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Reactions of 2-Iodo- and 1,2-Dihaloadamantanes with Carbanions in DMSO by the $S_{RN}1$ Mechanism

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The reaction of 2-iodoadamantane (**1**) with the potassium enolate of acetophenone (**2**) did not occur in the dark but succeeded under irradiation or in the presence of $FeBr_2$ to give the substitution product **3** in 62% and 88% yields, respectively. The photostimulated reaction was inhibited by *p*-dinitrobenzene (*p*-DNB). There was no reaction of **1** with the anion of nitromethane (**4**) in the dark or under irradiation. However, **4** reacted with **1** in the presence of acetone enolate ion (entrainment reaction) to yield 88% of the substitution product 2-adamantylnitromethane (**5**). The photostimulated reaction of **1** with anthrone (**6**), 2-naphthyl methyl ketone (**9**), and *N*-acetylthiomorpholine (**11**) anions afforded the substitution compounds **7** (37%), **10** (32%), and **12** (20%), respectively. There was no reaction of 1-chloro-2-iodoadamantane (**13**) with **2** in the dark (2 h), but under irradiation (5 min) it yielded 52% of the monosubstitution product α-(1-chloro-2-adamantyl)-acetophenone (**14**). Under longer irradiation time (3 h), the same yield of **14** (52%) was obtained but the disubstitution product **15** was formed in 45% yield. Product **15** was also formed in the photostimulated reaction of **14** with **2**. 2-Chloro-1-iodoadamantane (**18**) did not react with **2** in the dark (2 h), but the photostimulated reaction yielded the monosubstitution product α-(2-chloro-1-adamantyl)acetophenone (**19**) in 53% and **15** in 4% yield. Products **14** and **19** are intermediates in the formation of **15** in these reactions. There was a slow dark reaction of 1,2-diiodoadamantane (**20**) with **4** in the presence of acetone enolate ion to afford the iodomonosubstitution compound **21** (40%) and the disubstitution product **22** (13%). The photostimulated reaction (25 min) gave **21** (48%) and **22** (41%). On the other hand, after 3 h of irradiation, only traces of **21** could be detected (<5%) and the product distribution consisted mainly of **22**. The iodomonosubstitution product **21** is an intermediate in these reactions.

Several alkyl halides have been found to react with nucleophiles by the radical nucleophilic substitution or $S_{RN}1$ mechanism.[1] When there is no spontaneous electron transfer (ET) from the nucleophile to the substrate, the initiation step can be triggered by photostimulation[1] or by $FeBr_2$[2] (eq 1). The alkyl radical $R^{\cdot}$ thus formed couples with the nucleophile to yield a radical anion $(RNu)^{\cdot -}$ (eq 2), which by an intermolecular dissociative ET[3] to the substrate gives the substitution product and the alkyl radical $R^{\cdot}$ that propagates the chain (eq 3).

$$\begin{array}{llcll} \text{Initiation} & RX + Nu^{-} & \xrightarrow[\text{(or } FeBr_2)]{h\nu} & R^{\bullet} + X^{-} + Nu^{\bullet} & (1) \\ \text{Propagation} & R^{\bullet} + Nu^{-} & \longrightarrow & RNu^{-\bullet} & (2) \\ & RNu^{-\bullet} + RX & \longrightarrow & RNu + R^{\bullet} + X^{-} & (3) \end{array}$$

The alkyl halides that react by the $S_{RN}1$ mechanism are those that have a relatively low reactivity toward polar nucleophilic substitution.[1] For instance, 1-haloadamantanes as well as other bridgehead halides react with Ph_2P^-,[4] Ph_2As^-,[4a] and Me_3Sn^{-5} ions. Also, the reaction of 1-iodoadamantane (1-IAd) with carbanions,[6] PhS^-,[7,8] $PhSe^-$,[7] and $PhTe^{-\,7}$ ions has been reported.

The 2-position of the adamantane ring shows a lower reactivity in polar[9] and in free radical[10] reactions compared with that at the 1-position. Chloro and bromo cyclohexanes and derivatives also react under irradiation with Ph_2P^- ions by the $S_{RN}1$ mechanism.[11] Recently, it has been reported that 2-BrAd reacts with Ph_2P^- ions under irradiation whereas 2-ClAd does not. The latter

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reacts, however, with Me_3Sn^- ions, giving the substitution product in high yield.[12] In competition experiments, 1-BrAd was shown to be 1.4 times more reactive than 2-BrAd toward Ph_2P^- ions, while 1-ClAd is 12 times more reactive than 2-ClAd toward Me_3Sn^- ions.[12]

When an aromatic substrate bearing two leaving groups reacts by the $S_{RN}1$ mechanism, either the monosubstitution or disubstitution products can be formed, depending on the structure of the substrate, the nature of the nucleofugal group, the nucleophile, and the reaction conditions.[1b,13] The first reactive intermediate in these reactions is a haloaryl radical. The coupling reaction of this radical with the nucleophile forms a new radical anion, in which the π^* MO of the aromatic moiety is the bridge that mediates the ET to the σ^* MO of the remaining C−X bond. The rate of the intramolecular ET reaction depends on the energy difference between both MO's.[14]

