Reactivity of 1-Iodoadamantane with Carbanions by the $S_{RN}1$ Mechanism

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The photostimulated reaction of 1-iodoadamantane (**1**) with carbanions in DMSO has been studied. Acetone enolate ion (**2a**) reacted with **1** to give the substitution product (**4a**, 20%) and adamantane (**3**, 17%); acetophenone enolate ion (**2b**) gave the substitution product (**4b**, 65%) in the presence of 18-crown-6. In the reaction with propiophenone enolate ion (**2c**), the yield was lower (27%). Anthrone anion (**5**) gave good yields (75%) of the substitution product **6**. The anion of nitromethane (**7**) did not react with **1** under photostimulation, but in the presence of **2a** or **b**, 87% of 1-adamantylnitromethane (**8**) was obtained (entrainment reactions). Low amounts of substitution products were found with the fluorene anion and no substitution was observed with other carbanions. It is suggested that these reactions occurred by the $S_{RN}1$ mechanism.

By competition experiments, the following reactivity order toward 1-adamantyl radicals was determined: **2a** (1.0) < **2b** (11) < **7** (32) < **5** (80). The reactivity observed is explained on the basis of the pK_a of the conjugate acid of the anions and on the changes in π energy (HOMO carbanion − SOMO radical anion intermediate) that takes place in the coupling reaction.

By competition experiments of **1** and PhI toward **2b**, a $k_1 : K_{PhI}$ ratio of *ca.* 16 was found while 1-bromoadamantane and PhBr gave a $k_{1\text{-}BrAd} : k_{PhBr}$ ratio of *ca.* 0.13. This difference can be attributed to the capacity of phenyl radicals to abstract iodine atoms from **1** giving PhI and 1-adamantyl radicals, which ultimately results in an apparent greater reactivity of **1** *vs.* PhI.

The $S_{RN}1$ mechanism is a well known route in the substitution of unactivated aromatic halides by different types of nucleophiles.[1] The main reaction steps proposed involve the fragmentation of the radical anion of the substrate to give a radical and the nucleofugal group [eqn. (1)] and the reaction of the radical with the nucleophile to give the radical anion of the substitution product [eqn. (2)] which by an electron transfer (ET) to the substrate completes the chain propagation cycle of the proposed mechanism [eqn. (3)].

$$(RX)^{\cdot -} \longrightarrow R^{\cdot} + X^{-} \qquad (1)$$

$$R^{\cdot} + Nu^{-} \longrightarrow (RNu)^{\cdot -} \qquad (2)$$

$$(RNu)^{\cdot -} + RX \longrightarrow RNu + (RX)^{\cdot -} \qquad (3)$$

In aliphatic systems without a low lying π^* MO such as bridgehead, cyclopropyl, cyclohexyl and neopentyl halides, the radical anion $(RX)^{\cdot -}$ probably is not an intermediate and eqns. (1) and (3) occur simultaneously [eqn. (1, 3)].[2]

$$(RNu)^{\cdot -} + RX \longrightarrow RNu + R^{\cdot} + X^{-} \qquad (1, 3)$$

One of the initiation steps proposed for this process involves the formation of the radical anion of the substrate by thermal (spontaneous) or photo-assisted ET from a suitable electron donor such as the nucleophile present in the reaction media.

Different types of nucleophile react by this mechanism.[1,2] Although certain carbanions have been found to be efficient nucleophiles, stabilized carbanions such as enolate ions of acetophenone[3a,b] or the mono-anions of α,β-unsaturated ketones[3a,c] were found to be unreactive toward aryl halides under photostimulation in liquid ammonia. On the other hand, acetophenone[4] and 2-naphthyl methyl ketone[5] react in this solvent, but with more electrophilic substrates. Reaction of mono anions of β-dicarbonyl or β-cyanocarbonyl compounds with more electrophilic substrates has also been reported.[6,7]

Changing the solvent from liquid ammonia to dimethyl sulfoxide (DMSO) produced important modifications in the reactivity of the nucleophiles. Thus, we have recently reported that stabilized carbanions such as the anions of acetophenone, anthrone and nitromethane react with PhI under photostimulation in DMSO; their relative reactivities have also been determined.[8]

