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Reactions of halo- and dihaloadamantanes with nitromethane anions by the $S_{RN}1$ mechanism

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ABSTRACT: The reactions of 1-bromo-, 2-bromo-, 1,3-dibromo- and 1,4-dibromoadamantane with $^{-}CH_2NO_2$ anions were studied in DMSO and in liquid ammonia. The photostimulated reaction of 1-haloadamantane (1-AdX, X = Br, I) or 2-AdBr with $^{-}CH_2NO_2$ anions gave good yields of the substitution product 1-AdCH_2NO_2 and 2-AdCH_2NO_2, respectively, in the presence of the enolate anions of acetone (entrainment conditions). On the other hand, 1-adamantanol was the main product of the reaction performed in DMSO without irradiation, but not in liquid ammonia. 1,3-Dibromo and 1,4-dibromoadamantane reacted with $^{-}CH_2NO_2$ anions under irradiation in the presence of the enolate anions of acetone. The first compound gave the disubstitution product **11**, and the second the monobromo-substitution products **15** and **16**, together with the disubstitution product **17**. Compounds **15** and **16** were shown to be intermediates in the formation of **17**. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: $S_{RN}1$; haloadamantanes; nitromethane anion; electron transfer

INTRODUCTION

The reactivity of the bridgehead halides with different nucleophiles depends on the strain energy, the nature of the leaving group, the nucleophiles and the solvent. Bridgehead halides have a high-energy barrier for a polar mechanism owing to strain factors and some of these halides have been found to react by the $S_{RN}1$ mechanism.[1] The $S_{RN}1$ mechanism is a chain process. The initiation step [Eqn. (1)] is an electron transfer (ET) from the nucleophile or from a suitable electron source to give the radical and the halide ion by a dissociative ET.[2] The propagation steps consist in the coupling of the radical with the nucleophile to give a radical anion [Eqn. (2)], which by ET to the substrate [Eqn. (3)], forms the intermediates necessary to continue the propagation cycle.

$$RX \xrightarrow{\text{Electron Donor}} R^{\bullet} + X^{-} \qquad (1)$$

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

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

A reaction between a nucleophile and a substrate may show low efficiency in the initiation, but be fairly reactive at propagation. The addition of another nucleophile that is more reactive at initiation increases the generation of the reactive intermediates and allows the less reactive nucleophile to start its own propagation (entrainment reaction).[1]

In liquid ammonia solution, the photostimulated reaction of 1-iodoadamantane (1-AdI) with several carbanions such as those derived from acetone, *N*-acetylmorpholine, acetylacetone or acetonitrile afforded the reduction product adamantane (AdH) and the dimeric product 1,1′-biadamantane $(1\text{-Ad})_2$[3] as the only products. However, the reaction of 1-AdI with the anion from *N*-acetylthiomorpholine has been successfully achieved under irradiation or in the presence of $FeBr_2$ in DMSO.[4] In a detailed kinetic study, it has been shown that the reaction of 1-AdI with *N*-thioacetylmorpholine anion gave good yields of substitution products with as low as 0.6–1.6 mol% of $FeBr_2$ in DMSO.[5]

In DMSO solution, the photostimulated reaction of 1-AdI with acetone enolate anions gave AdH (17%) and 1-adamantylacetone (20%). Higher yields of substitution

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product were obtained with acetophenone enolate anions, which gave AdH in low yield, and 48% of 1-adamantyl-acetophenone (or 65% in presence of 18-crown-6 ether) under irradiation[6,7] or 85% in the reaction induced by $FeBr_2$.[8] The photostimulated reaction of 1-AdI with anthrone anion also gave good yields (75%) of the substitution product in DMSO.[7]

