at 0 °C for 2 h. The mixture was diluted with methanol (5 mL) at −78 °C and then treated with sodium borohydride (6.0 mmol) at 0 °C for 30 min. The mixture was then quenched with 10% aqueous HCl (50 mL) and extracted with benzene. The extracts were washed with brine and dried. Concentration and purification by silica gel column chromatography (hexane–ether, 5:1) afforded **3a** in 75% yield. The structure of **3a** was supported by spectroscopic[12] and analytical data.

Some of the reaction results are summarized in Table I. It is noteworthy that 1- and 2-naphthalenecarboxylates (**1**, **2**) were equally well converted to the corresponding dihydronaphthalenes (**3**, **4**, **5**) in good yields.

The one-flask process is constituted from a sequence of five chemical reactions: (1) addition of organolithium to naphthalene nucleus (**6**), (2) ketene formation (**7**) from BHA ester lithium enolate (**6**),[7] (3) in situ reduction of ketene with lithium triethylborohydride to aldehyde metal enolate (**8**),[13] (4) methylation of enolate with methyl iodide in the presence of HMPA (**9**), and finally (5) reduction of aldehyde with sodium borohydride in methanol to alcohol (**3**).[14]

Reductive generation of aldehyde metal enolate (**8**)[13] is apparent judging from the following results. Reduction of ester (**11**; R = Bu), prepared in 95% yield by treating **1** successively with butyllithium and methyl iodide–HMPA, afforded a mixture of complex products, being absent of alcohol **3**.[15] During the reduction of ester lithium enolate (**6**), disappearance of *cis*- and *trans*-esters[16] and at the same time appearance of BHA were detected by TLC analysis. Protonation of aldehyde metal enolate **8** with methanol and subsequent sodium borohydride reduction provided *trans*-1,2-disubstituted-1,2-dihydronaphthalenes (**5**) in high yields.[17] It is also important to note that although direct methylation of BHA ester enolate (**12**) generated from **2** provided a mixture of products (**13**, **14**), alkylated at the 4- and 2-positions, in a ratio of 2:1, probably due to the steric hindrance exhibited by BHA portion, methylation of aldehyde enolate afforded regio- and stereoselectively *cis*-alcohol (**4**).

In conclusion, we have developed for the first time a methodology for reductive generation and subsequent alkylation of aldehyde metal enolate. Since the present one-flask process to 1,2-disubstituted and 1,1,2- and 1,2,2-trisubstituted dihydronaphthalenes is an alternative to the elegant reaction scheme developed by Meyers based on the oxazoline[12,18] and imine chemistry,[19] our next goal is the development of an enantioselective one-flask process.[20,21]

Supplementary Material Available: Spectral and analytical data for **3**–**5**, **9**, **11a**,**c**, **13a**, and **14a** (6 pages). Ordering information is given on any current masthead page.

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(11) Reduction with diisobutyl aluminum hydride in place of super hydride provided **3a** in 30% yield.

(12) Meyers, A. I.; Lutomski, K. A.; Laucher, D. T. *Tetrahedron* **1988**, *110*, 3107.

(13) Actual metal species, lithium or borane enolate, or ate complexes shown in **8**, are not clear at the present time. Lithium enolates have been proposed not to form the corresponding enoxytrialkylborates. Negishi, E.; Idacavage, M. J. *Tetrahedron Lett.* **1979**, 845.

(14) Isolation of aldehyde caused a decreased yield, probably due to instability.

(15) Attempted oxidative removal of BHA of **11** with ceric ammonium nitrate (CAN)[9b] provided a mixture of coomplex products. However, catalytic hydrogenation of **11** and subsequent oxidative removal of BHA with CAN afforded the corresponding tetrahydronaphthalenecarboxylic acid.

(16) Addition reaction of organolithium with BHA naphthalenecarboxylate followed by aqueous workup provided the corresponding *cis*- and *trans*-dihydronaphthalenes in quantitative yield.

(17) After addition of methanol (5 mL) in the reaction at the stage of **8**, the whole mixture was warmed up to room temperature and then reduced with sodium borohydride to afford *trans*-**5** stereoselectively. Concomitant addition of methanol and sodium borohydride provided a mixture of *cis*- and *trans*-alcohols, indicating that initial protonation product is *cis*-aldehyde **10**.