On the other hand and with reference to the ET reaction from the carbanion to the substrate (initiation step) in DMSO, we have observed that the anions of acetone, acetophenone and anthrone initiate the process while the anion of nitromethane fails to do so.[8]

Certain unactivated alkyl halides have been shown to react by this mechanism with a variety of nucleophiles.[2] It has been proposed that whenever the polar nucleophilic substitutions are slow or prohibited for steric, geometric or electronic reasons, the reaction can take place by ET with radicals and radical anions as intermediates.[9] These substrates are less reactive towards carbanions in liquid ammonia compared with aromatic halides.[10]

Preliminary results obtained in the photostimulated reaction of 1-iodoadamantane (**1**) with carbanions in DMSO indicate that modifications in reactivity can be achieved by changing the solvent from liquid ammonia to DMSO.[11] We present here the reactions of **1** with carbanions as well as their relative reactivities in DMSO.

Results and Discussion

The photostimulated reaction of **1** with acetone enolate ion **2a** gave an 84% yield of I^- ions, 17% of adamantane **3** and 20% of 1-adamantylacetone **4a** (Expt. 1, Table 1).[11] Higher yields of substitution were obtained in the reaction of **1** with acetophenone enolate ion **2b**. In this reaction the substitution product α-(1-adamantyl)acetophenone **4b** was formed in 48% yield together with **3** (5%) (Expt. 3, Table 1). When this reaction was run in the presence of 18-crown-6 ether, the percentage of product **4b** was slightly increased (65%)[11] (Expt. 4, Table 1). Under the same experimental conditions, but with the enolate ion of propiophenone **2c** as the nucleophile, we found 2% of **3**

Table 1 Photostimulated reactions of **1** with carbanion nucleophiles in DMSO[a]

Expt.	Carbanion from	$h\nu$/min	X^- (%)	Substitution products[b] (%) AdH	 AdNu
1	Acetone	120	84	17	**4a** (20)
2	Acetone	120[c]	< 1		
3	Acetophenone	240	59	5	**4b** (48)
4[d]	Acetophenone	240	72	9	**4b** (65)
5[d]	Acetophenone	240[c]	< 1		
6[e]	Acetophenone	240	21	2	**4b** (8)
7[d]	Propiophenone	240	45	2	**4c** (27)
8	Anthrone	90	85	*f*	**6** (75)
9	Anthrone	90[c]	< 1		
10[d]	Nitromethane	120	9	*f*	*f*
11[d]	Nitromethane Acetophenone[g]	240	64	*f*	**8** (58) **4b** (< 1)
12	Nitromethane Acetone[h]	240	93	2	**8** (87) **4a** (< 1)
13[e]	Nitromethane Acetone[h]	240	45	*f*	**8** (38) **4a** (< 1)
14	Fluorene	120	99	14	**10** (21)

[a] 1-Iodoadamantane (**1**) 1.0 mmol, carbanions 3.0 mmol, unless otherwise indicated. [b] Yields determined by GLC using the internal standard method. [c] Dark reaction. [d] Added 18-crown-6 (3.0 mmol). [e] Added *p*-DNB (0.15 mmol). [f] Not quantified. [g] 1.0 mmol. [h] 2.0 mmol.

and 27% of the substitution product **4c**[11] (Expt. 7, Table 1). The reactions studied are summarized in eqn. (4).

$$\begin{array}{ccccccc} \text{1-IAd} & + & {}^-\text{CHR'COR} & \xrightarrow{h\nu} & \text{AdH} & + & \text{1-AdCHR'COR} \\ \mathbf{1} & & \mathbf{2} & & \mathbf{3} & & \mathbf{4} \end{array} \qquad (4)$$

a R = Me; R′ = H
b R = Ph; R′ = H
c R = Ph; R′ = Me

a R = Me, R′ = H
b R = Ph, R′ = H
c R = Ph; R′ = Me

It is suggested that these reactions occur according to the following mechanism.

