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NJC
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Reactions of 1-haloadamantanes and ethylmercury chloride with nitronate anions by the $S_{RN}1$ mechanism

Ana N. Santiago,* Silvana M. Basso, Carlos A. Toledo and Roberto A. Rossi*

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina.
E-mail: rossi@dqo.fcq.unc.edu.ar, santiago@dqo.fcq.unc.edu.ar;
Fax: +54 351 433 3030; Tel: +54 351 4334170

Received (in Montpellier, France) 3rd December 2004, Accepted 2nd February 2005
First published as an Advance Article on the web 6th May 2005

Secondary or tertiary nitro compounds can be easily obtained by photostimulated reaction of the anions corresponding to primary or secondary nitroalkanes with either 1-iodoadamantane (1-AdI) or ethylmercury chloride (EtHgCl) by the $S_{RN}1$ mechanism. Only 1-AdI requires the presence of the enolate anion of acetone as an entrainment reagent. The procedure works well with the nitroanions derived from 1-nitropentane, nitroethane or 6-nitrohex-1-ene, but with 2-nitropropane ion the outcome depends on the substrate and solvent.

Introduction

It has been observed that the reactivity of bridgehead halides with different nucleophiles depends on the strain energy, the nature of the leaving group, the nucleophile, and the solvent. Bridgehead halides have a high-energy barrier for a polar mechanism due to strain factors, and some of these halides have been found to react by the $S_{RN}1$ mechanism.[1] This mechanism is a chain process with radicals and radical anions as intermediates through which a bridgehead substitution is easily obtained. 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.

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

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

$$(\mathrm{RNu})^{\bullet-} + \mathrm{RX} \rightarrow \mathrm{RNu} + \mathrm{R}^{\bullet} + \mathrm{X}^{-1} \qquad (3)$$

It is known that 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,[3] as the only products. In these cases substitution products are not formed.

However, later it was observed that in DMSO the photostimulated reaction of 1-AdI with acetone enolate anions gave the substitution product 1-adamantylacetone (20%), together with AdH (17%). The substitution product was also obtained with acetophenone enolate anions, which gave 48% of 1-adamantylacetophenone under irradiation[4,5] or 85% in the reaction induced by $FeBr_2$.[6] The photostimulated reaction of 1-AdI with anthrone anion also gave good yields (75%) of the substitution product in DMSO.[5] 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.[7]

Even though no reaction has been observed under irradiation of 1-AdI with nitromethane ion, this anion gave the substitution product in the presence of acetophenone (58% yield) or acetone enolate anions (87% yield) as entrainment nucleophiles under irradiation[4,5] or in the presence of $FeBr_2$[6] in DMSO. The $1\text{-Ad}^{\bullet}$ radicals are formed under photostimulation with acetone enolate ion [eqn. (1)], but 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 nitromethane ion is unable to initiate the photostimulated $S_{RN}1$ reaction, but it does propagate the chain cycle very efficiently.[5]

In order to synthesize adamantylnitromethanes in good yields we decided to investigate the reaction of 1-bromo-, 2-bromo-, 1,3-dibromo- and 1,4-dibromoadamantanes with nitromethane ions in DMSO and in liquid ammonia.[8] The photostimulated reaction of 1-AdX (X = Br, I) or 2-AdBr with nitromethane ions gave good yields of the substitution product $1\text{-AdCH}_2\text{NO}_2$ or $2\text{-AdCH}_2\text{NO}_2$[9], respectively, in the presence of the enolate anions of acetone (entrainment conditions) in liquid ammonia. Although these reactions can be useful for preparing other nitroadamantyl derivates, a more thorough study is necessary so as to determine the scope of these reactions.

