The Journal of
Organic
Chemistry

VOLUME 55, NUMBER 12 JUNE 8, 1990

Communications

The Photostimulated Reaction of 1-Iodoadamantane with Carbanionic Nucleophiles in DMSO by the $S_{RN}1$ Mechanism

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Received February 27, 1990

Summary: 1-Iodoadamantane (**1**) reacts under irradiation with the enolate ions of acetone (**2**), acetophenone (**5a**), and propiophenone (**5b**) to give adamantane and the substitution products in variable yields. The anion of nitromethane (**7**) does not react under irradiation with **1**, but excellent yields of 1-adamantylnitromethane (**8**) are obtained in the photostimulated reaction of **1** and **7** in the presence of **2** or **5a** (entrainment reactions). We suggest that 1-iodoadamantane reacts with these nucleophiles by the $S_{RN}1$ mechanism of nucleophilic substitution.

The $S_{RN}1$ mechanism of nucleophilic substitution has been shown to be an important route in the nucleophilic substitution reactions of both aromatic[1] and aliphatic substrates.[2] This mechanism involves an initiation step, usually promoted by light (eq 1), and a propagation cycle (eqs 2–4).

$$\mathrm{RX} + \mathrm{Nu}^- \xrightarrow{h\nu} (\mathrm{RX})^{\bullet-} + \mathrm{Nu}^\bullet \tag{1}$$

$$(\mathrm{RX})^{\bullet-} \rightarrow \mathrm{R}^\bullet + \mathrm{X}^- \tag{2}$$

$$\mathrm{R}^\bullet + \mathrm{Nu}^- \rightarrow (\mathrm{RNu})^{\bullet-} \tag{3}$$

$$(\mathrm{RNu})^{\bullet-} + \mathrm{RX} \rightarrow \mathrm{RNu} + (\mathrm{RX})^{\bullet-} \tag{4}$$

It has been shown that several alkyl halides, such as bridgehead,[3] cyclopropyl,[4] and neopentyl halides,[5] are able to react by the $S_{RN}1$ mechanism in liquid ammonia with a variety of different nucleophiles, with the exception of the carbanionic ones.[6] For instance, in the photostimulated reaction of 1-iodo- or 1-bromoadamantane with acetone enolate ions, or other carbanionic nucleophiles, the main products were adamantane and 1,1′-biadamantyl. No substitution products were found in these systems.[7]

On the other hand, Russell has reported that *tert*-butylmercury halides react with carbanionic nucleophiles by the $S_{RN}1$ mechanism in DMSO, thus demonstrating that tertiary alkyl radicals are able to couple with this type of nucleophile.[8]

The different behaviors of haloaliphatic substrates compared with haloaromatics in liquid ammonia, (the latter react very easily with carbanionic nucleophiles, not only in liquid ammonia but also in DMSO), and with that of *tert*-butylmercury halides which react with carbanions in DMSO, has prompted us to study the photostimulated reactions of 1-iodoadamantane with different carbanionic nucleophiles in DMSO. Our primary goal, therefore, was

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(1) For review, see: (a) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanisms*; ACS Monograph 178, Washington DC, 1983. (b) Bowman, W. R. *Chem. Soc. Rev.* **1988**, *17*, 283.

(2) For reviews, see: (a) Kornblum, N. *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1982; Suplement F, Chapter 10. (b) Rossi, R. A.; Pierini, A. B.; Palacios, S. M. *J. Chem. Ed.* **1989**, *66*, 720. Also, it has been reported that certain alkyl halides react with nucleophiles by the SET mechanism, see: (c) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: New York, 1987. (d) Bordwell, F. G.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 1052 and references cited therein. (e) Santiago A. N.; Rossi, R. A. *J. Chem. Soc., Chem. Commun.* **1990**, 206.

(3) (a) Santiago, A. N.; Morris, D. G.; Rossi, R. A. *J. Chem. Soc., Chem. Commun.* **1988**, 220. (b) Santiago, A. N.; Iyer, V. S.; Adcock, W.; Rossi, R. A. *J. Org. Chem.* **1988**, *53*, 3016 and references cited therein.

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(5) (a) Ashby, E. C.; Argyropoulos, J. N. *J. Org. Chem.* **1985**, *50*, 3274. (b) Bornancini, E. R. N.; Peñéñory, A. B.; Palacios, S. M.; Rossi, R. A. *J. Phys. Org. Chem.* **1989**, *2*, 255 and references cited therein.