Initiation step

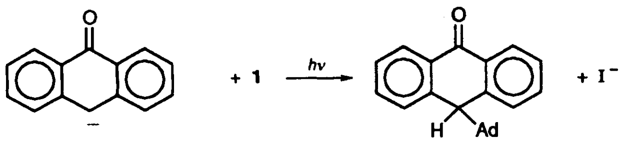
$$\begin{array}{ccccc} \text{1-IAd} & + & {}^-\text{CHR'COR} & \xrightarrow{h\nu} & \text{Ad}^\bullet + \text{I}^- \\ \mathbf{1} & & \mathbf{2} & & \end{array}$$

Propagation steps

$$\text{Ad}^\bullet + \mathbf{2} \longrightarrow \underset{\mathbf{4}^{\bullet -}}{(\text{1-AdCHR'COR})^{\bullet -}}$$

$$\mathbf{4}^{\bullet -} + \mathbf{1} \longrightarrow \underset{\mathbf{4}}{\text{1-AdCHR'COR}} + \text{Ad}^\bullet + \text{I}^-$$

The photostimulated reaction of anthrone anions with **1** gave the product **6** in 75% yield [eqn. (5)] (Expt. 8, Table 1).



5 **6** (5)

The $S_{RN}1$ mechanistic proposal is based on the facts that the reaction of **1** with anions **2a–c** and **5** did not take place without light (Expts. 2, 5, 9, Table 1) and that the photostimulated reaction with anion **2b** was inhibited by *p*-dinitrobenzene (*p*-DNB) (Expt. 6, Table 1).

The anion of nitromethane **7** is unable to initiate the process.[8,11] However, the reaction of **7** in the presence of good electron donors such as **2a** or **b** gave good yields of its substitution product **8** (entrainment reaction) (Expts. 11, 12, Table 1). Substitution with anion **2a** or **b** was not observed [eqn. (6)]. When the photostimulated reaction was carried out in the presence of *p*-DNB, inhibition occurred (Expt. 13, Table 1).

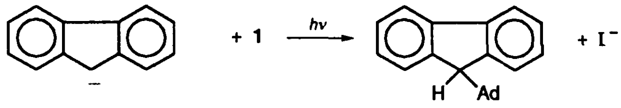
$$\begin{array}{ccccc} \mathbf{1} & + & {}^-\text{CH}_2\text{NO}_2 & \xrightarrow[(\mathbf{2a}\text{ or }\mathbf{b})]{h\nu} & \text{1-AdCH}_2\text{NO}_2 \\ & & \mathbf{7} & & \mathbf{8} \end{array} \qquad (6)$$

In this system, no fragmentation of the radical anion of the substitution product $\mathbf{8}^{\bullet -}$ was observed, while it has been shown that in the reaction of **7** with phenyl radicals, the radical anion formed dissociates in the sense indicated by eqn. (7).[8]

$$\text{Ph}^\bullet + \mathbf{7} \longrightarrow (\text{Ph-CH}_2\text{NO}_2)^{\bullet -} \longrightarrow \text{PhCH}_2{}^\bullet + \text{NO}_2{}^- \qquad (7)$$

The higher stability of benzylic *vs.* 1-adamantylmethyl radicals, which would be formed by fragmentation of $\mathbf{8}^{\bullet -}$, can explain the differences in behaviour between the aromatic and the aliphatic systems.

Low yields of the substitution product **10** (21%) were obtained in the photostimulated reaction of **1** with the anion of fluorene **9**, even though a 99% yield of I^- ion was found [eqn. (8), Expt. 14, Table 1]. This anion gave a *ca.* 40% yield of 9-phenylfluorene in its electron stimulated reaction with PhBr in liquid ammonia.[12]



9 **10** (8)

No substitution was found in the photostimulated reaction of **1** with the anion of acetonitrile, 2-naphthylmethylacetone enolate ion, the monoanion of acetylacetone or cyclohexanone enolate ion, even though some dehalogenation occurred.