Recently, it has been reported that cyanide ions also reacted by the $S_{RN}1$ mechanism with 1,3,5,7-tetrabromoadamantane in DMSO, affording the tetrasubstituted product in good yields (72%) in a photostimulated reaction (λ = 254 in quartz).[10]

On the other hand, alkylmercury halides (RHgX) are easily reduced to $\mathrm{R}^{\bullet}$, Hg^0 and X^- and can initiate a chain reaction by addition to an appropriate nucleophile.[1,11] Furthermore, the RHgX are reagents that have moderate reactivity in electrophilic substitution and low reactivity in S_N2 substitution at carbon because of the unfavorable polarity of the C–Hg bond (${}^{-\delta}\mathrm{R{-}Hg}^{\delta+}\mathrm{Cl}$).[12] Thus, RHgX has been proposed to react with primary or secondary nitronate ions by the $S_{RN}1$ mechanism [eqns. (4) and (5)]:[13]

$$\mathrm{R}^{\bullet} + {}^{-}\mathrm{CR}^1\mathrm{R}^2\mathrm{NO}_2 \rightarrow \mathrm{RR}^1\mathrm{R}^2\mathrm{CNO}_2^{\bullet-} \qquad (4)$$

DOI: 10.1039/b418305c

Table 1 Reaction of 1-AdX with **1** and acetone enolate ions in DMSO[a]

Entry	1-AdX	Conditions	% X^- [b]	Products (%)[c]
1	1-AdBr	*hν*	37	**2** (0), 1-AdOH (30)[d]
2[e]	1-AdBr	*hν*	77	**2** (75), 1-AdH (traces)[f]
3	1-AdI	Dark	30	**2** (0), 1-AdOH (15)
4	1-AdI	*hν*	98	**2** (85), 1-AdOH (8)
5[g]	1-AdI	*hν*	28	**2** (15), 1-AdOH (17)

[a] The concentration of substrate was 3.33×10^{-3} M. The concentration of **1** was 1×10^{-2} M and that of acetone enolate ion 6.67×10^{-3} M. The reaction time was 6 h. [b] Determined potentiometrically. [c] Quantified by GLC by the internal standard method with Ph_3As as reference. [d] Substrate recovered in 56%. [e] The solvent was liquid ammonia. [f] Substrate recovered in 15%. [g] *p*-DNB (20 mol %) was added.

$$RR^1R^2CNO_2^{\bullet -} + RHgX \rightarrow RR^1R^2CNO_2 + R^{\bullet} + Hg^0 + X^- \quad (5)$$

The procedure works well with alkylmercury chloride, bromide and iodide, even in the presence of other functionalities, without formation of alkyl nitrites. Tertiary nitro alkanes can be easily obtained by this method.

It was suggested that the ET to RHgX is dissociative, on the basis that the reactivity of RHgX in competitive reactions with 2-nitropropane ions is determined by the stability of the $R^{\bullet}$ radical.[14] This reaction is initiated by light and inhibited by radical scavengers or oxygen. Another piece of mechanistic evidence is the observation of products from the cyclization of the 5-hexenyl radical in the reaction of 5-hexenylmercury chloride with 2-nitropropane ions.[15] The nature of the photoinitiation appears not to involve homolysis, since simple RHgX do not absorb light above 310 nm. Russell *et al.* proposed an ET to RHgX from a photoexcited nitronate anion for the initiation path, due to the fact that no charge transfer complex was detected.[16]

In order to synthesize secondary or tertiary nitro compounds we decided to investigate the unreported reaction of 1-AdX (X = I, Br) and EtHgCl with some nitronate anions in DMSO and in liquid ammonia by the $S_{RN}1$ mechanism. This approach provides a facile preparation of 1-adamantyl compounds bearing a nitro group. Herein, we report on results that were obtained upon extension of our investigations on nitronate anions, different from nitromethane, so as to determine the scope and limitations of these reactions. Unfortunately, the classic substitution reactions of nitranions are impractical for the preparation of substituted nitroalkanes due to the formation of the O-alkylation product. The procedure we report here can be of great interest due to the absence of unwanted product. Also, we studied nitronate anions that can contain a double bond. In these cases, the substitution products bearing a double bond are not easy to synthesize by the standard procedures.

The synthesis of these nitro derivatives is of great interest since a nitro group is readily transformed into a number of other useful functional groups,[17] increasing the synthetic value of the reaction.