(18) Meyers, A. I.; Roth, G. P.; Hoyer, D.; Barner, B. A.; Laucher, D. *J. Am. Chem. Soc.* **1988**, *110*, 4611. Andrews, R. C.; Teague, S. J.; Meyers, A. I. *Ibid.* **1988**, *110*, 7854 and references cited therein.

(19) Meyers, A. I.; Brown, J.; Laucher, D. *Tetrahedron Lett.* **1987**, *28*, 5283 and 5297.

(20) Tomioka, K.; Shindo, M.; Koga, K. *J. Am. Chem. Soc.* **1989**, *111*, 8266.

(21) We are grateful to financial support from Grant in Aid for Scientific Research, Science and Culture, Ministry of Education, Japan (No. 63303013 and 01571143).

Carbon–Carbon Bond Cleavage by the Dianion Mechanism. Small Kinetic Advantage over the Radical Anion Cleavage

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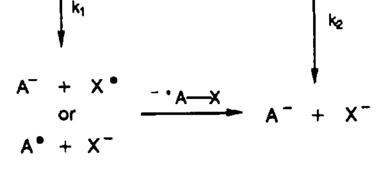
Received December 11, 1989

Summary: Carbon–carbon bond cleavage in dianions is faster than in radical anions as expected from thermodynamic considerations. However, in contrast to the radical anion fragmentation, where $\Delta G^{\ddagger} \cong \Delta G$, the dianion scission has a much larger intrinsic barrier ($\Delta G^{\ddagger} \gg \Delta G$).

Reductive cleavage of single C–C bonds by alkali metals has been postulated to involve radical anions, dianions, or even polyanions.[2,3] There are, however, only a few mechanistic studies published so far which provide data concerning the identity of the reactive species undergoing bond scission.[4-7] Two of these studies provided evidence

Scheme I



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(1) On leave from the Technical University of Łódź (Poland).

(2) For a summary of the relevant literature, see: (a) Grovenstein, E., Jr.; Bhatti, A. M.; Quest, D. E.; Sengupta, D.; VanDerveer, D. *J. Am. Chem. Soc.* **1983**, *105*, 6290 and references therein. (b) Staley, S. W. In *Selective Organic Transformations*; Thyagarajan, B. S., Ed.; Wiley Interscience: New York, 1972; Vol. 2, p 309. (c) Holy, N. L. *Chem. Rev.* **1974**, *74*, 243.

(3) (a) Marcinow, Z.; Hull, C. E.; Rabideau, P. W. *J. Org. Chem.* **1989**, *54*, 3602. (b) Schanne, L.; Haenel, M. *Tetrahedron Lett.* **1979**, *44*, 4245.

(4) Walsh, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 1511.

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Table I. Comparison[a] of the Kinetic and Thermodynamic Data for C–C Bond Scission in Neutral 1a and Its Anion and Dianion

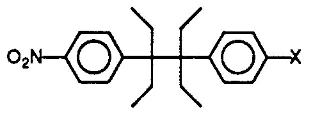
mode of cleavage		k (300 K)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$ (300 K)	ΔG^{b} (300 K)
homolysis[c]		6×10^{-10}	35.4 ± 1	17 ± 3	30.3 ± 2	30
radical anion cleavage	DMSO[d]	5×10^{-2}	17.0 ± 1	−8 ± 4	19.4 ± 2	17
	DMF	4×10^{-2}	18.8 ± 1	−2 ± 3	19.4 ± 2	17
dianion cleavage[e]		8×10^{1}	14.4 ± 1	−1 ± 2	14.8 ± 2	4

