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Regiochemistry of the Photostimulated Reaction of the Phthalimide Anion with 1-Iodoadamantane and *tert*-Butylmercury Chloride by the $S_{RN}1$ Mechanism

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Abstract: The photostimulated reaction of the phthalimide anion (**1**) with 1-iodoadamantane (**2**) gave 3-(1-adamantyl) phthalimide (**3**) (12%) and 4-(1-adamantyl) phthalimide (**4**) (45%), together with the reduction product adamantane (AdH) (21%). The lack of reaction in the dark and inhibition of the photoinduced reaction by *p*-dinitrobenzene, 1,4-cyclohexadiene, and di-*tert*-butylnitroxide indicated that **1** reacts with **2** by an $S_{RN}1$ mechanism. Formation of products **3** and **4** occurs with distonic radical anions as intermediates. The photoinduced reaction of anion **1** with *tert*-butylmercury chloride (**10**) affords 4-*tert*-butylphthalimide (**11**) as a unique product. By competition experiments toward **1**, 1-iodoadamantane was found to be ca. 10 times more reactive than *tert*-butylmercury chloride.

The radical nucleophilic substitution, or $S_{RN}1$, is an excellent means of effecting the nucleophilic substitution of different types of aromatic and aliphatic substrates with electron-withdrawing groups (EWG) possessing suitable leaving groups. Also, it has been reported that aliphatic substrates without EWG groups such as the cycloalkyl, bicycloalkyl, and neopentyl halides react by this mechanism.[1] This $S_{RN}1$ reaction involves radicals and radical anions as intermediates and proceeds by a chain mechanism, whose propagation steps are outlined in Scheme 1.

Scheme 1

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

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

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

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

In aliphatic systems without a π^* MO that stabilizes the radical anion $(RX)^{-\bullet}$, this is not an intermediate, and eqs 1 and 3 occur simultaneously (dissociative electron transfer) (eq 1,3).[2] However, this chain process requires an initiation step, that is, the generation of the radical ($R^{\bullet}$) or the radical anion $(RX)^{-\bullet}$ intermediates.[1] In a few systems, spontaneous electron transfer (ET) from the nucleophile to the substrate has been observed. When the ET does not occur spontaneously, it can be induced by light or by $FeBr_2$ in DMSO.

The alkyl halides that react by the $S_{RN}1$ mechanism are those that have a relatively low reactivity toward polar nucleophilic substitution.[1c,f] For instance, 1-haloadamantanes as well as other bridgehead halides react with Ph_2P^-,[3] Ph_2As^-,[3a] and Me_3Sn^- [4] ions. Also, the reaction of 1-iodoadamantane (1-IAd) with carbanions,[5] PhS^-,[6,7] $PhSe^-$,[6] and $PhTe^-$ [6] ions has been reported.

It is known that N-centered nucleophiles react with different substrates to give N-substitution or C-substitution and both N- and C-substitution. Thus, the photoinduced reaction of the anion of 2-aminonaphthalene with iodobenzene affords mainly 1-phenyl-2-aminonaphthalene (47%) and *N*-phenyl-2-aminonaphthalene (1%). However, with 1-iodonaphthalene only C-substitution is observed.[8] Several anions derived from nitrogen heterocycles react with aryl radicals on carbon. With the anion of pyrrole, only substitution at the carbon center is observed, the 2-position being more reactive than the 3-position.[9] For example, in the reaction of 4-chloropyridine with pyrrole anion induced by electrodes, 2-(4-pyridyl) pyrrole (60%) and 3-(4-pyridyl) pyrrole (3%) were obtained and no N-substitution is observed.[9] In contrast, it was found that alkyl substrates with EWG yield N-substitution products after reaction with N-centered nucleophiles derived from azoles,[10] nitroimidazoles,[11] pyrimidine,[12] purine,[13] etc. There is only one example in the literature of the reaction of an alkyl substrate without EWG with nitrogen nucleophiles in which *tert*-butyl-

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Table 1. Reactions of 1 with 2 in DMSO[a]

		products, yield %			
experiment	conditions	I^-	AdH	**3**	**4**
1	dark, 180 min	6	<1		
2	*hν*, 60 min	53	6	7	35[c]
3	*hν*, 300 min	67	10	11	40
4[b]	*hν*, 180 min	68	19	2[c]	35[c]
5[d]	*hν*, 180 min	72	21	12	45
6[e]	*hν*, 180 min	10	<1		
7[f]	*hν*, 180 min	50	3	<1	20
8[g]	*hν*, 180 min	48	7	2.5	18
9[h]	*hν*, 180 min	58	13[i]		
10[h]	dark, 180 min	<2	<1		
11[h,e]	*hν*, 180 min	<7	<1		