The photostimulated reaction of dihalobenzenes with PhS^- ions affords the disubstitution product without the formation of monosubstitution product, unless fluorine is the other leaving group.[15] In the reaction of dihaloarenes with different aromatic sulfanions, disubstitution, monosubstitution with retention of one leaving group, or a mixture of both products has been observed, depending on the stabilization of the halosubstituted radical anion.[16,17] Kinetics analysis led to the conclusion that the yield of the monosubstitution product is lower than that expected. The radical anion of the disubstitution product can either transfer the odd electron to the starting dihalide or to the monohalo substitution compound, decreasing its overall yield.[17]

The reaction of dihalobenzenes with $(EtO)_2PO^-$ ions yields the disubstitution product, except when fluorine is one of the leaving groups or with *m*-chloroiodobenzene.[18] The fact that *m*-chloroiodobenzene affords disubstitution with PhS^- ions but only monosubstitution with $(EtO)_2PO^-$ ions was ascribed to the higher stability (lower π^* MO) of the monosubstituted radical anions.[18] Several examples have been reported on the reaction of dihalobenzenes with carbanions as nucleophiles.[19]

When an alkyl substrate with two leaving groups reacts by the $S_{RN}1$ mechanism also monosubstitution or disubstitution products are formed.[1,20] The first reactive intermediate is an haloalkyl radical, and in the coupling reaction with the nucleophile a new radical anion is formed. However, in these cases only σ bonds or the space comprise the bridge between the radical anion formed and the σ^* MO of the C−X bond. The rate of the intramolecular ET not only depends on the energy difference between the MO's but also on the number of the intervening bonds, on the distance between them, and on the flexibility of the bridge.[21]

For example, in the photostimulated reaction of 1,3-dihaloadamantanes with Ph_2P^- ions mainly the disubstitution product is formed,[22] whereas with $NaMe_3Sn$ the product distribution depends on the leaving groups. Thus, when the halides are iodides or bromides the reaction proceeds with predominant formation of 1,3-adamantene, but with the dichlorides, or 1-chloro-3-bromo derivatives, disubstitution is achieved through the $S_{RN}1$ mechanism.[23] With these nucleophiles the rate of the intramolecular ET of the radical anion to the σ^* MO of the C−X bond is faster than the intermolecular ET to the substrate.

The photostimulated reaction of 1,3-dihaloadamantanes with various carbanions affords products which depend on the availability of α-hydrogens in the nucleophile. In this case the 1-halo-3-monosubstitution product formed undergoes deprotonation followed by a concerted fragmentation to afford 7-methylidenebicyclo[3.3.1]nonene derivatives.[21] With these nucleophiles the rate of the intramolecular ET of the radical anion to the σ^* C−X is a slow process and does not compete with the intermolecular ET to the substrate.

The reaction of 2-chloro-5-iodo and 2-bromo-5-fluoro adamantanes (*E* and *Z*) with $LiMe_3Sn$ gives mainly the monosubstitution product with retention of chlorine and fluorine, respectively. The disubstitution product is obtained in high yield when 2-bromo-5-iodoadamantane was made to react with $LiMe_3Sn$ (*E* and *Z*).[24]

The photostimulated reaction of 1,2-dichloroadamantane with Ph_2P^- ions leads to 1- and 2-adamantyldiphenylphosphine in 64% and 15% yields, respectively, isolated as the oxides. The disubstitution product was not formed with Ph_2P^- ions, but when 1,2-dichloroadamantane reacts with a nucleophile having less steric bulk, such as Me_3Sn^- ions,[25] 2-chloro-1-trimethylstannyladamantane and the disubstitution product are obtained. The formation of these products has been rationalized in terms of the different rates of the ET reactions from the radical anion intermediates.[20]

Due to the importance of the reaction of carbanions with 2-adamantyl radical to form a new C−C bond, we have undertaken the study of the reactions of 2-IAd and 1,2-dihaloadamantanes with these nucleophiles under $S_{RN}1$ conditions in order to gain more insight into the

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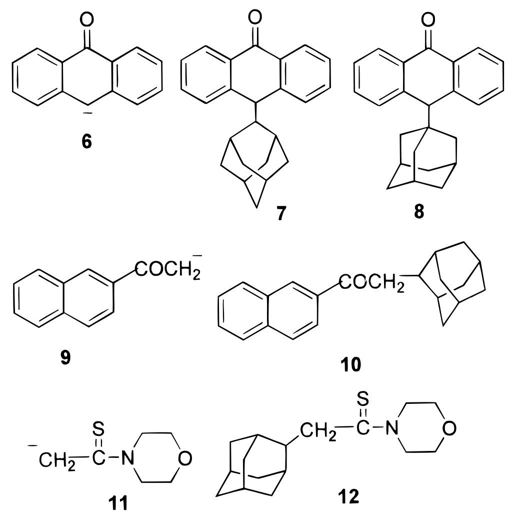
Table 1. Reactions of 2-Iodoadamantane (1) with Carbanions in DMSO