On the other hand, no reaction has been observed under irradiation of 1-AdI with $^-CH_2NO_2$ ion. However, this anion gave the substitution product in the presence of acetophenone (58%) or acetone enolate anions (87%) as entrainment nucleophiles under irradiation[6,7] or in the presence of $FeBr_2$[8] in DMSO. Even though the 1-Ad$^\bullet$ radicals are formed under photostimulation with acetone enolate ion [Eqn. (1)], they do not couple with the nucleophile to follow the $S_{RN}1$ mechanism at least at a rate to compete with other reactions (reduction or dimerization). The $^-CH_2NO_2$ ion is unable to initiate the photostimulated $S_{RN}1$ reaction, but it does propagate the chain cycle very efficiently.[7] The following relative reactivity order has been determined for the reaction of 1-Ad$^\bullet$ radical with the carbanions from anthrone (80)[7] $>CH_3NO_2$ (32)[7] $> CH_3COPh$ (11)[7] $>$ *N*-acetylthiomorpholine (3.3)[4] $> CH_3COCH_3$ (1.0).[7]

We have investigated the reactions of 1-bromo-, 2-bromo-, 1,3-dibromo- and 1,4-dibromoadamantane with $^-CH_2NO_2$ anions in DMSO and in liquid ammonia by the $S_{RN}1$ mechanism. This approach provides a facile preparation of adamantyl compounds bearing a nitro group. Since a nitro group is readily transformed into a number of other useful functional groups,[9] this extends the synthetic value of the reaction.

RESULTS AND DISCUSSION

Reactions of 1-halo- and 2-bromoadamantanes with $^-CH_2NO_2$ anions

1-AdCl did not react with $^-CH_2NO_2$ anions in liquid ammonia in the dark. There is a sluggish reaction under irradiation, even in the presence of acetone enolate anions as entrainment reagent, but in DMSO 20% yield of the substitution product was obtained (Table 1, expts 1 and 2). There was no dark reaction of 1-AdBr with $^-CH_2NO_2$ anions (in the presence of acetone enolate anions), but it reacted under photostimulation in the presence of acetone enolate anions to give the

Table 1. Reactions of haloadamantanes with nitromethane and acetonate anions[a]

Expt	Substrate	Conditions	X^- (%)[b]	$AdCH_2NO_2$ (%)[c]	Other products (%)[c]
1	1-AdCl	NH_3, *hv*, 300 min	8	4[d]	—
2	1-AdCl	DMSO, *hv*, 360 min	27	20	AdH (9)
3	1-AdBr	NH_3, dark, 360 min	<1	—[d]	—
4	1-AdBr	NH_3, *hv*, 360 min	96	83[e]	—
5	1-AdBr[f]	NH_3, *hv*, 360 min	<5	2[d]	—
6	1-AdBr	NH_3, *hv*, 360 min, *p*-DNB[g]	21	17	—
7	1-AdBr[f]	DMSO, dark, 360 min	36	—	1-AdOH (35)
8	1-AdBr	DMSO, *hv*, 360 min	82	50	1-AdOH (37)
9	1-AdBr	DMSO, dark, 360 min	38	—	1-AdOH (35)
10	1-AdBr[f]	DMSO, dark, 360 min, *p*-DNB[g]	58	—	1-AdOH (53)
11	1-AdBr[f]	DMSO, *hv*, 360 min	67	—	1-AdOH (66)
12	1-AdBr[f]	DMSO, dark, 360 min, *t*-BuOH[h]	69	—	1-AdOH (64)
13	1-AdBr[i]	DMSO, dark, 120 min	<1	—[d]	—
14	1-AdBr[i]	DMSO, *hv*, 360 min	98	—[j]	—
15	1-AdI	NH_3, dark, 240 min	<1	—[d]	—
16	1-AdI	NH_3, *hv*, 240 min	77	70[e]	AdH (10)
17	1-AdI[f]	DMSO, dark, 360 min	53	—	1-AdOH (57)
18	1-AdI	DMSO, *hv*, 360 min	93	87	1-AdOH ~4
19	2-AdBr	NH_3, dark, 300 min	<1	—[d]	—
20	2-AdBr	NH_3, *hv*, 300 min	77	68	AdH (11)
21	2-AdBr	DMSO, dark, 360 min	<5	—[d]	—
22	2-AdBr	DMSO, *hv*, 360 min	68	62	AdH (6)

[a] Substrate concentration, 2.5×10^{-3} M; nitromethane anion, 3×10^{-2} M; acetone enolate anion, 2×10^{-2} M, unless indicated otherwise.
[b] Determined potentiometrically.
[c] Quantified by GC using the internal standard method, unless indicated otherwise.
[d] Most of the substrate was recovered.
[e] Isolated yield.
[f] Only the nitromethane anion was present.
[g] *p*-Dinitrobenzene (20 mol%) was added.
[h] *tert*-Butanol (5 ml) was added.
[i] Only the acetone enolate anion was present.
[j] Adamantane (56%) was the only product found. Some adamantane is lost in the work-up.