Results

Reactions of 1-AdX with the anion of 1-nitropentane (1)

1-AdBr reacts with the anion of 1-nitropentane (**1**), in the presence of acetone enolate ion, in DMSO under irradiation to afford 1-AdOH and only a trace of the substitution product 1-(1-nitropentyl)adamantane (**2**). It was suggested that 1-AdOH is formed by a polar bromophilic type mechanism within a solvent cage reaction to furnish the observed product.[8] However, in liquid ammonia this bromophilic reaction did not occur, and 1-AdBr reacted with **1** under photostimulation in the presence of acetone enolate anion to give the substitution product **2** in 75% yield [eqn. (6), Table 1, experiments 1 and 2].

$$\underset{X = Br, I}{1\text{-}AdX} + \underset{\mathbf{1}}{{}^{-}CH(NO_2)(CH_2)_3CH_3} \xrightarrow[{}^{-}CH_2COMe]{h\nu} \underset{\mathbf{2}}{1\text{-}AdCH(NO_2)(CH_2)_3CH_3} \quad (6)$$

In the same way, under dark conditions 1-AdI reacted with **1** to afford 1-AdOH, but under photostimulation in the presence of acetone enolate anion, it affords the substitution product **2** in 85% yield [eqn. (6)]. No products derived from acetone enolate anion were found, and 1-AdOH was observed in 8% yield. The photostimulated reaction in the presence of acetone enolate ions was inhibited by *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of $S_{RN}1$ reactions[1] (Table 1, experiments 3–5).

Table 2 Reaction of 1-AdI and EtHgCl with nitranions in DMSO

Entry	Substrate[a]	Nucleophile[b]	Conditions	Time/min	% X^- [c]	Products (%)[d]
1[e]	1-IAd	**3a**	Dark	360	22	4a (0)[f], 1-AdOH (17%)
2[e]	1-IAd	**3a**	*hν*	360	99	**4a** (84), 1-AdOH (5%)
3[e]	1-IAd	**3b**	Dark	360	24	**4b** (0), 1-AdOH (13%)
4[e]	1-IAd	**3b**	*hν*	360	94	**4b** (77), 1-AdOH (4%)
5	EtHgCl	**3a**	Dark	180	nq	**5a** (0)
6	EtHgCl	**3a**	*hν*	180	nq	**5a** (68)
7	EtHgCl	**3b**	Dark	180	nq	**5b** (0)
8	EtHgCl	**3b**	*hν*	180	nq	**5b** (50)
9[e]	1-IAd	**3c**	Dark	360	32	1-AdOH (25)
10[e]	1-IAd	**3c**	*hν*	360	87	**6** (17), **7** (13), AdH (14)
11[eg]	1-IAd	**3c**	*hν*	360	37	**8** (21)
12[egh]	1-IAd	**3c**	*hν*	360	85	**8** (50), AdH (3)
13	EtHgCl	**3c**	*hν*	180	nq	**9** (65)
14[e]	1-IAd	**3d**	*hν*	360	85	AdH (55)

[a] The concentration of substrate was 3.33×10^{-3} M. [b] The concentration of nucleophile was 1.0×10^{-2} M. [c] Determined potentiometrically; nq = not quantified. [d] Quantified by GLC and the internal standard method. [e] Acetone enolate ions (6.67×10^{-3} M). [f] 1-AdI was recovered in 95%. [g] The solvent was liquid ammonia [h] The concentration of nucleophile was 1.67×10^{-2} M.

Reactions of 1-AdI and EtHgCl with nitranions in DMSO

1-AdI reacted under photostimulation with nitroethane (**3a**) or 6-nitrohex-1-ene (**3b**) ions in the presence of acetone enolate anion to give the substitution products **4a** and **4b** in 84% and 77% yields, respectively [eqn. (7)]. These nucleophiles afford 1-AdOH in the dark (Table 2, experiments 1–4).

$$1\text{-AdI} + {}^{-}CH(NO_2)R \xrightarrow[{}^{-}CH_2COMe]{h\nu,\ DMSO} 1\text{-AdCH}(NO_2)R \tag{7}$$

3a: R = CH_3 **4a**: R = CH_3
3b: R = $(CH_2)_3CH{=}CH_2$ **4b**: R = $(CH_2)_3CH{=}CH_2$

On the other hand, EtHgCl did not react with **3a** or **3b** in the dark; however, under irradiation the substitution products were found in 68% and 50% yields, respectively [eqn. (8); Table 2, experiments 5–8].

$$EtHgCl + \mathbf{3} \xrightarrow{h\nu,\ DMSO} Et\text{-}CH(NO_2)R \tag{8}$$

3a **5a**: R = CH_3
3b **5b**: R = $(CH_2)_3CH{=}CH_2$

5b was synthesized in order to be used later as a precursor of another nitroanion.