expt	carbanion, mmol	conditions[a]	I^-, yield (%)	substitution product, yield (%)[b]	AdH, yield (%)[b]
1	**2**, 3.0	dark, 3 h	<3	**3**, <1	
2	**2**, 3.0	$h\nu$, 2 h	51	**3**, 48	<5
3	**2**, 3.0	$h\nu$, 3 h	85	**3**, 62	10
4[c]	**2**, 3.0	$h\nu$, 3 h	69	**3**, 42	7
5[d]	**2**, 3.0	$h\nu$, 3 h (*p*-DNB)	28	**3**, 15	<5
6	**2**, 3.0	$FeBr_2$,[e] 1 h	*f*	**3**, 88	*f*
7[c]	**4**, 3.0	$h\nu$, 3 h	<1	**5**, −	
8[g]	**4**, 3.0	dark, 3 h ($^-CH_2COMe$)	<3	**5**, −	
9[h]	**4**, 3.0	$h\nu$, 1 h ($^-CH_2COMe$)	30	**5**, 29	*f*
10[g]	**4**, 3.0	$h\nu$, 3 h ($^-CH_2COMe$)	69	**5**, 68	*f*
11[d,h]	**4**, 3.0	$h\nu$, 3 h ($^-CH_2COMe$) (*p*-DNB)	14	**5**, 5	*f*
12[i]	**4**, 10.0	$h\nu$, 4 h ($^-CH_2COMe$)	91	**5**, 88	<5
13	**6**, 3.0	Dark, 3 h	<5	**7**, −	
14	**6**, 3.0	$h\nu$, 1 h	69	**7**, 28	28
15[d]	**6**, 3.0	$h\nu$, 1 h (*p*-DNB)	31	**7**, 11	15
16	**6**, 3.0	$h\nu$, 3 h	77	**7**, 37	35
17	**6**, 3.0	$FeBr_2$,[e] 1 h	*f*	**7**, <1	
18	**9**, 3.0	dark, 3 h	< 2	**10**, −	
19	**9**, 3.0	$h\nu$, 3 h	55	**10**, 32	20
20[d]	**9**, 3.0	$h\nu$, 3 h (*p*-DNB)	33	**10**, 10	10
21	**11**, 6.0	dark, 3 h	<2	**12**, −	
22	**11**, 6.0	$h\nu$, 3 h	40	**12**, 20[j]	*f*
23[k]	**2**, 3.0	$h\nu$, 3 h	<2		

[a] **1**: 1.0 mmol, *t*-BuOK: 4.0 mmol in 25 mL of DMSO. [b] Determined by GLC (internal standard method: C24 for **3**, phenanthrene for **5**, C32 for **7** and **10**, naphthalene for AdH). [c] 3.0 mmol of *t*-BuOK. [d] *p*-DNB (20 mol %) was added. [e] $FeBr_2$: 54 mol %. [f] Not quantified. [g] Acetone enolate ion: 2.0 mmol. *t*-BuOK: 6.0 mmol. [h] Acetone enolate ion: 1.0 mmol. *t*-BuOK: 5.0 mmol. [i] Acetone enolate ion: 10 mmol. *t*-BuOK: 22.0 mmol. [j] Isolated yield. [k] 1-Chloroadamantane: 1.0 mmol. *t*-BuOK: 4.0 mmol.

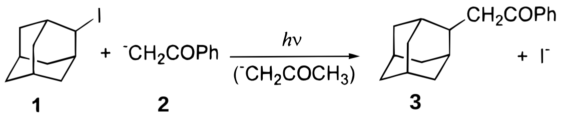
reactivity of the 2-position. 1,2-Dihaloadamantanes offer the possibility to study the competition between intra- and intermolecular ET reactions, as well as the substitution pattern of the 1- and 2-positions with carbanions.

Chart 1



Results and Discussion

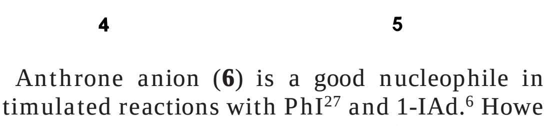
Reactions of 2-Iodoadamantane with Carbanions. There was no reaction of 2-IAd (**1**) with the enolate ion of acetophenone (**2**) in DMSO after 3 h in the dark, but it reacted under irradiation (3 h) or in the presence of $FeBr_2$ to give product **3** in 62% and 88% yields, respectively (eq 4).[26]



(4)

The photostimulated reaction was inhibited by *p*-dinitrobenzene (*p*-DNB), a good electron acceptor.[1] There was a decrease of the reactivity when the reaction was performed without excess of *t*-BuOK (used to form the carbanion) (Table 1, experiments 1−6). All these results show that **1** reacts with **2** by the $S_{RN}1$ mechanism.