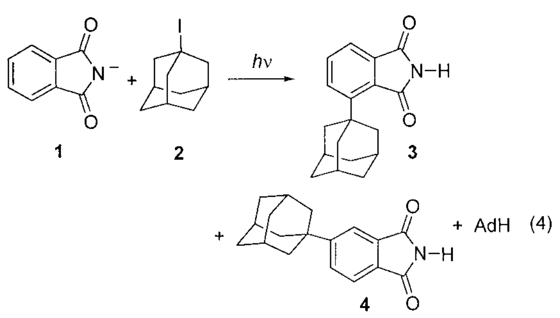
[a] Reactions were performed with **1** (16.4×10^{-2} M) and **2** (8.3×10^{-2} M) in DMSO and quantified by GC with the internal standard method. Part of AdH is lost during workup. [b] In the presence of 18-crown-6. [c] Isolated yield. [d] In the presence of 18-crown-6 and pinacolone enolate ion (16.4×10^{-2} M). [e] In the presence of *p*-dinitrobenzene (20 mol %). [f] In the presence of 1,4-cyclohexadiene (80 mol %). [g] In the presence of di-*tert*-butylnitroxide (20 mol %). [h] Reaction carried out with the anion of 1,3-indandione **12** (16.4×10^{-2} M) and **2** (8.3×10^{-2} M) in DMSO. [i] Together with 17% of the substitution product **13** and 1-adamantanol (3%).

mercury chloride was reported to react by the $S_{RN}1$ mechanism with the anion of the phthalimide to give substitution on the nitrogen.[14]

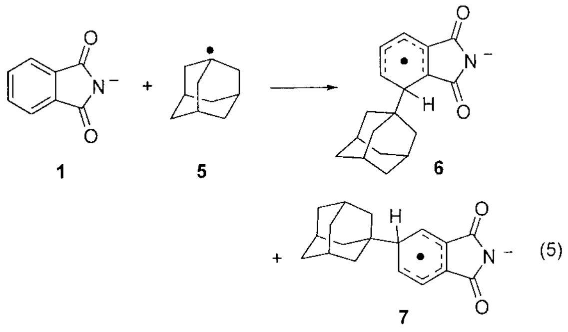
The lack of studies about the reactions of N-centered anions with radicals from aliphatic substrates without EWG has encouraged us to investigate the reactivity of the phthalimide anion with different substrates and the regiochemistry of the coupling reaction with radicals.

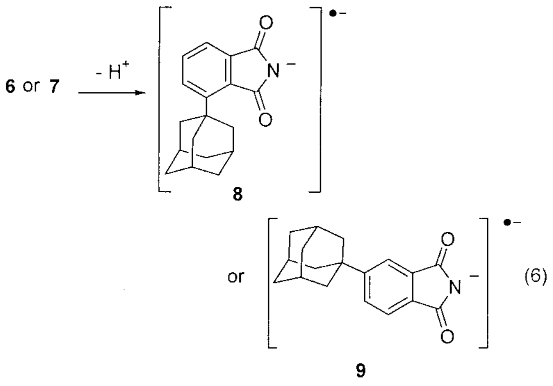
In the photoinduced reaction of the phthalimide anion **1** with 1-iodonaphthalene, we found no substitution products and only the reduction product naphthalene was formed (39%). This reaction does not proceed in the dark. These results can be ascribed to a poor reactivity of the 1-naphthyl radicals toward nucleophile **1**, in comparison with a competitive reduction process. Thus, a photoinduced ET from **1** to 1-iodonaphthalene followed by fragmentation of the C−I bond in the radical anion intermediate yields the 1-naphthyl radicals, which are reduced to the corresponding naphthalene by hydrogen atom abstraction from the solvent.[15]

The photostimulated reaction of **1** with 1-iodoadamantane **2** gave 3-(1-adamantyl) phthalimide (**3**) and 4-(1-adamantyl) phthalimide **4**, together with the reduction product adamantane (AdH) (eq 4). This reaction does not take place in the dark, and the photostimulated reaction was strongly inhibited by *p*-dinitrobenzene (radical anion trap) and partially by 1,4-cyclohexadiene and di-*tert*-butylnitroxide (as radical traps) (Table 1). These results indicate that **1** reacts with **2** by an $S_{RN}1$ mechanism.