Relative Reactivity Determinations of Carbanions toward 1-Adamantyl Radicals.—In order to determine the relative rate constants for the reactive nucleophiles toward 1-adamantyl radicals, we performed the photostimulated reactions of **1** with pairs of nucleophiles in excess. The relative reactivities were estimated as in previous works.* By this procedure and with enolate ions **2a** and **b** in excess, we determined that nucleophile **2b** is 11 times more reactive than enolate ion **2a** (Table 2).

Nitromethane ion **7** is 3.0 times more reactive than **2b**, while **5** is 2.6 times more reactive than **7** (Table 2). Thus, the following relative reactivity order for the reaction of carbanions with 1-adamantyl radicals can be estimated: monoanion of acetylacetone ≅ anion of acetonitrile (unreactive) ≪ acetone enolate ion (**2a**) (1.0) < acetophenone enolate ion (**2b**) (11) < nitromethane anion (**7**) (32) < anthrone anion (**5**) (80). The fact that **7** is 32 times more reactive than **2a**, explains the possibility

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* The equation used in the relative reactivity determination of pairs of nucleophiles *vs.* a radical is

$$\frac{k_{\text{Nu}}\mathbf{1}}{k_{\text{Nu}}\mathbf{2}} = \frac{\ln[\text{Nu}_1]_0/[\text{Nu}_1]_t}{\ln[\text{Nu}_2]_0/[\text{Nu}_2]_t}$$

where $[\text{Nu}_1]_0$ and $[\text{Nu}_2]_0$ are initial concentrations, and $[\text{Nu}_1]_t$ and $[\text{Nu}_2]_t$ are concentrations at time *t* of both nucleophiles. This equation is based on a first order reaction of both anions with the 1-adamantyl radicals, see ref. 13.

Table 2 Competition experiments between carbanions toward **1** in DMSO[a]

Expt.	Nucleophiles (mmol)	X^- (%)	Substitution product (%)[b]	Relative reactivity	
1	**2b** (3.00)	48	39	$k_{2b}:k_{2a}$ = 11	Average $k_{2b}:k_{2a}$ = 11
	2a (4.08)		7		
2	**2b** (3.00)	45	41	$k_{2b}:k_{2a}$ = 11	
	2a (2.99)		4		
3	**7** (2.98)	64	57	$k_7:k_{2b}$ = 3.0	Average $k_7:k_{2b}$ = 3.0
	2b (1.03)		7		
4	**7** (2.05)	46	27	$k_7:k_{2b}$ = 3.0	
	2b (3.00)		14		
5	**5** (2.98)	75	50	$k_5:k_7$ = 2.6	Average $k_5:k_7$ = 2.6
	7 (2.98)		20		
6	**5** (2.97)	76	50	$k_5:k_7$ = 2.5	
	7 (2.98)		21		

[a] Reactions carried out in 25 cm^3 of DMSO with 1 mmol of **1** and irradiated for 240 min. [b] Quantified by GLC.

Table 3 Relative reactivities, HOMO of the carbanions and SOMO of the radical anions formed in the coupling of methyl radicals with carbanions[a]

Carbanion derived from	Relative reactivity	pK_a	HOMO carbanion/eV	SOMO radical anion/eV	ΔE_π(SOMO − HOMO)
Acetylacetone	0	13.3	−3.21	−0.92	2.29
Acetonitrile	0	31.3	−1.40	0.01	1.41
Acetone	1.0	26.5	−1.96	−0.39	1.57
Acetophenone	11	24.7	−2.51	−1.72	0.79
Nitromethane	32	17.2	−3.08	−2.23	0.85[b]
Anthrone	80	—	−3.07	−2.14	0.93

[a] Calculation performed with the AM1/UHF method. [b] According to AM1/RHF this difference is equal to 1.04 eV (SOMO of the radical anion = −2.04 eV), while the difference calculated for acetophenone ion by the same procedure is 1.25 eV (SOMO = −1.26 eV).

of catalysing the photostimulated reaction with the latter nucleophile as well as the fact that the only substitution product observed is that derived from **7**.