There was no reaction under irradiation of **1** with nitromethane anion (**4**), but it reacted under photostimulation (3 h) in the presence of acetone enolate anion to give the product 2-adamantylnitromethane (**5**) in 68% yield. No products derived from acetone enolate ion were found (entrainment reaction). A similar entrainment reaction was found with 1-IAd and **4**.[6] This reaction was partially inhibited by *p*-DNB, and no reaction of **1** with **4** and acetone enolate ions in the dark was detected. When the concentration of **4** and that of the acetone enolate ions were increased and the irradiation time was prolonged (4 h), the yield of **5** rose to 88% (eq 5) (Table 1, experiments 7−12).



(5)

Anthrone anion (**6**) is a good nucleophile in photostimulated reactions with PhI[27] and 1-IAd.[6] However, the photostimulated reaction (1−3 h) of **6** with **1** gave a low yield of the substitution product **7** (28−37%) along with almost the same amount of the reduction product adamantane (Table 1, experiments 13−16). The photostimulated reaction of **6** with 1-IAd gave 75% of the substitution product **8**, and the amount of adamantane was low (Chart 1).[6b] The reaction of **1** with **6** was not induced by $FeBr_2$ (Table 1, experiment 17); as observed before with aromatic substrates, the reaction of highly conjugated

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(26) For a preliminary report, see: Lukach, A. E.; Santiago, A. N.; Szeimies, G.; Rossi, R. A. *Anal. Asoc. Quim. Arg.* **1998**, *86*, 281.

Table 2. Reactions of 1,2-Dihaloadamantanes with Carbanions in DMSO

expt	substr	carbanion	conditions[a]	I^-, yield (%)	Cl^-, yield (%)	monosubstitution product, yield (%)	disubstitution product, yield (%)
1	**13**	**2**	dark, 2 h	<2 (total)			
2	**13**	**2**	*hν*, 5 min	52	<2	**14**, 52	**15**, −
3[b]	**13**	**2**	*hν*, 5 min (*p*-DNB)	7 (total)		**14**, 5	**15**, −
4	**13**	**2**	*hν*, 40 min	90	12	**14**, 88	**15**, 10
5[b]	**13**	**2**	*hν*, 40 min, (*p*-DNB)	75	13	**14**, 68	**15**, 12
6[c]	**13**	**2**	*hν*, 3 h	94	45	**14**, 52	**15**, 45
7[d]	**14**	**2**	*hν*, 2 h		*e*	**14**, 66	**15**, 23
8	**18**	**2**	dark, 2 h	<3 (total)		**19**, −	**15**, −
9	**18**	**2**	*hν*, 2 h	87	23	**19**, 53	**15**, 4
10[b]	**18**	**2**	*hν*, 2 h, (*p*-DNB)	78	15	**19**, 39	**15**, <2
11[f]	**20**	**4**	dark, 3 h	72		**21**, 40	**22**, 13
12[b,f]	**20**	**4**	dark, 3 h (*p*-DNB)	16		**21**, 14	**22**, <2
13[b,f]	**20**	**4**	*hν*, 25 min	138		**21**, 48	**22**, 41
14[f]	**20**	**4**	*hν*, 25 min (*p*-DNB)	100		**21**, 68	**22**, 12
15[f]	**20**	**4**	*hν*, 3 h	164		**21**, <5	**22**, 68
16	**20**	**4**	*hν*, 3 h	105		**21**, 31	**22**, 37

[a] Carbanions were formed from neutral molecules (2.4 mmol) and *t*-BuOK (2.8 mmol); substrates (0.40 mmol) in 12.5 mL of DMSO. Substitution products quantified by GLC with internal standard (C24 for **14** and **19**, C32 for **15**, Ph_3Sb for **21** and **22**). [b] *p*-DNB (20 mol %) was added. [c] *t*-BuOK (2.4 mmol). [d] **2** (0.48 mmol) and **14** (0.16 mmol) in 5 mL of DMSO. [e] Not quantified. [f] *t*-BuOK (3.6 mmol) and acetone enolate ion (0.80 mmol).

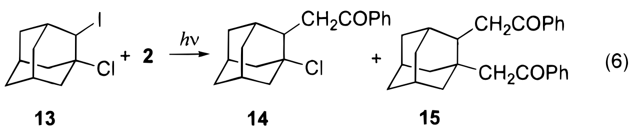
carbanions is not induced by $FeBr_2$.[28] Also, the photostimulated reaction of **1** with 2-naphthyl methyl ketone anion (**9**) gave a low yield of the substitution product **10** (32%) along with adamantane (20%) (Table 1, experiments 18−20).

The different reactivity pattern of **1** compared to that of 1-IAd toward **6** may be due to the steric hindrance encountered in the coupling reaction of **6** with the 2-adamantyl radical. Theoretical calculations show that the substitution product **7** is less stable than the substitution product with 1-IAd.[29] This steric hindrance renders the coupling process slow, and 2-adamantyl radicals are therefore reduced to adamantane.

Carbanions such as those derived from acetone[6] or *N*-acetylmorpholine[30] couple rather slowly with 1-adamantyl radicals. However, by changing the carbonyl group by a thiocarbonyl functionality, an increase in the reactivity occurs. Thus, 1-IAd reacted under irradiation or in the presence of $FeBr_2$ with *N*-acetylthiomorpholine anion **11** to give 60−65% yield of the substitution product.[30] The photostimulated reaction (3 h) of **1** with **11** gave only 20% yield of product **12** (Chart 1). There was no reaction in the dark (Table 1, experiments 21−22).