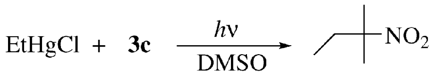
1-AdI reacts with 2-nitropropane (**3c**) and acetone enolate anions in the dark in DMSO to afford 1-AdOH; however, under irradiation, it affords the hydrocarbon **6** (17%) and the olefin **7** (13%), together with AdH (14%) (Table 2, experiments 9 and 10). No substitution product with the nitro group was found [eqn. (9)].

$$1\text{-AdI} + \bar{C}(NO_2)Me_2 \ (\mathbf{3c}) \xrightarrow[{}^{-}CH_2COMe]{h\nu,\ DMSO} 1\text{-Ad-CHMe}_2\ (\mathbf{6}) + 1\text{-Ad-C(Me)=CH}_2\ (\mathbf{7}) + AdH \tag{9}$$

Conversely, in liquid ammonia as solvent, 1-AdI reacted with **3c**, under photostimulation in the presence of acetone enolate anion, to give the substitution product **8** in 21% yield and only a trace of AdH was found [eqn. (10)]. When the concentration of the nucleophile was increased, **8** was obtained in 50% yield (Table 2, experiments 11 and 12).

$$1\text{-AdI} + \mathbf{3c} \xrightarrow[{}^{-}CH_2COMe]{h\nu,\ NH_3} 1\text{-Ad-C}(NO_2)Me_2\ (\mathbf{8}) \tag{10}$$

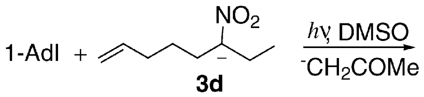
In contrast, the photostimulated reaction of **3c** with EtHgCl afforded the tertiary substitution product 2-methyl-2-nitrobutane (**9**) in 65% yield in DMSO [eqn. (11); Table 2, experiment 13].



9

(11)

Finally, a new nitroanion, 6-nitrooct-1-ene (**3d**), reacted under irradiation with 1-AdI in the presence of acetone enolate anion, affording AdH in 55% yield [eqn. (12)] and only traces of different substitution products (Table 2, experiment 14).



3d

(12)

Discussion

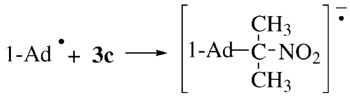
The photostimulated reactions of 1-AdI with primary nitranions, such as **1**, **3a** and **3b**, afforded the substitution products in good yields in DMSO. The presence of acetone enolate ion as entrainment reagent is necessary for these reactions to occur. A reaction between a nucleophile and a substrate may be rather unreactive at initiation, but quite reactive at propagation. The addition of small amounts 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).

The facts that these reactions did not occur in the dark and were inhibited by *p*-DNB are indicative that 1-AdI reacts with these nitranions by the $S_{RN}1$ mechanism.

The dark reaction of 1-AdI with nitranions only afforded 1-AdOH, whereas under irradiation, the substitution products were formed in high yields, along with small amounts of 1-AdOH. These results indicate that in dark conditions 1-AdI only reacts by a polar mechanism to furnish 1-AdOH; however, under irradiation the $S_{RN}1$ mechanism takes over the polar reaction to give mainly the substitution products.

On the other hand, the reaction of **1** with 1-AdBr, which is a less reactive substrate than the iodo derivative in ET reactions, only yielded 1-AdOH in the photostimulated reaction in DMSO. This result indicates that the polar reaction is faster than the radical one. Conversely, a different product distribution was observed in the reaction of 1-AdBr with **1** in liquid ammonia. Thus, the photostimulated reaction affords the substitution product in high yield, and no 1-AdOH is found. In these experimental conditions, the $S_{RN}1$ mechanism is faster than the polar one.

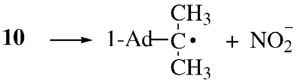
As regards the anions of a secondary nitro compound, such as **3c**, the photostimulated reaction in DMSO gave the hydrocarbon **6**, the olefin **7** and the reduction product AdH. The formation of these products is depicted in eqns. (13)–(15).