1-AdCH_2NO_2 in 83% isolated yield [Eqn. (4)].

$$\text{1-AdBr} + {}^{-}CH_2NO_2 \xrightarrow[{}^{-}CH_2COMe]{h\nu,\ NH_3} \text{1-Ad}CH_2NO_2 \qquad (4)$$

As the $^{-}CH_2NO_2$ anion reacts 32 times faster than acetone enolate anion,[7] no substitution products derived from the latter were found (entrainment reactions). The photostimulated reaction in presence of acetone enolate anions was inhibited by *p*-dinitrobenzene, (*p*-DNB), a well-known inhibitor of $S_{RN}1$ reactions[1] (Table 1, expts 3–6).

Similar entrainment has been described previously in the reaction of 1-AdI[7] and also 2-AdI[10] with $^{-}CH_2NO_2$ anions by the $S_{RN}1$ mechanism in DMSO.

Another feature that emerged from the reaction of 1-AdBr with $^{-}CH_2NO_2$ anions (with or without acetone enolate anions) in DMSO, either in the dark or under irradiation, is the formation of significant amounts of 1-adamantanol (1-AdOH) (360 min, 35–37% yield). This 'solvolytic' product was unexpected, owing to the low reactivity of 1-AdBr in S_N1 substitution reactions.

In order to determine if an ET was involved in the formation of 1-AdOH, we performed the reaction of 1-AdBr and $^{-}CH_2NO_2$ anions in the presence of *p*-DNB to inhibit the radical reaction. In this case there was an *increase* in the percentage of 1-AdOH (53% yield) and no substitution by $^{-}CH_2NO_2$ anions. This result shows that 1-AdOH is formed through a polar pathway.

One possibility is a bromophilic reaction to give 1-adamantyl anion, which is attacked by the oxygen of the nucleophile to give an oxime, which then is hydrolyzed to 1-AdOH in the work-up. When we carried out the reaction of 1-AdBr and $^{-}CH_2NO_2$ anions in the presence of *t*-BuOH to trap any carbanion derived from adamantane, 1-AdOH was formed in 64% yield, and no AdH was found. Also, the yield of 1-AdOH increased when the reaction of 1-AdBr and $^{-}CH_2NO_2$ anions was irradiated in the absence of acetone enolate anions (Table 1, expts 10–12). 1-AdBr did not react in the dark with acetone enolate anions, nor was 1-AdOH formed, whereas under irradiation the main product was AdH, as has been reported previously[3] (Table 1, expts 13 and 14).

Although the mechanism of formation of 1-AdOH is still unknown, it seems to operate only with $^{-}CH_2NO_2$ anions in the dark at room temperature in DMSO. The fact that 1-AdBr did not react with acetonate anions in DMSO, and that when it reacts with $^{-}CH_2NO_2$ anions the formation of 1-AdOH was not inhibited by *p*-DNB or by *t*-BuOH, suggest that 1-AdOH is formed by a polar bromophilic type mechanism within a solvent cage reaction to furnish the observed product. More experimental studies remain to be undertaken to elucidate this novel substitution of 1-AdBr.

There was no reaction in the dark of 1-AdI with $^{-}CH_2NO_2$ anions (in the presence also of acetone enolate anions) in liquid ammonia. Under the same experimental conditions, but under photostimulation, 1-AdCH_2NO_2 was obtained in 70% isolated yield together with 10% of AdH (Table 1, expts 15 and 16).