The formation of the substitution products **3** and **4** can be rationalized as follows. The 1-adamantyl radicals **5**, formed by a dissociative ET to **2**, react with the nucleophile **1** at positions 3- and 4- affording distonic radical anions **6** and **7**, respectively (eq 5). No addition to the nitrogen is observed. As far as we know there are few examples of the formation of distonic radical anion in the coupling of a radical and a nucleophile.[16] To yield the observed products, the intermediate radical anions **6** and **7** should lose a proton to afford radical dianions **8** and **9** (eq 6), which continue the chain propagation cycle. The driving force of this reaction is the aromatization to the benzene ring. Radical dianions have also been reported as intermediates in the propagation cycle of the $S_{RN}1$ reaction of the nucleophiles derived from 2-naphthol and analogues with *o*-dihalobenzenes.[17]





$$\mathbf{8} \text{ or } \mathbf{9} \xrightarrow{\text{ET}} \mathbf{3} \text{ or } \mathbf{4} \qquad (7)$$

The unexpected regiochemistry of this reaction could be ascribed to differences in the activation energy for the coupling reactions leading to the C−N or C−C bond formation, although the C−N product is thermodynamically more favorable.[18]

There is a slight increase in products **3** and **4** when the reaction is carried out in the presence of 18-crown-6 and pinacolone enolate ions as an entrainment reagent. (Table 1, experiments 4 and 5). The formation of products **3** and **4** is opposite to those reported on the reaction of **1**

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[16] In the reaction of **1** with isobutirophenone anion, the main product is the coupling of adamantyl radicals in the para position of the nucleophile to give also a distonic radical anion. See: Lukach, A. E.; Santiago, A. N.; Rossi, R. A. *J. Org. Chem.* **1997**, *62*, 4262−4265.

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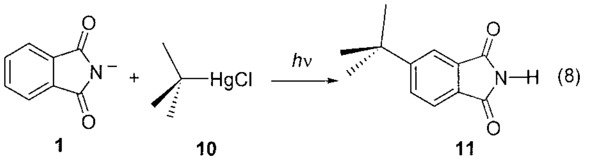
with *tert*-butylmercury chloride (**10**) in which *tert*-butyl radicals couple on the nitrogen.[14] We repeated the reaction under the same experimental conditions, and we found that the only substitution product formed is 4-*tert*-butylphthalimide (**11**) (20% isolated yield) (eq 8).[19] The crude reaction product was analyzed by GC-MS, and not even traces of other possible coupling products were observed.

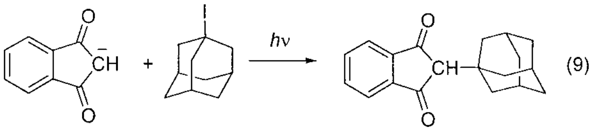


1 **10** **11**

To assess the relative reactivity of **2** and **10** toward anion **1**, we performed the corresponding competition experiment in DMSO, using 8.3×10^{-2} M in both substrates, and 6.7×10^{-2} M in the anion **1**.[20] After 3 h of irradiation, 47.5% of product **4** and 5% of product **11** was quantified by GC with the internal standard method. We found that **2** was ca. 10 times more reactive than **10**; this can be rationalized as **2** being a better electron acceptor than **10**.

No coupling products were formed in the photostimulated reaction of **1** with neopentyl iodide and with 7-iodonorcarane, primary and secondary alkyl halides, respectively. Nevertheless, dehalogenations were observed in acceptable yields (60 and 62% iodide ion, respectively).

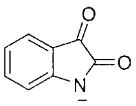
The anion of 1,3-indandione **12**, analogue to the phthalimide anion (**1**) in which the NH moiety is replaced by a methylene group, shows a different regiochemistry. Thus, in the photostimulated reaction with **2** only the C-substitution product **13** was obtained (17%), together with adamantane (13%), adamantanol (3%), and iodide ions (58%) (eq 9). This reaction does not occur in the dark and is strongly inhibited by the presence of *p*-dinitrobenzene (<2 and 5% iodide ion, respectively) (Table 1).