(6) It has been reported that cyclopropyl halides react with ketone enolate ions, although in low overall yield; see ref 4a.

(7) Palacios, S. M.; Santiago, A. N.; Rossi, R. A. *J. Org. Chem.* **1984**, *49*, 4609.

(8) Russell, G. A.; Khanna, R. K. *Tetrahedron* **1985**, *41*, 4133.

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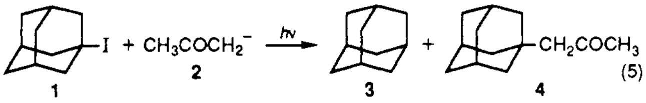
Table I. Photostimulated Reactions of 1-Iodoadamantane with Carbanion Nucleophiles in DMSO[a]

expt	Nu^-	added compound (M)	$h\nu$, min	yield,[b] % I^-	yield,[b] % AdH	yield,[b] % Ad–Nu
1[c]	**2**		120	34[d]	7	*e*
2	**2**		120	84	17	4, 20[f]
3	**2**		120[g]	0		
4	**5a**		240	59	5	**6a**, 48[h]
5	**5a**	18-C-6[i] (0.12)	240	72	9	**6a**, 65[h]
6	**5a**	18-C-6[i] (0.12)	240[g]	0		
7	**5a**	p-DNB[j] (0.006)	240	21	2	**6a**, 8[h]
8	**5a**	**2** (0.12)	240	45	4	**6a**, 41[h] 4, 7[f]
9	**5b**	18-C-6[i] (0.12)	240	45	2	**6b**, 27[k]
10	**7**		120	0		
11	**7**	18-C-6[i] (0.12)	120	9	*e*	*e*
12	**7**	*t*-BuOK (0.24)	240	30	*e*	8, 27[k]
13	**7**	18-C-6[i] (0.16) **5a** (0.04)	240	64	*e*	8, 58[k] **6a**, 0
14	**7**	**2** (0.08)	240	93	2	8, 87[k] 4, 0
15	**7**	**2** (0.08) *p*-DNB[j] (0.008)	240	45	*e*	8, 38[k] 4, 0

[a] 1-Iodoadamantane, 0.04 M; carbanions, 0.12 M. [b] Yields determined by GLC using the internal standard method. [c] 1-Bromoadamantane, 0.027 M. [d] Bromide ions. [e] Not quantified. [f] Internal standard, naphthalene. [g] Dark conditions. [h] Internal standard, triphenylstibine. [i] 18-Crown-6. [j] *p*-Dinitrobenzene. [k] Internal standard, diphenyl disulfide.

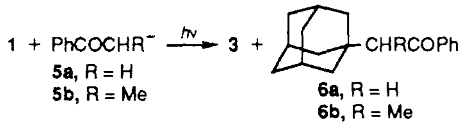
to build a new C–C bond in a bridgehead position.

In the photostimulated reaction of 1-iodoadamantane **1** with acetone enolate ion **2**,[9] we obtained an 84% yield of iodide ion, 17% of adamantane **3**, and 20% of 1-adamantylacetone **4**[10] (expt 2, Table I) (eq 5).[11] There was no reaction in the dark under the same experimental conditions (expt 3, Table I). When the photostimulated reaction was carried out with 1-bromoadamantane as substrate, we obtained only a 34% yield of bromide ion (expt 1, Table I).



(5)

In the photostimulated reaction of **1** with the enolate ion of acetophenone **5a**, we obtained iodide ion (59% yield), together with **3** (5%), and the substitution product α-(1-adamantyl)acetophenone (**6a**) (48%) (expt 4, Table I).[12]



(6)

When this photostimulated reaction was performed in the presence of 18-crown-6, a 72% yield of iodide ion was obtained, together with 9% of **3** and 65% of the substitution product **6a** (expt 5, Table I). There was no reaction in the dark (expt 6, Table I), and the photostimulated reaction was inhibited by *p*-dinitrobenzene (expt 7, Table I). In the photostimulated reaction of **1** with the enolate ion of propiophenone **5b** in the presence of 18-crown-6, we obtained 45% of iodide ion, 2% of **3**, and 27% of the substitution product **6b** (expt 9, Table I).[13]

The fact that there was no reaction in the dark, that light catalyzed these reactions, and that the photostimulated reaction was inhibited by *p*-dinitrobenzene suggests that **1** reacts with carbanions **2** and **5** by the $S_{RN}1$ mechanism of nucleophilic substitution.