In DMSO, the dark reaction of 1-AdI with $^{-}CH_2NO_2$ anions afforded 1-AdOH (57%) in the same fashion as did 1-AdBr. In contrast, under irradiation, 1-AdCH_2NO_2 was formed (87% yield), along with small amounts of 1-AdOH. These results indicate that in the dark 1-AdI reacted only by a polar mechanism with $^{-}CH_2NO_2$ anions to furnish 1-AdOH, but under irradiation the $S_{RN}1$ mechanism takes over the polar reaction to give mainly the substitution product. On the other hand, 1-AdCl did not give 1-AdOH in the reaction with $^{-}CH_2NO_2$ anions in DMSO.

Entrainment was also needed in order to substitute 2-AdBr in liquid ammonia and DMSO with $^{-}CH_2NO_2$ anions to give the substitution product 2-AdCH_2NO_2 in 68 and 62% yields, respectively, together with a small amount of AdH (6–11%). No dark reactions were detected (Table 1, expts 19–22). Again, the 2-position of the adamantane ring shows a lower reactivity in Polar[11] and free radical reactions compared with that of the 1-position.[12,13] It has been reported that 2-AdBr reacts with Ph_2P^{-} ions under irradiation whereas 2-AdCl does not. The latter reacts, however, with Me_3Sn^{-} ions to give the substitution product in high yield.[13] In competition experiments, 1-AdBr was shown to be 1.4 times more reactive than 2-AdBr toward Ph_2P^{-} ions, whereas 1-AdCl is 12 times more reactive than 2-AdCl toward Me_3Sn^{-} ions.[13] Previously, the photostimulated reaction of 2-AdI in DMSO with carbanionic nucleophiles to afford substitution products by the $S_{RN}1$ mechanism has been described.[10]

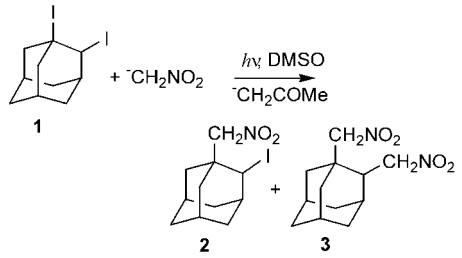
Reactions of 1,3- and 1,4-dibromoadamantanes with $^{-}CH_2NO_2$ anions in DMSO

The $S_{RN}1$ reactions of nucleophiles with substrates bearing two leaving groups afford either the monosubstitution or disubstitution product depending on the structure of the substrate, the nature of the nucleofugal groups and their spatial separation, or the nucleophile.[1]

1-Iodo-2-chloroadamantane and 1-chloro-2-iodoadamantane are known to react with acetophenone enolate anions under irradiation to afford the chloro monosubstitution product and small amounts of the disubstitution product. The chloro monosubstitution products have been shown to be intermediates in the formation of disubstitution compounds.[10]

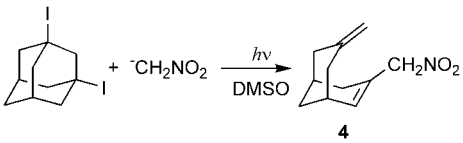
A similar behavior has been found with 1,2-diiodoadamantane (**1**), which reacted with $^{-}CH_2NO_2$ anions under irradiation to give the monosubstitution product with retention of iodine **2** (traces of iodine in the 2-position were found, indicating that the radical anion fragment faster at the 1-position) and the disubstitution

product **3** [Eqn. (5)]. In this reaction acetone enolate anions were used as the entrainment reagent. At short irradiation times, the main product is **2**, but at longer irradiation times, the disubstitution product **3** is the main product, indicating that **2** is an intermediate to furnish **3**.[10]



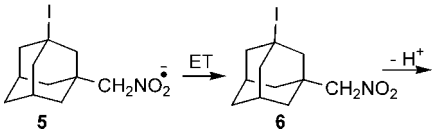
(5)

Different results were obtained in the photostimulated reaction of 1,3-diiodoadamantane with nitromethane anion in DMSO [Eqn. (6)]. In this case, the only product obtained by the $S_{RN}1$ mechanism, is the ring opened **4**.[14]