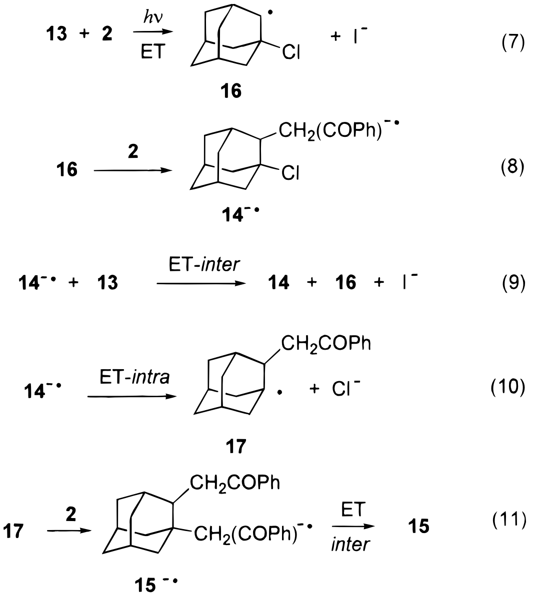
Reactions of 1,2-Dihaloadamantanes with Carbanions. When 1,2-dichloroadamantane receives an electron, the 1-position fragments ca. four times faster than the 2-position.[12] However, in the case of 1-chloro-2-iodoadamantane (**13**) the 2-position has a lower LUMO value (iodide is the best leaving group), and it would fragment faster than the 1-position, with chlorine as the substituent.

No dark reaction of **13** with **2** (2 h) occurred in DMSO, but in 5 min of irradiation, the monosubstitution product with retention of chlorine (**14**) was obtained (52%). No disubstitution product **15** was found under the experimental conditions employed. The reaction was almost completely inhibited by adding *p*-DNB (Table 2, experiments 1−3) (eq 6).



Under the same experimental conditions but when irradiation took place for 40 min, the yield of **14** was 88% and **15** was 10%. This reaction was also inhibited by *p*-DNB. When the irradiation time was 3 h, the yield of **14** was 52%, whereas the yield of **15** increased up to 45% (Table 2, experiments 4−6). These results indicate that this is a stepwise mechanism, as shown in Scheme 1.

Scheme 1



Upon irradiation, **2** transfers one electron to **13** to give the radical **16** (eq 7), which further reacts with **2** to yield the radical anion intermediate $\mathbf{14}^{-\cdot}$ (eq 8). This radical anion intermediate would have two competing reaction pathways: intermolecular ET to **13** to afford product **14** and radical **16** that continues the chain reaction (eq 9)

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[27] Borosky, G. L.; Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1992**, *57*, 247.

[28] Galli, C.; Gentili, P. *J. Chem. Soc. Perkin Trans. 2* **1993**, 1135.

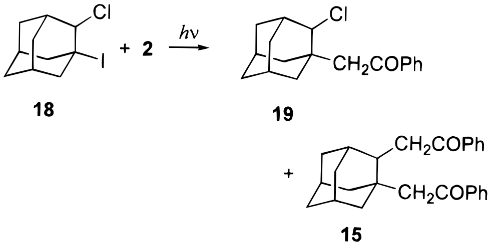
[29] The heats of formation (ΔH, kcal/mol) are as follows: −7.67 for **7**, −10.31 for **8**; for the radical anions, −40.86 for $\mathbf{7}^{\cdot -}$ and −42.52 for $\mathbf{8}^{\cdot -}$. The activation energies E_a for the coupling process between adamantyl radicals and **6** are as follows: 17.1 kcal/mol and 10.82 kcal/mol for the 2- and 1-adamantyl radicals, respectively. The calculations were carried out with the AM1 method.

[30] Murguía, M. C.; Rossi, R. A. *Tetrahedron Lett.* **1997**, *38*, 1355.

or an intramolecular ET to the C−Cl bond to give radical **17** (eq 10). Radical **17** would give by reaction with **2** ultimately the disubstitution product **15** (eq 11). Since after a short irradiation time only **14** was obtained, the intermolecular ET to **2** (eq 9) should be faster than the intramolecular ET (eq 10).

At longer irradiation times, the disubstitution product **15** is formed, showing that **14** is an intermediate of these reactions. To ascertain that **14** is an intermediate, the photostimulated reaction of **14** with **2** was performed. The disubstitution product **15** was obtained in 23% yield (Table 2, experiment 7). The outcome of this reaction is quite surprising, since 1-ClAd does not react with **2** under irradiation (Table 1, experiment 23).