The relative reactivity reported for the reaction of these anions with PhI is: monoanion of β-dicarbonyl compounds (unreactive) ≪ acetone enolate ion (**2a**) (1.0) < acetophenone enolate ion (**2b**) (7.5) < anthrone anion **5** (16.5). According to these results, 1-adamantyl radicals are more selective than phenyl radicals in their reaction with carbanions.

The $S_{RN}1$ mechanism is a chain process with initiation, propagation and termination steps, and the reactivity of a nucleophile is not necessarily the same for all these reactions. Thus, in the initiation step carbanions show a different reactivity from that shown in the coupling reaction of the propagation cycle.

In the initiation step, we determined qualitatively, based on the percentage of dehalogenation *vs.* irradiation time,* the following order of ET capability: acetone enolate ion (**2a**) > anthrone anion (**5**) ≈ fluorene anion (**9**) ≈ acetophenone enolate ion (**2b**) > monoanion of acetylacetone ≈ nitromethane anion (**7**). This sequence follows roughly the same order of the pK_a of the conjugated acids of the carbanions as has been proposed previously.[8]

On the other hand, the reactivity in the coupling reaction [eqn. (2)], which corresponds to the reactivity determined experimentally in competition experiments, does not follow the same order of the pK_a of the conjugate acid of the nucleophile.

We have previously proposed that the rate of this reaction depends on the pK_a of the conjugated acid as well as on the HOMO (carbanion) − SOMO (radical anion intermediate) energy difference which can be considered an indication of the loss in π energy for the process.[8]

In Table 3 are presented the HOMO energy of the carbanions and SOMO energy of the radical anions derived from coupling with methyl radicals. The 1-adamantyl group was replaced by methyl in order to simplify the calculations which were performed with the AM1 method as implemented in AMPAC.†

It can be seen that the HOMOs of the calculated carbanions become lower in energy as the pK_a of the corresponding conjugated acids decreases, which corresponds to an increase of the oxidation potentials as determined experimentally.[14]

Changing the pK_a from 26.5 (acetone)[15] to 24.7 (acetophenone)[15] increases the relative reactivity of the conjugated base toward 1-adamantyl radicals by 11. In going from **2a** to **b** the HOMO of the nucleophile as well as the SOMO of the formed radical anion decrease in energy, but the latter decreases even more in the case of acetophenone ion (lower E_π destabilization). In the radical anion formed with this nucleophile the extra electron is located in a SOMO that belongs to the COPh group, of lower energy than the SOMO formed with acetonate ion which belongs to the CO group.

The radical anion formed between 1-adamantyl radical and **7** (conjugated acid pK_a = 17.2) has its extra electron in a very good acceptor group such as the $-NO_2$. The π destabilization that accompanies this radical anion formation should be lower than the one that takes place with **2b**. This is the case for AM1/RHF calculations with the methyl substituted radical anions. Thus, **7** is three times more reactive than **2b**, and 32 times more reactive than **2a**. The reactivity of **5** cannot be explained only on an E_π basis, at least with the method used in our calculations.

From inspection of Table 3, we can conclude that neither the change in E_π nor the pK_a of the conjugated acids of the

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* These reactions have been carried out with Bu^{t}OK in excess, which is also able to initiate these photostimulated reactions.

† The calculations were carried out with the semiempirical AM1 method available from the *QCPE*, program 506. The replacement of the 1-adamantyl moiety by the methyl group will affect neither the SOMO energy order nor the change in π energy calculated.

nucleophiles (measured through the energy of their HOMO) explain the reactivity observed, but a combination of both can do so. From these data we propose that the reactivity of a carbanion toward a radical increases as the pK_a decreases whenever the ΔE_π of the reaction follows a similar tendency.

On the contrary, the monoanions of β-dicarbonyl compounds such as acetylacetone enolate ion, expected to be highly reactive on the basis of their pK_a, have a HOMO − SOMO energy difference for the coupling higher than for the other anions. For this type of nucleophile the structure that determines the pK_a (two conjugated carbonyl groups) changes considerably in the radical anion intermediate in which the two carbonyl groups are separated by an sp^3 carbon atom. This fact produces a large HOMO − SOMO energy difference (an important loss in π energy). This effect is sufficiently important to retard the reaction and these carbanions do not couple with phenyl or 1-adamantyl radicals.