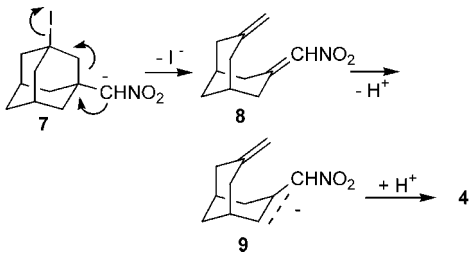


(6)

The formation of **4** has been explained considering that once the 3-iodoadamantyl radical is formed, it couples with the nucleophile to give the radical anion intermediate **5**, which by an intermolecular ET to the substrate forms the halomonosubstitution product **6**. This compound is deprotonated in the basic reaction conditions to give the carbanion **7**, which by a ring-opening reaction renders **8**, which is deprotonated to give the carbanion **9**. This carbanion transforms into the most stable isomer **4** after acidification of the reaction [Eqns (7) and (8)].



(7)



(8)

1,3-Dibromo- and 1-bromo-3-chloroadamantane did not react with $^{-}CH_2NO_2$ anions (<5%) under irradiation (3 h) in DMSO.[14] There is no reaction of 1,3-dibromoadamantane (**10**) with $^{-}CH_2NO_2$ and acetone enolate anions in DMSO in the dark, but under irradiation it affords the disubstitution product **11**, in yields that depend on the experimental conditions. When the substrate concentration is decreased from 10×10^{-3} to 2.5×10^{-3} M, the yield of **11** increases from 25 to 84% [Eqn. (9)] (Table 2, expts 1–4).

(9)

In liquid ammonia, **10** did not react with $^{-}CH_2NO_2$ and acetone enolate anions, but under irradiation it afforded the disubstitution compound **11** in high yields (80%) (Table 2, expts 5–7).

Table 2. Reaction of dibromoadamantanes with $^{-}CH_2NO_2$ and acetone enolate anions in DMSO

Expt	Substrate (M × 10^3)	$^{-}CH_2COCH_3/^{-}CH_2NO_2$ (M × 10^3)	Conditions (min)	Br^- (%)[a]	Disubstitution product (%)
1	**10**, 2.5	20/30	Dark (360)	<1	—[b]
2	**10**, 10	20/60	*hv* (360)	36	**11**, 25[c]
3	**10**, 5	20/30	*hv* (300)	73	**11**, 49[c]
4	**10**, 2.5	20/30	*hv* (360)	89	**11**, 84[c]
5[d]	**10**, 2.5	20/30	*hv* (300)	81	**11**, 80[c]
6[d]	**10**, 2.5	20/30	Dark (300)	<5	—[e]
7	**14**,[f] 1.8	20/30	Dark (360)	<5	—[b]
8	**14**,[f] 1.8	20/30	*hv* (360)	72	**17**, 47[g]
9[d]	**14**,[f] 1.8	20/30	*hv* (360)	82	**17**, 77[h]

[a] Determined potentiometrically considering two bromide ions per molecule of substrate.
[b] Substrate (97%) was quantified with 1-bromonaphthalene as reference.
[c] Quantified by GC using the internal standard method with Ph_3As as reference.
[d] In liquid ammonia as solvent.
[e] Substrate (88%) was quantified with 1-bromonaphthalene as reference.
[f] A mixture of *E*- and *Z*-isomers was used.
[g] Quantified by GC with 1-bromonaphthalene as reference. 1-$AdCH_2NO_2$ (5%), 2-$AdCH_2NO_2$ (2%) and a mixture of (*E*)- and (*Z*)-4-bromo-1-nitromethyladamantane (**15**) and 1-bromo-4-nitromethyladamantane (**16**) isomers (32%) were quantified.
[h] Isolated yield.