10

(13)

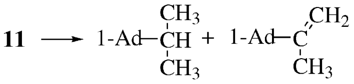
$$1\text{-Ad}^{\bullet} + \mathbf{3c} \longrightarrow \left[1\text{-Ad}{-}C(CH_3)_2{-}NO_2\right]^{\bullet -}$$



11

(14)

$$\mathbf{10} \longrightarrow 1\text{-Ad}{-}\dot{C}(CH_3)_2 + NO_2^{-}$$



6 **7**

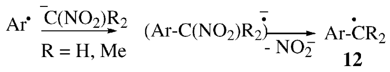
(15)

$$\mathbf{11} \longrightarrow 1\text{-Ad}{-}CH(CH_3)_2 + 1\text{-Ad}{-}C(CH_3){=}CH_2$$

Once the 1-Ad$^{\bullet}$ radical is formed in the initiation step, it couples with **3c** to give the radical anion **10** [eqn. (13)]. This radical anion, instead of transferring the odd electron to the substrate in the sense of eqn. (3) of the propagation cycle, fragments faster to give the radical **11** and nitrite ions [eqn. (14)]. Radical **11** does not couple with **3c**, but by a disproportion reaction it affords the products **6** and **7** [eqn. (15)].

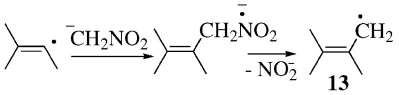
The fact that the main product is the reduction product AdH indicates that the coupling reaction of 1-Ad$^{\bullet}$ radical with the secondary anion **3c** is not efficient, probably due to steric reasons, and 1-Ad$^{\bullet}$ radicals are reduced to AdH.

The driving force of radical anion **10** fragmentation is the formation of the tertiary radical **11** and nitrite ions. There are precedents in the literature of fragmentation process of radical anions during the $S_{RN}1$ cycle. Thus, nitromethane anion and other nitranions react with aryl radicals [eqn. (16)],[18,19] or vinyl radicals [eqn. (17)],[20] and the radical anions formed fragment to give radicals and nitrite ions faster than ET to the substrates can occur. The driving force of these fragmentation reactions is the formation of the stable benzylic **12** and allylic **13** radicals and nitrite ions.



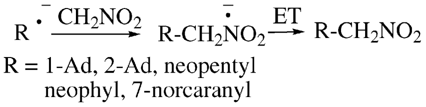
$$Ar^{\bullet} \xrightarrow[R = H,\ Me]{^{-}C(NO_2)R_2} (Ar\text{-}C(NO_2)R_2)^{\bullet -} \xrightarrow[-\ NO_2^-]{} Ar\text{-}\dot{C}R_2 \quad \mathbf{12}$$

(16)



(17)

On the other hand, straightforward substitution is achieved by reaction of nitromethane ions with 1-AdX,[4,5,8,] 2-IAd,[8,9] neopentyl[21] and neophyl[22] iodides, and 7-iodonorcarane,[6] in liquid ammonia or DMSO. In these cases, the fragmentation would give a primary radical and the ET reactions to the substrates are faster than the fragmentation rates [eqn. (18)].



$$R^{\bullet} \xrightarrow{^{-}CH_2NO_2} R\text{-}CH_2NO_2^{\bullet -} \xrightarrow{ET} R\text{-}CH_2NO_2$$

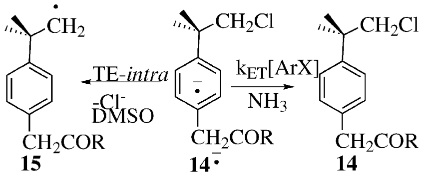
R = 1-Ad, 2-Ad, neopentyl
neophyl, 7-norcaranyl

(18)

In our study, in the reaction of 1-IAd with secondary nitranions, the fragmentation reaction led to a stable tertiary radical, such as **11**. Under these conditions this reaction prevails over the ET to the substrate. The reaction of secondary nitronate anions with aliphatic substrates bearing electron-withdrawing groups, such as 2-bromo-2-nitropropane[23] or 4-nitrobenzylbromide,[17b] afforded the substitution products (90% and 92% yields, respectively) in the reaction with 2-nitropropane anion. No fragmentation was observed due to the formation of stabilized radical anions.[1]

On the other hand, in liquid ammonia the photostimulated reaction of 1-IAd with **3c** gave only the straightforward substitution product. In this case the ET reaction is faster than the fragmentation reaction.