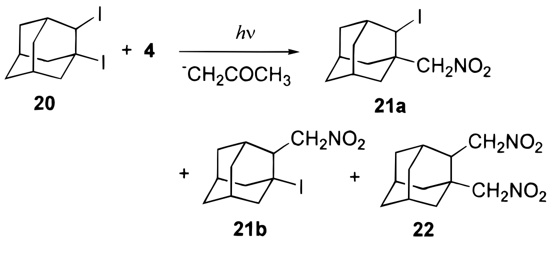
1-Iodo-2-chloroadamantane (**18**) does not react with **2** in the dark, but under irradiation (2 h) it affords the monosubstitution product **19** and small amounts of the disubstitution product **15** (eq 12). This reaction was slightly inhibited by *p*-DNB (Table 2, experiments 8−10). There is some decomposition of the products under these experimental conditions, and there is unbalance between the halide ion yields and the products obtained.[31]



(12)

These observations show that **18** also reacts with **2** by the $S_{RN}1$ mechanism in a fashion similar to that of **14** and in the radical anion formed by the coupling of 2-chloro-1-adamantyl radical with **2** the intermolecular ET to the substrate is faster than the intramolecular ET to the σ^* MO of the C−Cl bond. Due to their partial decomposition, these reactions were not studied further.

The reaction of 1,2-diiodoadamantane (**20**) with **4** and with acetone enolate ion in the dark gave monosubstitution products with retention of iodine in the 2-position (**21a**) and in the 1-position (**21b**) in ca. 40% yield[32] and the disubstitution product **22** in 13% yield (eq 13).[33]



(13)

This dark reaction was inhibited by *p*-DNB, and these reactions were light-catalyzed. Thus, the photostimulated reaction (25 min) gave **21** (48%) and **22** (41%). The inhibition with *p*-DNB for **22** decreased the yield to 12%. Product **21** increases the yield to 68%. Under a longer irradiation time (3 h) almost all the product formed was the disubstitution product **22** (68%) with mere traces of **21** (<5% yield). In the photostimulated reaction (3 h) of **20** with **4** without acetone enolate ion as the entrainment reagent, the yields were lower and **21** was formed (31%) together with **22** (37%) (Table 2, experiments 11−16).

These data are consistent with the $S_{RN}1$ mechanism. As **20** has a low reduction potential,[34] the dark reaction occurs by spontaneous ET from the nucleophile and is inhibited by *p*-DNB. Since mainly products **21a** and **21b** are formed, it appears that **21** are intermediates in the formation of **22**. In the photostimulated reaction there is an increase in the yield of **22**, and in the photostimulated reaction in the presence of *p*-DNB the yield of **21** increases, which suggests that *p*-DNB inhibited the formation of **22**, resulting in an overall increase in the yield of **21**.

Conclusions

Substrate **1** is able to react with carbanions **2** and **4** by the $S_{RN}1$ mechanism under irradiation, by entrainment with the enolate ion of acetone or by induction with $FeBr_2$. A decrease in the reactivity of 2-adamantyl radicals with bulky carbanions (such as **6** and **9**) and with a less reactive nucleophile such as **11** was observed.

The reaction of the chloroiodoadamantanes **13** and **18** with **2** affords the monosubstitution products **14** and **19** as intermediates, the intramolecular ET of the radical anion intermediates being a slow process. Product **14** with chlorine in the 1-position reacts further to give the disubstitution product **15**, whereas **19** with chlorine in the 2-position is quite unreactive under these experimental conditions showing that position 1 is more reactive than position 2, as found previously.[12]

The formation of the monosubstitution compounds **21a** and **21b** as intermediates in the reaction of **20** with **4** indicated that the intramolecular ET of the radical anion intermediates is a slow process. The fact that **21a** was formed as the major monosubstitution product and that a small amount of **21b** was obtained also shows that when **20** accepts an electron, the 1-position fragments faster than the 2-position. Monosubstitution products **21** react further to give the disubstitution compound **22**.

Experimental Section

General Methods. Irradiation was conducted in a reactor equipped with two 400-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water-refrigerated). Column chromatography was performed on silica gel (70−270 mesh ASTM).

Synthesis of 2-Iodoadamantane. A mixture of 2-adamantanol (1.2 g), sodium iodide (4.9 g), and hydriodic acid (58%, 13.2 mL) was stirred at 90−100 °C for 48 h. The mixture was cooled and diluted with 200 mL of water, obtaining a white solid after filtration. Recrystallization from acetone−water gave pure 2-iodoadamantane: mp 46−47 °C (lit.[35] mp 46−47 °C) (1.4 g, 81% yield).

Synthesis of 1,2-Dihaloadamantes. These compounds were obtained from the procedure described in the literature.[36]

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(31) Small amount of unidentified olefins were found.

(32) Compound **21a** was formed in major proportion, with mere traces of **21b**. These two compounds were quantified together; **21a** was purified and the structure determined.

(33) There was no reaction of **20** with **2** in the dark (3 h), but under irradiation there was a very fast process (5 min) which gave **15** in low yield (28%) although iodide ions were quantified to be 162%. The reaction was inhibited by *p*-DNB. There were substantial amounts of several unidentified olefins. These reactions were not studied further.

(34) The LUMO value of **20** is 0.149 eV, compared with 1-IAd (0.446 eV) and **1** (0.523 eV) (AM1 method).