12 **2** **13**

Anion **12** was not reactive toward *tert*-butylmercury chloride (**10**) after 3 h of irradiation under the same experimental conditions employed for the reaction with **2**. This result is in agreement with the lower reactivity shown by **10** in regard to **2**, as was observed by competition experiments toward anion **1** (see above).

Other nucleophiles related to **1** such as the anions **14** and **15** were studied, but in the photostimulated reaction with **2** only reduction to adamantane was obtained.



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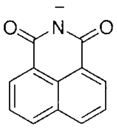

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From these results, it is concluded that alkyl radicals without EWG react sluggishly with nitrogen-centered nucleophiles. The phthalimide anion (**1**) couples with 1-adamantyl and *tert*-butyl radicals mainly at the 4-position to give a new C−C bond, and no coupling at the nitrogen took place.

Experimental Section

General Methods. Irradiation was conducted in a reactor equipped with two 250 W UV lamps emitting maximally at 350 nm (Philips Model HPT, water-refrigerated). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 200 spectrometer, and all spectra are reported in δ (parts per million) relative to Me_4Si, with $CDCl_3$, CD_2Cl_2, CD_3SOCD_3, or CD_3COCD_3 as solvents. HRDEIMS were recorded at Mc Master Regional Centre for Mass Spectrometry, Mc Master University, Canada. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II apparatus with a flame-ionization detector and the data system Hewlett-Packard 3396 Series II integrator, on a 5 m capillary column packed with methyl silicone gum of a 0.53 mm × 2.65 μm film thickness. GS/MS analyses were carried out on a Shimadzu GC-MS QP 5050 spectrometer, employing a 30 m × 0.12 mm DB-5 MS column. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer. The column chromatography was performed on silica gel (70−230 mesh ASTM). Potentiometric titration on halide ions was performed in a pH meter (Orion, model 420 A), using an Ag/Ag$^+$ electrode and a $AgNO_3$ solution as a standard. Melting points were obtained on an Electrothermal 9100 apparatus and were not corrected.

Materials. *tert*-Butylmercury chloride[21] (**10**) and 7-iodonorcarane[22] were synthesized as previously reported. Phthalimide (Aldrich), *t*-BuOK (Aldrich), 18-crown-6 ether (ICN), 1-iodoadamantane (Aldrich), 1,3-indandione (Aldrich), isatin (Aldrich), and 1,8-naphthalimid (Aldrich) were commercially available and used as received. DMSO (Carlo Erba) was distilled under vacuum and stored over molecular sieves (4Å). The anions were generated in situ by acid−base deprotonation using *t*-BuOK.

Photoinduced Reactions of Anion 1 with 2 (General Procedure). The photochemical reaction was carried out in a three-necked, 50 mL round-botton flask equipped with a nitrogen gas inlet, a condenser with a cooling jacket, and a magnetic stirrer. The flask was dried under vacuum, filled with nitrogen, and then loaded with 30 mL of dried DMSO. To the degassed solvent under nitrogen was added 7.5 mmol of *t*-BuOK, 5.0 mmol of the nucleophile precursor, 7.5 mmol of 18-crown-6 ether, and 2.5 mmol of **2**. After 3 h of irradiation, the reaction was quenched with addition of ammonium nitrate in excess and 10 mL of water, and then the mixture was extracted with diethyl ether. The iodide ions in the aqueous solution were determined potentiometrically. The ether extract was washed twice with water and dried, and the products were quantified by GC with the internal standard method.

3-(1-Adamantyl) Phthalimide (3). Compound **3** was isolated in 7% yield by silica gel chromatography with petroleum ether/diethyl ether (80:20) as the eluent from the crude product reaction. Compound **3** is a white solid: ^{1}H NMR (CD_3SOCD_3) δ 1.27 (s), 1.81 (s), 2.17 (s), 7.65−7.81 (m) 11.33 (s); ^{13}C NMR (CD_3COCD_3) δ 19.38, 27.04, 27.77, 31.16, 111.72, 120.05, 122.50, 125.46, 125.95, 142.58, 159.85, 160.88; IR (KBr) cm^{-1} 3182, 1766, 1730, 1714, 1359, 1302, 1077, 743; MS (EI+) 282 (19.96), 281 (100.00) M$^+$, 238 (13.23), 224 (61.61), 160 (13.45), 135 (5.90), 121 (69.05), 93 (31.60), 79 (50.35); HRMS (EI+) calcd 281.1416, found 281.1359.