The differences in relative reactivities for pairs of nucleophiles toward phenyl and 1-adamantyl radicals can be explained on the basis of the higher stability of the bicyclic *vs.* the phenyl radicals. 1-Adamantyl radicals are more stable than phenyl radicals* and should therefore be more selective in reacting with nucleophiles. This behaviour can also be explained on the basis of the differences in E_π that accompany the coupling reactions.

Therefore, the anion of acetonitrile (conjugated acid pK_a = 31.3)[15] does not couple with 1-adamantyl radicals but reacts with aromatic radicals[1] due to the lower destabilization in E_π for the aromatic system where a low lying energy SOMO is available to receive the extra electron.

On going from acetone enolate ion (**2a**) to acetophenone enolate ion (**2b**) the relative reactivity toward phenyl radicals increases by 7.5 while it increases by 11 with 1-adamantyl radicals. In the reaction of phenyl radicals with **2a** the extra electron in the attachment product radical anion is located in the phenyl group while in the reaction with **2b** it is located in the COPh moiety of energy lower than the phenyl and CO groups. When these anions react with 1-adamantyl radicals, the extra electron locates in the CO group in the reaction with **2a** and in the COPh group in the reaction with **2b**. Thus, while the change in E_π is approximately the same for acetophenone, independently of the radical, the destabilization is lower in the reaction of **2a** with phenyl than with 1-adamantyl radicals.

Relative Reactivity of 1-*Haloadamantane* vs. *Halobenzenes toward* **2b**.—In order to determine the relative reactivity of halobenzenes compared with 1-haloadamantanes toward **2b**, we performed the photostimulated reactions of this anion with PhBr and **1** in excess. Under these conditions there was almost no reaction. The reaction of **1** and PhI with **2b** in excess of Bu^{t}OK† gave 45% of I$^-$ ions with a ratio of $k_{1\mathrm{Ad}}:k_{\mathrm{PhI}}$ *ca.* 16. These results strongly suggest that **1** is more reactive than PhI, an unprecedented reactivity taking into account the calculated LUMO MO values for both substrates.‡

One possibility is that PhI receives one electron faster than **1**, and by fragmentation of its radical anion gives phenyl radicals, which are able to abstract iodine atoms from **1**, forming PhI again and 1-adamantyl radicals [eqn. (9)]. This reaction results in an apparent lower relative reactivity for PhI *vs.* **1**.

$$\mathrm{Ph}^{\bullet} + \mathbf{1} \longrightarrow \mathrm{PhI} + 1\text{-}\mathrm{Ad}^{\bullet} \qquad (9)$$

It is known that phenyl radicals react with aliphatic iodides by iodine atom abstraction with a rate constant of 1.1 × 10^9 (45 °C).[17] As the rate of bromine atom abstraction is much slower than that of iodine atom abstraction, we studied the competition reaction between PhBr and 1-bromoadamantane toward **2b**. Although this reaction is sluggish (16% yield of Br$^-$ ions), the $k_{\mathrm{BrAd}}:k_{\mathrm{PhBr}}$ is now *ca.* 0.13, which demonstrates that in the competition reaction of the iodides, the atom abstraction reaction plays an important role. Thus, this system is not useful for determining the relative reactivity of iodide substrates in S$_{\mathrm{RN}}$1 reactions.

Conclusions.—We conclude that the reactivity of carbanion nucleophiles in photostimulated reactions with **1** varies according to the nature of the reaction step. Thus, the carbanion reactivity in the photostimulated ET to **1** increases with the pK_a of the corresponding conjugated acids.

In the propagation cycle, the reactivity of the carbanions would depend on the pK_a of the conjugated acids as well as on the energy difference between the HOMO of the anion and the SOMO of the radical anion formed which is a measurement of the loss in π energy of the reaction. The reactivity order is the same on going from the phenyl to the 1-adamantyl radical; however, the latter radical is more selective in its reaction with carbanions. This difference in selectivity can be explained on the basis of the higher stability of 1-adamantyl radicals and on the π energy change that takes place during the reaction.