These results also indicate that carbanions **5a** and **5b** are more effective in trapping 1-adamantyl radicals than is **2** (there is a lower yield of the reduction product adamantane associated with a significant yield of the substitution products **6a** and **6b** in the case of the first two nucleophiles); however, **2** is more effective in initiating the photostimulated reaction than **5** (the overall yield of reaction is higher, as measured by iodide ion liberated, despite the fact that less substitution product **4** is formed). Therefore, a competition reaction between **2** and **5a** in the same concentrations was performed. In this reaction we found that **6a** was formed in 41% yield while only a 7% yield of **4** was detected (expt 8, Table I). This result shows that **5a** is indeed more effective (about 6 times more reactive) in trapping 1-adamantyl radicals than **2**.

On the other hand, in the photostimulated reaction of **1** with nitronate ion **7** there was no reaction at all after 120 min of irradiation (≤1% yield of iodide ion) (expt 10, Table I). When this reaction was performed in the presence of 18-crown-6, only a 9% yield of iodide ion was obtained (expt 11, Table I) (eq 7).

$$1 + \underset{7}{{}^-CH_2NO_2} \xrightarrow{h\nu} \text{no reaction} \qquad (7)$$

This lack of reactivity could be explained by the fact that nucleophile **7** is unable to initiate the reaction (no photostimulated electron transfer in the sense of eq 1), or that **7** is unable to couple with bridgehead radicals. However, as we pointed out before, it has previously been shown that nucleophile **7** couples with *tert*-butyl radicals,[8]

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[9] Irradiation was conducted in a reactor equipped with two 400-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated).

[10] Sauers, R. R.; Gorodetsky, M.; Whittle, J. A.; Hu, C. K. *J. Am. Chem. Soc.* **1971**, *93*, 5520.

[11] Several other minor products were detected by GLPC and TLC, probably as the aldol condensation products of 1-adamantylacetone and acetone, as suggested by ^1H NMR and mass spectra analyses.

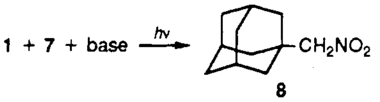
[12] Lewis, F. D.; Johnson, R. W.; Kory, D. R. *J. Am. Chem. Soc.* **1974**, *93*, 6100.

[13] α-(1-Adamantyl)propiophenone was isolated by column chromatography (silica gel) eluted with hexane–diethyl ether, 95:5: ^1H NMR (δ, relative to TMS) 0.90 (3 H, d), 1.32–1.92 (16 H, m), 7.10–7.80 (5 H, m); mass spectrum, *m/e* (relative intensity) 269 (6), 268 (31), 250 (3), 239 (3), 202 (7), 163 (14), 147 (7), 136 (14), 135 (100), 119 (7), 105 (89), 93 (19), 77 (17), 57 (19), 43 (10); high-resolution mass spectrum,[14] *m/e* 268.1828 (M^+, calcd 268.1827).

[14] The high-resolution mass spectra were run in the Chemical Instrumentation Center of the Yale University.

which suggests that it should be able to do so with bridgehead radicals.

As potassium *tert*-butoxide was shown to be a good electron donor in DMSO under photostimulation, we performed the photostimulated reaction of **1** with **7** in the presence of an excess of this base. We found a 30% yield of iodide ion, a small amount of **3** and a 27% yield of the substitution product 1-adamantylnitromethane (**8**)[15] (eq 8, base = t-BuO$^-$) (expt 12, Table I). These results suggest that even though **7** is unable to initiate the photostimulated $S_{RN}1$ reaction, it does propagate very efficiently the chain reactions.



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(8)

In order to augment the photostimulated initiation step, we carried out the same experiment, but in the presence of **5a** together with 18-crown-6 (eq 8, base = $PhCOCH_2^-$). Under these reaction conditions we obtained a 64% yield of iodide ion, 58% yield of the substitution product **8** and a complete absence of the substitution product **6a** (expt 13, Table I). When the reaction was performed in the presence of **2** (eq 8, base = $CH_3COCH_2^-$), once again we obtained a high yield of iodide ion (93%) and the substitution product **8** (87% yield), with only a 2% yield of adamantane, and no substitution product **4** (expt 14, Table I). When the photostimulated reaction was carried out in the presence of *p*-dinitrobenzene, inhibition occurred (expt 15, Table I).