(35) Udding, A. C., Strating, J., Wynberg, H. *Tetrahedron Lett.* **1968**, *11*, 1345.

(36) Abdel-Sayed, A. N., Bauer, L. *Tetrahedron* **1988**, *44*, 1873.

Photostimulated Reaction of 2-Iodo- and 1,2-Dihaloadamantanes with Carbanions in DMSO. The procedure is described in a previous publication.[14]

Isolation and Identification of the Products: **α-(Adamant-2-yl)acetophenone (3):** isolated as a white solid after radial chromatography on silica gel, eluted with petroleum ether−diethyl ether (98:02); mp = 68−70 °C. ^{1}H NMR (CDCl$_3$): δ 1.66−2.14 (14H, m), 2.36−2.57 (1H, m), 3.09 (2H, d, J = 7.7 Hz), 7.38−7.65 (3H, m), 7.92−8.07 (2H, m). ^{13}C NMR (CDCl$_3$): δ 27.9, 31.9; δ 32.1, 38.3, 39.0, 40.6, 41.9, 128.1, 132.8, 137.6, 200.5. MS (EI+) m/z (%): 255 (43.7), 254 (M$^+$, 44.8), 236 (8.3), 179 (9.0), 149 (9.8), 120 (16.2), 106 (21.4), 105 (100), 91 (11.8), 77 (32.0), 56(9.3). HRMS: calcd 255.174891, found 255.174731.

(Adamant-2-yl)nitromethane (5): isolated as an oil after chromatography on silica gel, eluted with petroleum ether−diethyl ether (98:02). ^{1}H NMR (CDCl$_3$): δ 1.56−2.05 (14H, m), 2.49−2.64 (1H, m), 4.53 (2H, d, J = 7.7 Hz). ^{13}C NMR (CDCl$_3$): δ 27.6, 30.0, 31.6, 37.7, 38.3, 43.5, 79.0. MS (EI+)[37] m/z (%): 195 (3), 178 (8), 175 (22), 165 (12), 163 (24), 149 (32), 147 (22), 135 (100), 123 (10), 121 (17), 119 (28), 113 (12), 111 (10), 109 (16), 107 (40), 105 (35), 101 (10).

9-(Adamant-2-yl)anthrone (7): isolated as a white-pink solid after radial chromatography on silica gel, eluted with petroleum ether−diethyl ether (98:02); mp = 186−7 °C. ^{1}H NMR (CDCl$_3$): δ 1.18−1.44 (3H, m), 1.53−1.82 (9H, m), 2.17−2.34 (3H, m), 4.24 (1H, d, J = 10.6 Hz), 7.33−7.53 (6H, m), 8.07−8.20 (2H, m). ^{13}C NMR (CDCl$_3$): δ 27.5, 27.9, 29.8, 32.1, 37.9, 39.0, 45.6, 58.8, 126.8, 127.7, 128.4, 131.1, 133.0, 145.7, 186.5. MS (EI+) m/z (%): 329 (5.5), 328 (M$^+$, 5.8), 196 (5.9), 195 (35.4), 194 (100), 193 (14.8), 166 (6.7), 165 (17.1), 136 (18.4), 135 (32.0), 93 (10.4), 81 (6.1), 67 (12.4). HRMS: calcd 329.190541, found 329.191514.

(Adamant-2-yl)methyl 2-naphthyl ketone (10): isolated as a white solid after radial chromatography on silica gel, eluted with petroleum ether−diethyl ether (98:02); mp = 110−111 °C. ^{1}H NMR (CDCl$_3$): δ 1.70−2.10 (14H, m), 2.42−2.53 (1H, m), 3.24 (2H, d, J = 6.9 Hz), 7.49−7.67 (2H, m), 7.82−8.10 (4H, m), 8.49 (1H, s). ^{13}C NMR (CDCl$_3$): δ 27.9, 31.9, 32.1, 38.2, 39.0, 40.8, 42.0, 124.1, 126.7, 127.7, 128.3, 128.4, 129.57, 129. 61; δ 132.6, 134.9, 135.5, 200.5. HRMS: calcd 305.190541, found 305.189850.

(Adamant-2-yl)-*N*-thioacetylmorpholine (12): isolated as a white solid after chromatography on silica gel, eluted with petroleum ether−diethyl ether (70:30); mp = 94−96 °C. ^{1}H NMR (CDCl$_3$): δ 1.47−2.17 (15H, m), 3.05 (2H, d, J = 6.5 Hz); δ 3.64−3.84 (6H, m); δ 4.27−4.44 (2H, m). ^{13}C NMR (CDCl$_3$): δ 27.8, 28.0, 31.8, 38.2, 39.2, 44.7, 46.6, 50.1, 50.5, 66.6, 203.4. HRMS: calcd 280.173511, found 280,173774.