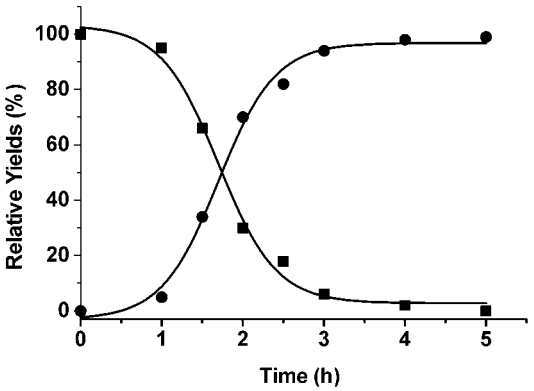
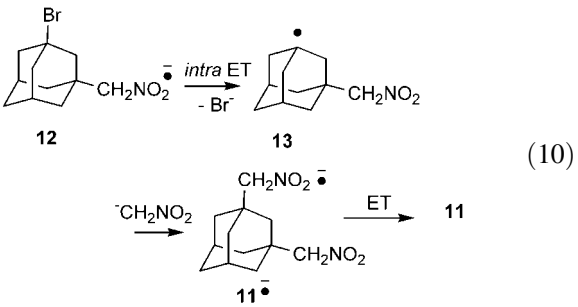


Figure 1. Relative yields of the decrease of substrate **10** (■) and the formation of **11** (●) in DMSO vs time.

To fact that the formation of **11** does not occur through the intermediacy of the monosubstitution product 1-bromo-3-nitromethyladamantane is shown by a plot of product formation vs time, which indicates that the production of **11** and the decrease of **10** occur simultaneously (Fig. 1).

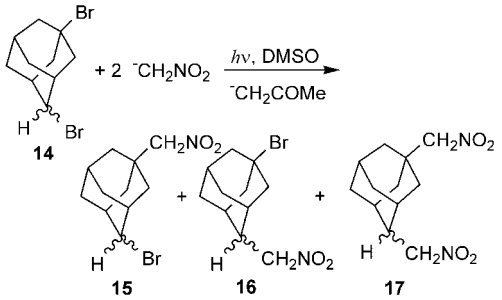
Under irradiation, **10** receives an electron from the acetone enolate ion and fragments to afford 3-bromoadamantyl radical, which couples with $^{-}CH_2NO_2$ anions to give the radical anion intermediate **12**, which by an *intramolecular* ET to the other C—Br bond forms the radical **13** to continue the chain propagation step and ultimately give **11** [Eqn. (10)].



(10)

The fact that with 1,3-diiodoadamantane the *intermolecular* ET to the substrate to give 1-iodonitromethyladamantane as an intermediate is faster than the *intramolecular* ET to the other C—I bond might be ascribed to the better electron acceptor capability of 1,3-diiodoadamantane with respect to the dibromo derivative **10**. The lack of formation of ring opening product, in the sense of Eqn. (6), is another factor which indicates that 1-bromo-3-nitromethyladamantane is not an intermediate in these reactions,

On the other hand, a mixture of isomers (*E* and *Z*) of 1,4-dibromoadamantane (**14**) did not react in the dark with $^{-}CH_2NO_2$ and acetone enolate anions in DMSO, but under irradiation it gave (32%) of the monosubstituted compounds 1-bromo-4-nitromethyladamantane (**15**) and 4-bromo-1-nitromethyladamantane (**16**) (a mixture of *E*- and *Z*-isomers) together with 47% yield of the disubstitution product **17** (*E*- and *Z*-isomers in a 1:1 ratio) [Eqn. (11)] (Table 2, expts 7 and 8).



(11)

These results indicate that **14** also reacts with $^{-}CH_2NO_2$ anions (with acetone enolate anions as entrainment reagent) by the $S_{RN}1$ mechanism. When **14** receives one electron, it fragments either at the 1- (major) or at the 4-position (minor) to give radicals that react with $^{-}CH_2NO_2$ anions to furnish the radical anions $\mathbf{15}^{\bullet -}$ and $\mathbf{16}^{\bullet -}$; the main reaction pathway of these radical anion intermediates is the *intermolecular* ET to **14** to give **15** and **16** as products the ratio of products **15** and **16** is ca 4:1, which indicates that the 1-position fragments faster than the 4-position, as found previously[15]. This ET is faster than the *intramolecular* ET to the C—Br bond, in contrast to the behavior shown by the 1,3-dibromo isomer **10**, for which the *intramolecular* ET is faster than the *intermolecular* ET. The same behavior has been found in the photostimulated reactions of **10** and **14** with Me_3Sn^{-} ions in liquid ammonia.[15]

On the other hand, the photostimulated reaction of **14** with $^{-}CH_2NO_2$ and acetone enolate ion furnishes **17** in 77% isolated yield in liquid ammonia (Table 2, expt 9).