[a] Rate constants are in s^{-1} (estimated or measured); the estimated errors in the measured rate constants are ±15%. Activation enthalpy and free-energy data are in kcal/mol, activation entropy values are in cal/mol K [b] Free-energy of the reaction (±2 kcal/mol), assuming $\Delta G(\mathbf{1a}) = \Delta G^{\ddagger}(\mathbf{1a})$ and estimating from the redox data: $\Delta G(\mathbf{1a}^{\bullet-}) = \Delta G(\mathbf{1a}) - 23[E(\mathbf{2}^{-}/\mathbf{2}^{\bullet}) - \mathrm{E}(\mathbf{1a}^{\bullet-}/\mathbf{1a})]$ and $\Delta G(^{-\bullet}\mathbf{1a}^{\bullet-}) = \Delta G(\mathbf{1a}) - 46[E(\mathbf{2}^{-}/\mathbf{2}^{\bullet}) - E(\mathbf{1a}^{\bullet-}/\mathbf{1a})]$, where $E(\mathbf{2}^{-}/\mathbf{2}^{\bullet}) = -0.61$ V and $E(\mathbf{1a}^{\bullet-}/\mathbf{1a}) = -1.21$ V, both in DMSO at 300 K vs SCE (refs 8, 11). [c] Thermolysis in xylene in the presence of excess thiophenol (refs 8 and 18), $k(400\ \mathrm{K}) = 2 \times 10^{-3}\ s^{-1}$. [d] The data are for $\mathbf{1d}^{\bullet-}$ Li^{+} in DMSO (ref 5). The activation free energy for $\mathbf{1a}^{\bullet-}$ should be slightly smaller (ref 17). [e] The rate constant and the activation parameters correspond to $k_{app} = 2k_2k_e/k_{-e}$. At 252 K in DMF, $k_{app} = 0.81\ s^{-1}$.

for radical anion fragmentation[4,5] and two others implicated dianions as the reactive species.[6,7] We describe here the first comparison of these two modes of cleavage and provide kinetic and thermodynamic analysis of the mechanistic options. In both cases, the kinetic activation of the bond for scission (as compared to homolysis) is due to the increased driving force for fragmentation. However, in contrast to the radical anion, wherein most of the thermodynamic advantage is expressed in the lowering of the transition state energy,[8] only a relatively small fraction of the increased driving force contributes to the lowering of the dianion fragmentation barrier.

The mechanistic alternatives for reductive cleavage in homogeneous solution are summarized in Scheme I. The initially formed radical anions may undergo fragmentation (k_1) or can disproportionate (k_e/k_{-e}), giving dianions and neutral molecules. In the dianion the extra electrons can occupy the same π-system ($^{2-}$A–X) or can be distributed between the π-systems on both sides of the scissile bond ($^{-\bullet}$A–X$^{\bullet-}$).

We have recently explored[5,8] the C–C bond fragmentation in radical anions of nitro-substituted diphenylethane derivatives **1a–d**. We have found that the unimolecular fragmentation of $\mathbf{1b}$–$\mathbf{d}^{\bullet-}$ was tremendously accelerated[5] in comparison to the corresponding homolytic cleavage of **1b–d**, and that this C–C bond activation was due to thermodynamic factors.[8] The dinitro derivative, $\mathbf{1a}^{\bullet-}$, decayed at least 10^3 times faster than any other derivative ($\mathbf{1b}$–$\mathbf{d}^{\bullet-}$), however, the decay followed *second-order* kinetics.



1a: X = NO_2
b: X = H
c: X = NMe_2
d: X = CN

The radical anions of **1a** were produced by electron transfer from Li^{+} 2,4,6-tri-*tert*-butylnitrobenzenide[5,9] in DMF to minimize ion pairing.[10] The decay of $\mathbf{1a}^{\bullet-}$ could be followed by ESR spectroscopy only at low temperatures (215–252 K) in the presence of an excess of unreduced **1a**. The ESR spectrum of $\mathbf{1a}^{\bullet-}$ was characteristic of nitroaromatic radical anions, with the unpaired electron delocalized on only one of the nitroaryl moieties.[5] The 3-(4′-nitrophenyl)pentyl anion ($\mathbf{2}^{-}$) was the only product observed by NMR or UV/vis spectroscopy, and after quenching with deoxygenated $MeOH/H_2O$ the corresponding pentane was recovered quantitatively. One molar equivalent of the reducing agent led to consumption of only 0.5 molar equiv of the nitro compound.