Based on the results herein obtained, we conclude that substrate **1** is able to react with carbanionic nucleophiles by the $S_{RN}1$ mechanism under irradiation in DMSO, thus opening an interesting synthetic route to build a new C–C bond in a bridgehead position.

Other features related to these reactions imply that the stronger the base used, the more it catalyzes the photostimulated initiation step (the pK_a's in DMSO are: acetone, 26.5; acetophenone, 24.7; and nitromethane, 17.2).[16] Furthermore, 1-adamantyl radicals are quite selective with these carbanionic nucleophiles; the apparent reactivity decreases in the order **7** > **6a** > **2** (inverse order of the respective pK_a's in DMSO). Further study on both the scope and limitations of this novel radical nucleophilic substitution at the bridgehead position with different carbanionic nucleophiles and different bridgehead halides is planned.

Acknowledgment. G.L.B. gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). This work was partially supported by CONICET, Antorchas Foundation, and the Consejo de Investigaciones de la Provincia de Córdoba, Argentina.

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(15) 1-Adamantylnitromethane was isolated by column chromatography (silica gel) eluted with petroleum ether–diethyl ether, 95:5: ^{1}H NMR (δ, relative to TMS) 1.70–2.50 (15 H, m), 4.30 (2 H, s); mass spectrum, *m/e* (relative intensity) 195 (0.29), 179 (0.48), 163 (8), 149 (100), 135 (13), 121 (17), 119 (23), 107 (26), 105 (23), 93 (53), 91 (28), 81 (61), 79 (61), 67 (75), 55 (38), 43 (27), 41 (33); high-resolution mass spectrum,[14] *m/e* 195.1249 (M$^+$, calcd 195.1259).

(16) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

Acidities of Arenium Ions in Acetonitrile[1]

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Received February 20, 1990

Summary: The pK_a's of benzenium, 1-naphthalenium, and 9-anthracenium in acetonitrile have been estimated to be −24.0, −19.7, and −9.1, respectively, by using a thermochemical cycle.

Carbocations derived by protonation of aromatic hydrocarbons—*arenium ions*—are important intermediates in organic chemistry. These species exist only as short-lived intermediates except in strongly acidic solutions. Consequently, all of the available thermochemical[3] and spectroscopic[4] measurements have been made in solvent systems such as superacids or liquid HF. Clearly, these data may not necessarily apply to polar organic solvents.

Table I. Oxidation and Reduction Potentials of Dihydroaromatic Derived Radicals[a]

radical	V vs SCE $E_{1/2}^{ox}$	V vs SCE $E_{1/2}^{red}$
1a	−0.04	−1.78
1b	0.30	−1.70
2a	0.03	−1.69
2b	0.3[b]	*c*
3a	0.18	−1.40
3b	0.20	−1.36

[a] Measured by modulation voltammetry in acetonitrile/di-*tert*-butyl peroxide (9:1) containing 0.1 M tetrabutylammonium perchlorate using 53-Hz modulation and detection of the out-of-phase component. The potentials have an uncertainty of ±50 mV. [b] Reference 9, ±100 mV. [c] Reduction wave not observed due to high background current.

While it is not possible to make direct thermochemical determinations of the pK_a's of these intermediates in organic solvents, the values can be derived by using a thermochemical cycle (eqs 1–4).[5–8] In this work we report

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(4) For example, see: (a) Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299. (b) Buchanan, A. C., III; Dworkin, A. S.; Byrnestad, J.; Gilpatrick, L. O.; Poutsma, M. L.; Smith, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5430. (c) Buchanan, A. C., III; Dworkin, A. S.; Smith, G. P. *J. Am. Chem. Soc.* **1980**, *102*, 5262. (d) Farcasiu, D. *Acc. Chem. Res.* **1982**, *15*, 46. (e) Farcasiu, D. *Adv. Chem. Ser.* **1987**, 285. (f) Farcasiu, D.; Marino, G.; Miller, G.; Kastrup, R. V. *J. Am. Chem. Soc.* **1989**, *111*, 7210.

(5) Griller, D.; Martinho Simoes, J. A.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7872.

(6) A similar approach has been used to estimate the pK_a's of radical cations[7] and dications.[8]

0022-3263/90/1955-3707$02.50/0 Published 1990 by the American Chemical Society