There are precedents that changing the solvent from DMSO to liquid ammonia modifies the product distribution in $S_{RN}1$ reactions.[24] This behavior is attributed to differences in the rate constant of intra-ET *vs.* inter-ET of the radical anion $\mathbf{14}^{\bullet -}$ [eqn. (19)].



(19)

While dissociative intra-ET is the main reaction of radical anion $\mathbf{14}^{\bullet -}$ in DMSO to yield radical **15**, the main reaction of $\mathbf{14}^{\bullet -}$ in liquid ammonia is intermolecular ET to afford **14**. It has been reported that unsubstituted benzyl halides do not form radical anions in acetonitrile and follow a concerted dissociative pathway.[25] The fact that the main product is the substitution one, **14**, indicates that the radical anion $\mathbf{14}^{\bullet -}$ is indeed an intermediate in liquid ammonia and survives to transfer its odd electron to the substrate. We do not know if it is formed in DMSO or if the ET reaction follows a concerted dissociative pathway.

The coupling reaction of 1-Ad$^{\bullet}$ radical with **3c** afforded radical anion **10**. In DMSO as solvent, it fragmented in the sense of eqn. (14) faster than intermolecular ET to the substrate; however, in liquid ammonia as solvent, the intermolecular ET was faster than its fragmentation. In order to trap the radical formed in the sense of eqn. (14), we performed the reaction of 1-IAd with the secondary nitronate anion **3d**, prepared from **5b**. But this nucleophile did not couple with the 1-Ad$^{\bullet}$ radical, probably for steric reasons; AdH was the main product obtained and only traces of different products were observed by GC-MS. Thus, we can conclude that **3c** gives the substitution product in liquid ammonia.

In the photostimulated reaction of EtHgCl with **3a** and **3b** it was not necessary to entrain the reactions with acetone enolate ions, which indicates that EtHgCl is easier to reduce (peak potential −0.6 V *vs.* SCE)[26] than 1-AdI (peak potential −2.20 *vs.* SCE[27] or −2.01 *vs.* SHE[28]). The radical anion formed in the coupling of Et$^{\bullet}$ radical with **3c** did not fragment in DMSO, which indicates that intermolecular ET to the substrate was faster than its fragmentation. The higher rate for intermolecular ET is due to the fact that EtHgCl is easier to reduce than 1-AdI.

The fact that EtHgCl does not react with nitranions in the dark, but that it does under irradiation, suggests that these reactions occur by the $S_{RN}1$ mechanism. This synthetic approach is important to obtain secondary or tertiary nitro compounds from primary ones. Tertiary nitro alkanes can be easily obtained by this method. These reactions are compatible with many functional groups, as compared to the drastic experimental conditions of other C-alkylation processes such as the reaction of alkyl halides with the dianion of the primary nitro compound.[29]

Conclusion

We have reported the conversion of EtHgCl and 1-AdX to nitroalkanes by reaction with nitranions under irradiation ($S_{RN}1$ reactions). These results can be of great interest to obtain aliphatic nitro compounds as precursors in organic synthesis.

Compared with the standard procedures, our method offers a series of important advantages, such as better yields, reactions compatible with some functional groups, less drastic experimental conditions, and the absence of formation of unwanted alkyl nitrites.

Experimental

Methods and materials

Irradiation was conducted in a reactor equipped with two 400 W UV lamps emitting with a maximum at 350 nm (Philips Model HPT, water-refrigerated). The HRMS were recorded at Santiago of Compostela University (RIAIDT), Spain.

1-AdBr, 1-AdI, ethyl chloride, magnesium, acetone, nitroethane, nitropropane, 6-nitrohex-1-ene, 1-nitropentane and potassium *t*-butoxide were commercially available and were used as received. DMSO was distilled under vacuum and stored under molecular sieves (4 Å).