The observed[11] second-order rate constant (k_{obs}) was inversely proportional to the concentration of **1a**. For example, in DMF at 215 K, k_{obs} for disappearance of $\mathbf{1a}^{\bullet-}$ Li^{+} was 0.093 $M^{-1}\ s^{-1}$ at [**1a**] = 0.0522 M and 0.19 $M^{-1}\ s^{-1}$ at [**1a**] = 0.0275. These observations are consistent with the mechanism presented in Scheme I, wherein the disproportionation equilibrium (k_e/k_{-e}) is followed by the rate-limiting fragmentation of a dianion of **1a** (k_2). According to this kinetic scheme, $k_{obs} = 2k_2k_e/k_{-e}[\mathbf{1a}]$. Several runs at various concentrations of **1a** and at different temperatures allowed us to determine the concentration independent apparent rate constants[11] ($k_{app} = 2k_2k_e/k_{-e}$) and the corresponding activation parameters (Table I). These activation parameters are a composite of the thermodynamic parameters (ΔH and ΔS) describing the equilibrium (k_e/k_{-e}) and the kinetic parameters of the dianion fragmentation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$).

The observed activation parameters exclude involvement of the dianion with the two electrons delocalized on the same aromatic moiety. The second reduction potential of nitrotoluene is 0.86 V higher than the first.[12] Therefore, the disproportionation equilibrium would be ca. 20 kcal/mol uphill, much more than the apparent activation energy of the process (Table I). It can be safely concluded that the reacting dianion has one electron on each of the two nitroaryl rings. Furthermore, the energy required to reduce the second ring should be essentially identical with that of the first reduction, a small charge-repulsion effect notwithstanding. To a first approximation, the ΔH of the disproportionation equilibrium should be very close to zero, and the position of the equilibrium should be only weakly affected by entropic terms. The entropic contribution will be due to symmetry factors[13,14] and also to any solvation changes associated with the accumulation of charge on one molecule.[15] Overall, the ΔG for the equilibrium should

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[5] Maslak, P.; Narvaez, J. N. *J. Chem. Soc., Chem. Commun.* **1989**, 138.

[6] Lagendijk, A.; Szwarc, M. *J. Am. Chem. Soc.* **1971**, *93*, 5359.

[7] Walsh, T. D.; Megremis, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 3897.

[8] Maslak, P., Narvaez, J. N. *Angew. Chem.*, in press.

[9] Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2628.

[10] Ion pairing may affect the rate of bond scission, the disproportionation equilibrium (k_e/k_{-e}) and influence the evaluation of the reaction thermodynamics. A polar solvent will minimize these complications (compare refs 13, 16, and 20).

[11] Kinetic data, Eyring plots, and thermodynamic cycles are provided as supplementary material.

[12] Maki, A. H.; Geske, D. H. *J. Am. Chem. Soc.* **1961**, *83*, 1852.

[13] In the ideal case, if there is no interaction between reducible groups, the additional difficulty of adding the second electron arises purely from statistical reasons (symmetry factors, refs 14a,c). In practice, these entropic considerations are complicated by solvent reorganization effects and by the fact that the dianion ($^{-\bullet}\mathbf{1a}^{\bullet-}$) can exist in a singlet or triplet states. Although, these states most likely do not differ significantly in energy, only the singlet state of $^{-\bullet}\mathbf{1a}^{\bullet-}$ can undergo fragmentation.

[14] (a) Benson, S. W. *J. Am. Chem. Soc.* **1958**, *80*, 5151. (b) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; p 232. (c) Ammar, F.; Savéant, J. *Electroanal. Chem.* **1973**, *47*, 215.

be small, amounting to no more than ±2 kcal/mol, as evidenced by a single-reduction wave observed for the related dinitro compounds.[16] In consequence, the observed $\Delta G^{\ddagger}$ is a good approximation for the activation parameters of the dianion cleavage. Most likely, it overestimates the true value by no more than 1–2 kcal/mol, primarily in the entropic term.[13,14,16]