CONCLUSIONS

In the photostimulated reaction of 1-iodo-, 1-bromo-, 2-bromo- and 1,3-dibromoadamantane with $^{-}CH_2NO_2$ anions in the presence of an entrainment reagent (acetonate anion) it is possible to achieve the synthesis of mono- and disubstitution products in very good yields by the $S_{RN}1$ mechanism either in liquid ammonia or DMSO. In DMSO and under similar reaction conditions 1-AdBr gives 1-AdOH through a competitive process.

On the other hand, a very low yield of substitution is obtained by reaction of 1-AdCl with $^{-}CH_2NO_2$ anions (in the presence of acetone enolate anions) under irradiation in either liquid ammonia or DMSO.

The reaction of 1,4-dibromoadamantane with $^{-}CH_2NO_2$ and acetone enolate anions under irradiation renders the bromo monosubstitution product as an intermediate, in contrast to the similar reaction of 1,3-dibromoadamantane where no intermediate was observed.

The procedure here reported is an easy method for preparing adamantyl compounds containing nitro groups, which will allow the synthesis of other adamantyl derivatives. Therefore, we will continue the study with other nitranions to define the scope and limitations of these reactions.

EXPERIMENTAL

General methods

NMR spectra were recorded on a Bruker AC-200 NMR spectrometer. Mass spectral measurements were obtained with a Shimadzu GCMS QP5050 GC-17A gas chromatograph–mass spectrometer system. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5890 Series II instrument with a flame-ionization detector and a Hewlett-Packard 3396 Series II data system, using an HP5 (5% methylsilicone, 0.5 m × 0.53 mm i.d.) column. 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). Potentiometric titration of halide anions was performed with a pH meter (Orion Model 420A), using an Ag/Ag^+ electrode and $AgNO_3$ as standard. Melting-points were obtained with a Büchi 510 apparatus and are not corrected.

Materials

1- and 2-AdBr, 1-AdI, 1-AdCl, 1,3- and 1,4-dibromoadamantane, acetone, nitromethane, and potassium *tert*-butoxide were commercially available and used as received.

Photostimulated reactions of 1-halo-, 2-halo- and 1,3- and 1,4-dibromoadamantanes with $^-CH_2NO_2$ in liquid ammonia

The following procedure is representative of these reactions. To 300 ml of distilled ammonia were added CH_3NO_2 (3 mmol) and $(CH_3)_2CO$ (2 mmol) and then *t*-BuOK (5 mmol) and 10 min after the last addition when no more solid was present, $^-CH_2NO_2$ and $^-CH_2COCH_3$ anions were ready for use. The haloadamantane (1 mmol) dissolved in 1 ml of anhydrous diethyl ether was added to the solution and the reaction mixture was irradiated. Then, the reaction was quenched with an excess of ammonium nitrate and the ammonia was allowed to evaporate. The residue was dissolved with water and then extracted with diethyl ether. The products were isolated by column chromatography. In the other experiments the products were quantified by GC using the internal standard method.

Photostimulated reactions of 1-halo-, 2-halo- and 1,3- and 1,4-dibromoadamantanes with $^-CH_2NO_2$ anion in DMSO

The following procedure is representative. The reactions were carried out in a 250 ml three-necked round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 100 ml of dry and degassed DMSO under nitrogen were added CH_3NO_2 (3 mmol) and acetone (2 mmol) and then *t*-BuOK (5 mmol) and 10 min after last addition when no more solid was present, $^-CH_2NO_2$ and $^-CH_2COCH_3$ anions were ready for use. After 15 min, 1-AdX (1.0 mmol) was added and the reaction mixture was irradiated. Then, the reaction was quenched with an excess of ammonium nitrate. The residue was dissolved with water (300 ml) and then extracted with diethyl ether (100 ml). The products were isolated by column chromatography. In the other experiments the products were quantified by GC using the internal standard method.