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(19) The spectroscopic data from ^{1}H NMR are essentially the same as those previously reported in ref 14, but probably due to an incomplete analysis of the reaction product (no ^{13}C NMR or MS data were available), the structure assignment was not correct.

(20) The following is the equation used in the evaluation of the relative reactivity of 1-iodoadamantane (**2**) and *tert*-butylmercury chloride (**10**) toward phthalimide anion (**1**): $k_{\mathrm{Ada}}/k_{t\mathrm{-Bu}} = [\ln(\mathrm{AdaI})_o/(\mathrm{AdaI})_o - (\mathrm{AdaNu})_t]/[\ln(t\text{-}\mathrm{BuHgCl})_o/(t\text{-}\mathrm{BuHgCl})_o - (t\text{-}\mathrm{BuNu})_t]$, where $(\mathrm{AdaI})_o$ and $(t\text{-}\mathrm{BuHgCl})_o$ are the initial concentrations and $(\mathrm{AdaNu})_t$ and $(t\text{-}\mathrm{BuNu})_t$ are the concentrations of the products at time *t*. See: Bunnett, J. F. *Investigation of Rates and Mechanism of Reactions,* 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part I.

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(22) Dehmlow, E. V.; Stütten, J. *Tetrahedron Lett.* **1991**, *43*, 6105−6108.

4-(1-Adamantyl) Phthalimide (4). Compound **4** was isolated in 35% yield by silica gel chromatography with petroleum ether/diethyl ether (80:20) as eluent from the crude product reaction. Compound **4** is a white solid: mp 251−252 °C; ^{1}H NMR (CD_3SOCD_3) δ 1.79 (6H, s), 1.96 (6H, s), 2.12 (3H, s), 7.77−7.95 (3H, m) 11.24 (1H, s); ^{13}C NMR ($CDCl_3$) δ 28.67, 36.43, 37.32, 42.93, 120.50, 123.41, 129.90, 131.01, 132.84, 159.09, 168.26, 168.66; IR (KBr) cm^{-1} 3250, 1765, 1710, 1622, 1437, 1301, 1099, 1041, 751; MS (EI+) 282 (20.27), 281 (100.00) M$^+$, 238 (17.33), 224 (46.06), 181 (63.64), 152 (18.48), 135 (16.52), 94 (65.16), 79 (49.89); HRMS (EI+) calcd 281.1416, found 281.1386.

4-*tert*-Butylphthalimide (11). Compound **11** was isolated in 20% yield by silica gel chromatography with petroleum ether/diethyl ether (90:10) as the eluent from the crude product reaction. Compound **11** is a white solid: mp 142−143 °C; ^{1}H NMR ($CDCl_3$) δ 1.44 (9H, s), 7.76−7.99 (3H, m) 10.00 (1H, s); ^{13}C NMR (CD_3COCD_3) δ 32.18, 37.04, 121.44, 124.40, 132.24, 132.89, 135.05, 160.05, 170.01, 170.34; IR (KBr) cm^{-1} 3218, 1769, 1717, 1608, 1475, 1297, 1084, 1034, 725; MS (EI+) 204 (3.53), 203 (14.15) M$^+$, 188 (100.00), 160 (50.82), 145 (20.99), 115 (15.81), 102 (4.57), 89 (9.35), 71 (5.61), 57 (14.92); HRMS (EI+) calcd 203.0946, found 203.0935.

2-(1-Adamantyl)-1,3-indandione (13). Compound **13** was isolated in 17% yield by silica gel chromatography with petroleum ether/diethyl ether (80:20) as the eluent from the crude product reaction. Compound **13** is a yellow solid: ^{1}H NMR ($CDCl_3$) δ 1.82 (6H, s), 1.99 (6H, s), 2.14 (3H, s), 3.20 (1H, s) 7.74−8.07 (4H, m); ^{13}C NMR (CD_2Cl_2) δ 29.02, 36.56, 42.95, 43.92, 45.59, 119.31, 132.97, 141.33, 197.90; IR (KBr) cm^{-1} 2901, 2850, 1714, 1602, 1574, 1453, 1254; MS (EI+) 281 (17.85), 280 (100.00) M$^+$, 237 (9.08), 223 (28.91), 181 (34.58), 135 (8.42), 94 (23.93), 79 (20.65); HRMS (EI+) calcd 280.1463, found 280.1491.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, and mass spectra of compounds **3**, **4**, **11**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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