The dianion cleavage reaction can be compared with the analogous fragmentation of $\mathbf{1d}^{\bullet -}$ which may serve as a model[17] for the unimolecular fragmentation of $\mathbf{1a}^{\bullet -}$ (Table I). This comparison is especially illuminating in the context of the thermodynamic considerations. As usual, the homolytic bond strength ($\Delta G(\mathbf{1a})$) may be approximated[8,18] by the activation energy for this process, $\Delta G^{\ddagger}(\mathbf{1a})$. The free energy change for the radical anion scission[8] ($\Delta G(\mathbf{1a}^{\bullet -})$) is smaller than $\Delta G(\mathbf{1a})$ by the difference (ΔE) between redox potentials of $\mathbf{2}^{-}/\mathbf{2}^{\bullet}$ and $\mathbf{1a}/\mathbf{1a}^{\bullet -}$. On the other hand, $\Delta G({}^{-\bullet}\mathbf{1a}^{\bullet -})$ is smaller than $\Delta G(\mathbf{1a})$ by *twice* the same difference in redox potentials.[11]

As shown in Table I, the observed acceleration of both radical anion and dianion cleavages have thermodynamic origin. However, in contrast to the radical anion scission, wherein almost all of the thermodynamic advantage is expressed in the lowering of transition-state energy[8] (i.e. $\Delta G(\mathbf{1a}^{\bullet -}) \approx \Delta G^{\ddagger}(\mathbf{1a}^{\bullet -})$), the dianion cleavage shows a distinct intrinsic barrier[19] ($\Delta G({}^{-\bullet}\mathbf{1a}^{\bullet -}) \ll \Delta G^{\ddagger}({}^{-\bullet}\mathbf{1a}^{\bullet -})$). A similar conclusion is obtained from the thermodynamic evaluation of the mechanistically equivalent dianion cleavage in 1,2-dinaphthylethane (**3**) reported by Szwarc.[6] In contrast to our study, the activation barrier for this system was measured in THF, where ion pairing complicates the analysis.[10,20] An approximate evaluation[21] yields $\Delta G(\mathbf{3}^{\bullet -}) = 28$ kcal/mol for the radical anion and $\Delta G({}^{-\bullet}\mathbf{3}^{\bullet -}) = 1$ kcal/mol for the dianion fragmentations. Not surprisingly the radical anion fragmentation was not observed in this case,[6] but the activation energy measured[6] for the dianion cleavage was 20 kcal/mol, i.e. almost 20 kcal/mol above the free energy change for this process.

The observed difference between the mono- and dianion scissions cannot be ascribed to the different endergonicity of the two processes. For example,[22] the radical anion of 2-(4′-cyanophenyl)-3-cyano-2-methyl-3-phenylbutane ($\mathbf{4}^{\bullet -}$) undergoes unimolecular fragmentation with a rate constant of ca. $9 \times 10^{6}\ \mathrm{s}^{-1}$ at 300 K ($\Delta G^{\ddagger}(\mathbf{4}^{\bullet -}) \approx 6$–$8$ kcal/mol). The free energy change accompanying this reaction ($\Delta G(\mathbf{4}^{\bullet -})$) is estimated[23] at 5 ± 2 kcal/mol. The central C–C bond cleavage in $\mathbf{4}^{\bullet -}$ has the activation barrier smaller than the corresponding process in ${}^{-\bullet}\mathbf{1a}^{\bullet -}$ by ca. 7 kcal/mol despite the fact the driving force is essentially identical for both processes. We conclude that the fragmentation reactions of dianions have much larger intrinsic barriers ($\Delta G({}^{-\bullet}\mathrm{AX}^{\bullet -}) \ll \Delta G^{\ddagger}({}^{-\bullet}\mathrm{AX}^{\bullet -})$) than analogous radical anion scissions for which $\Delta G(\mathrm{AX}^{\bullet -}) \approx \Delta G^{\ddagger}(\mathrm{AX}^{\bullet -})$.[8,22] Regardless of the origin and precise magnitude of the barrier, dianion formation can, however, increase the kinetic advantage of bond fragmentation over that of the monoanion.

These observations can be generalized to other than C–C bond cleavage reactions. As a rule, the fragmentation of radical anions will dominate in systems with relatively weak bonds ($\Delta G(\mathrm{AX}^{\bullet -}) = \Delta G(\mathrm{AX}) - \Delta E$),[24] such as in benzylic halides, ethers, and thioethers where stable anions are the products. The cleavage of dianions with extra electrons on both sides of the scissile bond should be of importance in systems where A and X (Scheme I) are electronically similar. In these cases, the ion pairing may, however, shift the disproportionation equilibrium significantly.[15] Dianions with two electrons on one aromatic system (AX^{2-}) will generally have the largest driving force (more negative ΔG). However, they will be accessible only in special cases of easily reducible AX molecules or in heterogeneous media, where the presence of undissolved alkali metals will provide high local concentration of electrons.

