that for the $\text{S}_{\text{N}}2$ transition structure. Indeed, the orbital interaction associated with electron transfer may not be at C-9 of the fluorenyl anion but at the more unhindered C-3 position.⁸ This regioselective electron transfer has precedence in the calculations of Shaik, who predicts a difference in

(8) Electron transfer induced alkylation of triphenylmethyl anions occur at both para and α positions: Tolbert, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 6808.

regioselectivity for alkylation of carbonyl radical anion for one- vs two-electron processes.⁹ In any event, this distance dependence for the electron transfer associated with nucleophilic substitution provides further permissive evidence for the intervention of SET in these substitutions and provides a further complication for distinguishing between SET and $\text{S}_{\text{N}}2$ pathways. That is, an innersphere SET pathway will have similar stereochemical constraints to the $\text{S}_{\text{N}}2$ pathway. Admittedly, the observation of SET is invariably the result of sterically inhibiting the normal presumptive $\text{S}_{\text{N}}2$ pathway and reducing its rate. We note, however, that this is apparently the first example of methyl iodide acting as an oxidant in this fashion.

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