Preparation of ethyl mercury chloride

The ethyl mercury chloride (EtHgCl) was obtained by a modification of the Marvel[30] method. The Grignard compound was prepared from 2.7 g (77 mmol) of magnesium turnings and EtCl in excess. The Grignard solution was added to 18.7 g (69 mmol) of powdered $HgCl_2$ suspended in 30 mL of dry THF. After all the Grignard solution had been added, the mixture was stirred and refluxed for 24 h. EtHgCl could not be recrystallized by conventional methods, since it decomposes readily. Acetone was added to the solid at room temperature and the suspension was filtered. The acetone was then evaporated under vacuum at room temperature. The EtHgCl was obtained as long needles crystals, mp 192–193 °C (lit.[31] mp 192.5 °C).

Photostimulated reactions

1-Adx with nitronate anions in liquid ammonia. The following procedure is representative. The reactions were carried out in a 500 mL three-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 300 mL of distilled ammonia were added *t*-BuOK (5.1 mmol), the nitroalkane (3 mmol), and acetone (2 mmol). The 1-AdX (1 mmol) dissolved in 1 mL of anhydrous ether was added to the solution and the reaction mixture was irradiated. 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 other similar experiments the products were quantified by GC using the internal standard method.

1-Adx with nitronate anions in DMSO. The following procedure is representative. The reactions were carried out in a 250 mL three-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 100 mL of dry and degassed DMSO under nitrogen were added *t*-BuOK (5.1 mmol), the nitroalkane (3 mmol), and acetone (2 mmol). After 15 min 1-AdX (1.0 mmol) was added and the reaction mixture was irradiated. The reaction was quenched with an excess of ammonium nitrate. The residue was dissolved with water and then extracted with diethyl ether. The products were isolated by column chromatography. In similar experiments the products were quantified by GC using the internal standard method.

EtHgCl with nitronate anions in DMSO. The following procedure is representative. The reactions were carried out in a 25 mL three-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 12 mL of dry and degassed DMSO under nitrogen were added *t*-BuOK (2.1 mmol) and the nitroalkane (2 mmol). EtHgCl (1 mmol) was added and the reaction mixture was irradiated. The reaction was quenched with an excess of ammonium nitrate. The residue was dissolved with water and then extracted with diethyl ether. The products were isolated by column chromatography. In similar experiments the products were quantified by GC using the internal standard method.

Reactions with nitronate anions in the dark. The procedure was similar to that for the previous reactions, except that the reaction flask was wrapped with aluminum foil.

Inhibited reactions with nitronate anions. The procedure was similar to that for the previous reactions, except that 20 mol % of *p*-DNB was added to the solution of nucleophile prior to substrate addition.

Isolation and identification of the products[32]

1-(1-Nitropentyl)adamantane (2). Isolated as a yellow oil after column chromatography on silica gel, eluted with petroleum ether–ethyl ether (98 : 2). ^{1}H-NMR ($DCCl_3$) δ: 0.89 (3H, t, J = 6.9 Hz); 1.45–2.02 (21H, m); 4.09 (1H, dd, J = 12.1, 2.2 Hz). ^{13}C-NMR ($DCCl_3$) δ: 13.74, 22.13, 26.54, 28.24, 28.62, 35.90, 36.60, 38.51, 99.26. MS (EI+) m/z (%): 204 (2), 136 (11), 135 (100), 107 (6), 93 (12), 91 (9), 79 (16), 67 (8), 55 (4), 41 (6). HRMS (EI) exact mass calcd for $C_{15}H_{25}NO_2$: 251.1885, found 251.1878.

1-(1-Nitroethyl)adamantane (4a). Isolated as a white solid after column chromatography on silica gel, eluted with hexane–ethyl ether (98 : 2). Mp: 46–47.5 °C. ^{1}H-NMR ($DCCl_3$) δ: 1.42–1.46 (3H, d, J = 6.9 Hz); 1.49–2.04 (15H, m); 4.21–4.31 (1H, q, J = 6.9 Hz). ^{13}C-NMR ($DCCl_3$) δ:12.80; 28.22; 36.54; 38.16; 92.93. MS (EI+) m/z (%): 163 (100), 135 (33), 121 (15), 107 (33), 93 (46), 91 (30), 79 (55), 67 (29), 55 (27). Anal. found: C, 68.7; H, 8.9; N, 6.5%; calcd for $C_{12}H_{19}NO_2$: C, 68.87; H, 9.15; N, 6.69%.