Acknowledgment. Financial support for this work was provided by the National Science Foundation. P.M. is a recipient of the Camille and Henry Dreyfus Foundation New Faculty Award.

Supplementary Material Available: Kinetic data, Eyring plots, and thermodynamic cycles (4 pages). Ordering information is given on any current masthead page.

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(15) Szwarc, M.; Jagur-Grodzinski, J. In *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; J. Wiley and Sons: New York, 1974; Vol. 2, p 1.

(16) Dinitrobicumene (reversible) and **1a** (irreversible) give single waves at ca. 1.2 V vs SCE. Two peaks with separation of ca. 100 mV could be detected under similar conditions (ref 14b). These results indicate that the addition of the second electron requires no more than 2 kcal/mol more energy than the first reduction.

(17) A series of radical anions of **1** with various X substituents have been investigated in DMSO (Maslak, P.; Narvaez, J. N.; Kula, J.; Malinski, D. S., submitted). For electron-withdrawing substituents there is a linear correlation between $\Delta G^{\ddagger}(\mathbf{1}^{\bullet -})$ and σ^{-} (or σ) extrapolation of which yields $\Delta G^{\ddagger}(\mathbf{1a}^{\bullet -}) = 18.6$ kcal/mol at 300 K. Also, the homolytic C–C bond strength in **1a** should be similar to that in **1d** (i.e. $\Delta G(\mathbf{1a}) \leq \Delta G(\mathbf{1d})$). Thus, $\mathbf{1d}^{\bullet -}$ provides a lower limit for the kinetics and thermodynamics of $\mathbf{1a}^{\bullet -}$.

(18) Compare: Krat, G.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1984**, *117*, 1748.

(19) The actual disparity between the two cleavage modes might be slightly smaller, in part due to the fact that the processes are evaluated at different driving forces and in part to the fact that the observed activation parameters based on k_{app} may overestimate slightly the true activation energy for the dianion cleavage.

(20) In this case ion pairing may have increased $k_{\mathrm{e}}/k_{-\mathrm{e}}$, since no cleavage has been observed in HMPA (ref 6). The effect of solvent (ion pairing and polarity) on ΔE should be rather small since the radical anion of **2** and the naphthylmethyl anion resulting from cleavage should be similarly solvated.

(21) This estimate is based on $\Delta G(\mathbf{3}) = 56$ kcal/mol (Sato, Y. *Fuel* **1979**, *58*, 318), the reduction potential of 1-methylnaphthalene (−2.48 V vs SCE; Streitwieser, A., Jr.; Schwager, I. *J. Phys. Chem.* **1962**, *66*, 2316) and the reduction potential of naphthylmethyl radical (−1.27 V vs SCE; Dr. D. D. M. Wayner, private communication; compare: Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132).

(22) Maslak, P.; Kula, J., unpublished results.

(23) The thermodynamic estimate is based on $\Delta G(\mathbf{4}) = 41$ kcal/mol (ref 22), the reduction potential of *p*-cyanotoluene (−2.38 V vs SCE; Rieger, P. H.; Bernal, I.; Reinmuth, W. H.; Fraenkel, G. *J. Am. Chem. Soc.* **1963**, *85*, 683) and the redox potential of α-methyl-α-cyanobenzyl anion (−0.82 V vs SCE, ref 22. Compare: Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986** *108* 1979. Arnett, E. M.; Harvey, H. G.; Amarnath, K.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 4143).

(24) $\Delta G(\mathrm{AX})$ stands for the free energy of homolysis of AX, and $\Delta E = E(\mathrm{AX}^{\bullet -}/\mathrm{AX}) - E(\mathrm{A}^{-}/\mathrm{A}^{\bullet}$ or $\mathrm{X}^{-}/\mathrm{X}^{\bullet})$.