α-(1-Chloroadamant-2-yl)acetophenone (14): isolated as a white solid after radial chromatography on silica gel, eluted with petroleum ether−diethyl ether (98:02); mp = 80−83 °C. ^{1}H NMR (CDCl$_3$): δ 1.45−2.37 (13H, m), 2.73−2.85 (1H, m), 2.97−3.14 (1H, m), 3.61−3.75 (1H, m), 7.41−7.62 (3H, m), 7.95−8.07 (2H, m). ^{13}C NMR (CDCl$_3$): δ 29.9, 31.4, 31.8, 34.3, 36.2, 37.4, 38.6, 42.5, 47.7, 49.8, 72.7, 128.2, 128.6, 132.9, 137.3, 199.5. MS (EI+) m/z (%): 290 (7.8), 289 (23.7), 288 (14.2), 253 (29.1), 252(28.0), 251 (19.0), 149 (7.0), 106 (42.9), 105 (100), 104 (27.7), 91 (13.8), 79 (13.6), 78 (12.1), 77 (40.2), 76 (10.8). HRMS: calcd 289.135918, found 289.136247.

α-(2-Chloroadamant-1-yl)acetophenone (19): isolated as a white solid after radial chromatography on silica gel, eluted with petroleum ether−diethyl ether (98:02). ^{1}H NMR (CDCl$_3$): δ 1.36−2.35 (13H, m), 2.81−3.13 (2H, m), 4.70−4.84 (1H, m), 7.38−7.63 (3H, m), 7.88−8.03 (2H, m). ^{13}C NMR (CDCl$_3$): δ 27.9, 30.5, 36.5, 36.9, 37.1, 37.7, 38.3, 41.7, 47.0, 71.4, 128.0, 128.5, 132.8, 138.3, 199.3. MS (EI+) m/z (%): 290 (5.7), 289 (16.2), 288 (11.3), 253 (13.2), 252(10.3), 251 (4.8), 107 (5.4), 106 (47.2), 105 (100), 104 (41.2), 91 (9.0), 79 (4.8), 78 (8.6), 77 (24.2), 76 (8.5). HRMS: calcd 289.135918, found 289.135024.

1,2-Bis(benzoylmethylene)adamantane (15): isolated as an solid after radial chromatography on silica gel, eluted with petroleum ether−diethyl ether (95:05); mp = 81−83 °C. ^{1}H NMR (CDCl$_3$): δ 1.49−1.72 (10H, m), 2.05−2.17 (1H, m), 2.20−2.31 (2H, m) δ 2.97−3.21 (5H, m), 7.38−7.58 (6H, m), 7.92−7.97 (4H, m). ^{13}C NMR (CDCl$_3$): δ 35.4, 37.4, 37.6, 41.6, 42.5, 44.0, 46.6, 53.3, 128.1, 128.4, 132.7, 137.4, 200.1. MS (EI+) m/z (%): 372 (2.7), 254 (12.5), 253 (63.2), 252 (28.4), 251 (11.0), 234 (4.4), 106 (13.8), 105 (100), 104 (73.1), 91 (12.5), 79 (10.9), 78 (7.9), 77 (56.1), 76 (22.2). HRMS: calcd 373.216755, found 373.215966.

(2-Iodoadamant-1-yl)nitromethane (21a): isolated as a white solid after radial chromatography on silica gel, eluted with petroleum ether−diethyl ether (99:01) and recrystallized from petroleum ether; mp = 123−4 °C. ^{1}H NMR (CDCl$_3$): δ 1.36−2.48 (13H, m), 4.14−4.48 (2H, m), 4.84−4.93 (1H, m). MS (EI+) m/z (%): 321 (1), 196 (3), 195 (34), 194 (100), 164 (22), 148 (20), 136 (14), 135 (97), 133 (16), 131 (6), 127 (4), 126 (4), 121 (3), 120 (8), 119 (48), 105 (54). ^{13}C NMR (CDCl$_3$): δ 27.7, 28.1, 32.7, 35.7, 37.0, 38.0, 38.4, 38.8, 49.3, 88.5. HRMS: calcd 321.0226, found 312.0220.

1,2-Bis(nitromethyl)adamantane (22): isolated as a white solid after recrystallization from petroleum ether; mp = 115−6 °C ^{1}H NMR (CDCl$_3$): δ 1.44−1.96 (11H, m), 2.02−2.16 (2H, m), 2.53−2.68 (1H, m), 4.04−4.33 (2H, m), 4.48−4.88 (2H, m). MS (EI+) m/z (%): 254 (2), 208 (6), 194 (3), 193 (10), 178 (7), 177 (40), 176 (10), 163 (14), 162 (10), 161 (37), 160 (10), 159 (37), 150 (13), 149 (100), 148 (6), 147 (20), 145 (9), 135 (26), 133 (42), 132 (5), 131 (17), 121 (18), 120 (15), 119 (73), 117 (22), 107 (40), 105 (69). ^{13}C NMR (CDCl$_3$): δ 27.4, 27.6, 30.0, 30.4, 35.4, 36.4, 37.1, 41.1, 43.5, 75.5, 84.0. HRMS: calcd 254.1267, found 254.1259.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **3**, **5**, **7**, **10**, **12**, **14**, **15**, **19**, **21a**, and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[37] The HRMS could not be determined by EI or FAB.