1-(1-Nitrohex-5-enyl)adamantane (4b). Isolated as an oil after column chromatography on silica gel, eluted with pentane–ethyl ether (98 : 2). ^{1}H-NMR ($DCCl_3$) δ: 1.25–2.12 (21H, m); 4.10 (1H, dd, J = 12, 2.3 Hz); 4.96–5.06 (2H, m); 5.65–5.85 (1H, m). ^{13}C-NMR ($DCCl_3$) δ: 25.60, 26.17, 28.24, 32.93, 36.57, 38.51, 99.05, 115.35, 137.59. MS (EI+) m/z (%): 175 (1), 135 (100), 119 (2), 107 (10), 93 (14), 91 (8), 79 (18), 67 (13), 55 (19), 41 (37). HRMS (CI) exact mass calcd for $C_{16}H_{25}NO_2$: 263.1885, found 263.1874.

2-Nitrobutane (5a). Isolated as a colorless oil after column chromatography on silica gel, eluted with pentane–ethyl ether (98 : 2). MS (EI+) m/z (%): 58(3), 57 (64), 56 (8), 55 (6), 42 (6), 41 (100), 40 (6), 39 (23), 30 (9), 29 (99), 28 (16), 27 (38). Identified by comparison with literature data.[33]

6-Nitrooct-1-ene (5b). Isolated as a solid after column chromatography on silica gel, eluted with pentane–ethyl ether (99 : 1). ^{1}H-NMR ($DCCl_3$) δ: 0.95 (3H, t, J = 7.6); 1.38–2.09 (8H, m); 4.32–4.46 (1H, m); 4.96–5.07 (2H, m); 5.65–5.85 (1H, m). ^{13}C-NMR ($DCCl_3$) δ:. 10.21, 24.95 (m), 27.16, 29.67, 32.80, 90.23, 115.41, 137.45. MS (EI+) m/z (%): 109 (2), 95 (4), 90 (7), 81 (18), 69 (100), 68 (18), 55 (91). HRMS (CI) exact mass calcd for $C_8H_{15}NO_2$: 157.1103, found 157.1108.

1-Isopropyladamantane (6). Isolated as an oil after column chromatography on silica gel, eluted with petroleum ether (100) and identified by comparison with literature data.[34] ^{13}C-NMR ($DCCl_3$) δ: 16.27, 28.84, 34.33, 37.49, 39.27. MS (EI+) m/z (%): 178 (3), 135 (100), 107 (9), 93 (15), 79 (20), 67 (8), 55 (5), 41 (11).

1-Isopropenyladamantane (7). Isolated as an oil after column chromatography on silica gel, eluted with petroleum ether (100) and identified by comparison with literature data.[34] ^{13}C-NMR ($DCCl_3$) δ: 18.51, 28.76, 37.06, 41.04, 107.37, 154.73. MS (EI+) m/z (%): 176 (100), 161 (21), 147 (8), 133 (25), 119 (45), 105 (26), 93 (43), 91 (60), 79 (54), 55 (18), 41 (43).

1-(1-Methyl-1-nitroethyl)adamantane (8). Isolated as a white solid after column chromatography on silica gel, eluted with petroleum ether–ethyl ether (98 : 2). The product was recrystallized from pentane. Mp: 136–139 °C. ^{1}H-NMR ($DCCl_3$) δ: 1.52 (6H, s); 1.56–1.73 (12H, m); 1.97–2.11 (3H, m). ^{13}C-NMR ($DCCl_3$) δ: 21.40, 28.54, 36.52, 95.22. MS (EI+) m/z (%): 177 (36), 176 (21), 135 (100), 107 (17), 93 (35), 91 (21), 81 (15), 79 (43), 67 (18), 55 (11), 41 (20). HRMS (CI) exact mass calcd for $C_{13}H_{21}NO_2$: 223.1572, found 223.1577.

Acknowledgements

This work was supported in part by Agencia Córdoba Ciencia (ACC), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Antorchas Foundation, SECYT, Universidad Nacional de Córdoba and FONCYT. C.A.T. gratefully acknowledges receipt of a fellowship from FONCYT and S.M.B. gratefully acknowledges receipt of a fellowship from the Council of the Province of Neuquén and Repsol-YPF.

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