The determination, through competition experiments, of the relative reactivity of 1-iodoadamantane *vs.* PhI toward nucleophiles was not possible in the system studied due to the iodine atom abstraction reaction between the radical intermediates.

Experimental

General Method.—^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT-200 spectrometer, and all spectra are reported relative to Me$_4$Si (δ), with CCl$_4$ as the solvent, unless otherwise indicated. Mass spectra were obtained with a Finnigan 3300 f-100 mass spectrometer. IR spectra were recorded on a Nicolet FTIR 5-SXC spectrophotometer. GC analyses were performed on Shimadzu GC-8A or Konik instruments with flame ionization detectors and a data system Shimatzu CR-3A, using a column packed with 5% OV17 on Chromosorb G (1.5 m × 3 mm) and another with 6% SE30 (0.35 m × 3 mm). Column chromatography was performed on silica gel (70–270 mesh ASTM). Irradiation was conducted in a reactor equipped with two 250 W lamps ($\lambda_{\max}$ 350 nm) (Philips Model HPT, air refrigerated). Potentiometric titration of halide ions was performed in a pH-meter (Seybold Wien) using an Ag/Ag$^+$ electrode. M.p.s were obtained with a Büchi 510 apparatus and are not corrected. The high resolution mass spectra were run in the Chemical Instrumentation Center of Yale University, USA and in the Institute of Scientific and Industrial Research, Osaka University, Japan.

Materials.—Potassium *tert*-butoxide (Fluka), cyclohex-2-enone (Aldrich), ammonium nitrate (Carlo Erba), and fluorene (Sigma) were commercially available and used as received.

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* $\Delta_f H$[1-Ad$^\bullet$] = 14.8 kcal mol^{-1}, $\Delta_f H$[AdH] = −32.51 kcal mol^{-1}, see ref. 16(*a*). $\Delta_f H$[Ph$^\bullet$] = 77.7 ± 2 kcal mol^{-1}, $\Delta_f H$[PhH] = 19.82 kcal mol^{-1}, see ref. 16(*b*). According to these values, 1-Ad$^\bullet$ is ≈10 kcal mol^{-1} more stable than Ph$^\bullet$. The values calculated with AM1/RHF (MNDO/RHF) are: $\Delta_f H$[1-Ad$^\bullet$] = −2.98 (10.01) kcal mol^{-1}; $\Delta_f H$[1-AdH] = −43.21 (−26.37) kcal mol^{-1}. $\Delta_f H$[Ph$^\bullet$] = 79.51 (78.15) kcal mol^{-1}; $\Delta_f H$[PhH] = 22.03 (21.33) kcal mol^{-1}. According to AM1 (MNDO) 1-Ad$^\bullet$ is ≈17 (20) kcal mol^{-1} more stable than Ph$^\bullet$.

† These reactions have been carried out with Bu^{t}OK in excess, which is also able to initiate these photostimulated reactions.

‡ The LUMO values calculated with AM1 are 0.062 eV for PhI, whereas **1** has a LUMO of 0.444 eV. The lower the LUMO energy the easier it is to reduce the compound.

DMSO (Carlo Erba) was distilled under vacuum and stored over molecular sieves (4 Å). Acetone (Merck) and acetonitrile (Carlo Erba) were distilled and stored over molecular sieves (4 Å). Acetophenone (Carlo Erba) was distilled. Nitromethane (Aldrich) and acetylacetone (Aldrich) were distilled and dried ($MgSO_4$). Anthrone (Carlo Erba) and 2-naphthylmethylacetone (Alfa) were recrystallized by techniques described in the literature.[18] 1-Iodoadamantane was synthesized by the technique described in ref. 19.