Reaction with $^-CH_2NO_2$ anion in the dark

The procedure was similar to that for the previous reaction, except that the reaction flask was wrapped with aluminum foil.

Inhibited reaction with $^-CH_2NO_2$ anion

The procedure was similar to that for the previous reaction, except that *p*-DNB was added to the solution of nucleophile prior to substrate addition.

Isolation and identification of the products

1-AdCH_2NO_2. Isolated as a yellow oil after column chromatography on silica gel, eluted with petroleum ether–diethyl ether (98:2) and identified by comparison with an authentic sample.[7]

2-AdCH_2NO_2. Isolated as a yellow oil after column chromatography on silica gel, eluted with petroleum ether–diethyl ether (98:2) and identified by comparison with an authentic sample.[10]

*1,3-*Bis*(nitromethyl)adamantane.* Isolated as a white solid after column chromatography on silica gel, eluted with petroleum ether–diethyl ether (90:10); m.p. decomp. >185 °C. ^1H NMR (CD_3COCD_3), δ: 1.26–2.52 (14H, m); 4.35 (4H, s). ^{13}C NMR (CD_3COCD_3), δ: 28.32, 35.46,

35.60, 38.94, 41.88 and 87.32. MS (EI+), *m/z* (%): 208 (19), 177 (13), 161 (27), 160 (12), 147 (26), 133 (29), 131 (15), 119 (39), 117 (18), 107 (16), 106 (14), 105 (77), 93 (42), 91 (100), 81 (42), 79 (66), 77 (42), 69 (12), 67 (35), 65 (17), 55 (23), 53 (17).

(E)- *and* (Z)-*1,4*-bis*(nitromethyl)adamantane.* Isolated as a mixture of *E*- and *Z*-isomers (ratio 1:1) as a light yellow liquid after column chromatography on silica gel, eluted with petroleum ether–diethyl ether (90:10). ^{1}H NMR ($CDCl_3$), δ: 1.34–2.14 (26 H, m); 2.45–2.57 (2H, m); 4.11 (2H, s); 4.13 (2H, s); 4.44 (2H, d); 4.53 (2H, d). ^{13}C NMR ($CDCl_3$), δ: 27.33, 29.73, 29.97, 30.35, 33.98, 34.09, 36.92, 39.83, 39.99, 40.45, 42.10, 42.20, 78.13, 78.21, 86.81 and 87.00. MS (EI+), *m/z* (%): 209 (4), 208 (15), 207 (20), 162 (6), 161 (19), 149 (26), 148 (4), 147 (16), 135 (21), 134 (10), 133 (54), 119 (59), 105 (73), 91 (100), 79 (91), 67 (48), 55 (30), 41 (26) and 209 (10), 207 (13), 162 (5), 161 (22), 149 (24), 148 (5), 147 (14), 135 (20), 134 (4), 133 (58), 119 (52), 105 (89), 91 (100), 79 (89), 67 (54), 55 (37), 41 (20).

(E)- *and* (Z)-*1-(nitromethyl)-4-bromoadamantane.* Isolated as a mixture of *E*- and *Z*-isomers (ratio 1:1) as a light yellow liquid after column chromatography on silica gel, eluted with petroleum ether–diethyl ether (96:4). ^{1}H NMR ($CDCl_3$), δ: 1.21–2.61 (13H, m); 4.16 (2H, s); 4.57 (1H, m). ^{13}C NMR ($CDCl_3$), δ: 26.73, 34.14, 34.20, 36.33, 37.35, 39.86, 60.51, 87.00. MS (EI+), *m/z* (%): 194 (67), 147 (81), 135 (32), 119 (53), 105 (65), 91 (100), 79 (61), 67 (40), 55 (19), 41 (22).

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