Photostimulated Reaction of Anthrone Anion with **1**.—The following procedure is representative of these reactions. The reactions were carried out in a 100 cm^3 three-necked round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 25 cm^3 of dry and degassed DMSO under nitrogen were added 3.44 mmol of Bu^tOK, 3.0 mmol of anthrone and 1.06 mmol of **1**. After 120 min of irradiation the reaction was quenched by adding ammonium nitrate in excess, water (50 cm^3) and methylene chloride (50 cm^3). The iodide ions in the aqueous solution were determined potentiometrically. The ether extract was washed twice with water, dried and quantified by GLC by the internal standard method. The solvent was removed under reduced pressure. The residue, after column chromatography on silica gel [eluted with hexane–methylene chloride (70:30)] gave 10-(1-adamantyl)-9-anthrone, m.p. 212–214 °C (lit.,[20] m.p. 214–216 °C); δ_H 2.10–1.10 (15 H, m), 3.70 (1 H, s), 7.40 (6 H, m) and 8.10 (2 H, m); *m/z* 328 (M^+, 3%), 327 (2), 165 (8), 135 (100), 93 (12) and 79 (14).

1-*Adamantylacetone*.[21] Liquid isolated by column chromatography on silica gel (eluted with hexane); δ_H 1.48–1.98 (18 H, m) and 2.08 (2 H, s); *m/z* 192 (M^+, 2%) 191 (4), 175 (4), 149 (7), 136 (12), 135 (100), 123 (5), 107 (7), 93 (11), 82 (26), 67 (16), 55 (17), 43 (61) and 41 (29).

α-(1-*Adamantyl*)*acetophenone*. Solid isolated by column chromatography on silica gel [eluted with light petroleum–diethyl ether (90:10)]; m.p. 61–64 °C (lit.,[22] m.p. 64–65 °C); δ_H 1.58–2.30 (15 H, m), 2.59 (2 H, s) and 7.12–7.91 (5 H, m); *m/z* 256 (16%), 254 (M^+, 81), 236 (46), 179 (27), 135 (76), 105 (100), 93 (33), 91 (30), 79 (31) and 77 (40).

α-(1-*Adamantyl*)*propiophenone*. Liquid isolated by column chromatography on silica gel [eluted with light petroleum–diethyl ether (95:05)]; $\delta_H(CDCl_3)$ 1.10–1.20 (3 H, d), 1.50–2.00 (15 H, m), 3.25–3.35 (1 H, q) and 7.40–8.05 (5 H, m); δ_C 11.47, 28.59, 35.89, 36.93, 40.09, 49.21, 128.15, 128.45, 132.58, 139.06 and 205.18; *m/z* 269 (6%), 268 (M^+, 31), 250 (3), 239 (3), 202 (7), 163 (14), 147 (7), 136 (14), 135 (100), 119 (7), 105 (89), 93 (19), 77 (17), 57 (19) and 43 (10) (M^+, 268.1828; *M*, 268.1827).

1-*Adamantylnitromethane*. Liquid isolated by column chromatography on silica gel [eluted with light petroleum–diethyl ether (95:05)]; $\delta_H(CDCl_3)$ 1.63–2.05 (15 H, m) and 4.10 (2 H, s); δ_C 28.06, 34.53, 36.29, 39.91 and 87.78; *m/z* 195 (M^+, 0.29%), 179 (0.48), 168 (8), 149 (100), 135 (13), 121 (17), 119 (23), 107 (26), 105 (23), 93 (53), 91 (28), 81 (61), 79 (61), 67 (75), 55 (38), 43 (27) and 41 (23) (M^+, 195.1249; *M*, 195.1259).

9-(1-*Adamantyl*)*fluorene*. Solid isolated by column chromatography on silica gel (eluted with light petroleum); m.p. 130–131 °C; δ_H 1.50–2.00 (15 H, m), 3.5 (1 H, s) and 7.09–7.69 (8 H, m); δ_C 28.75, 36.83, 39.99, 43.40, 59.30, 119.33, 125.57, 126.80, 126.94, 142.21 and 145.15 (M^+, 300.1855; *M*, 300.1872).

Supplementary Material Available.—^1H and ^{13}C NMR spectra for compounds **4c**, **8** and **10** and DEPT for compound **10** (7 pages) are available from the authors on request.

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