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$S_{RN}1$ Reactions of 7-Iodobicyclo[4.1.0]heptane, 1-Iodoadamantane, and Neopentyl Iodide with Carbanions Induced by $FeBr_2$ in DMSO

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There was no reaction of 7-iodobicyclo[4.1.0]heptane (7-iodonorcarane, **1**) (*exo*−*endo* ratio of *ca.* 1) with acetophenone enolate ions **2** in DMSO at 25 °C; however, with the addition of SmI_2 or $FeBr_2$ and under the same experimental conditions, the substitution product **3** was obtained in 9% and 72% yields, respectively, with an *exo*−*endo* ratio of *ca.* 16 similar to the product ratio from photostimulated reactions. Thus, it seems that 7-norcaranyl radicals are intermediates of these reactions. With $FeBr_2$ at 60 °C the yield of **3** was as high as 90%. Reactions of **1** with the enolate ion of 2-naphthyl methyl ketone **4** induced by $FeBr_2$ gave substitution product **5** in 60% yield (96% of it the *exo* isomer). In competition experiments, **4** was 1.7 times more reactive than **2**, and the anion of nitromethane (**7**) was 6.5 times more reactive than **2** toward 7-norcaranyl radicals. The reactions of 1-iodoadamantane (**9**) and neopentyl iodide (**11**) with carbanion **2** induced by $FeBr_2$ gave the substitution products in 85% and 92% yields, respectively. These observations indicate that all these reactions induced by $FeBr_2$ occur by the $S_{RN}1$ mechanism.

Radical nucleophilic substitution, or $S_{RN}1$, has been found to be an excellent method for many types of aromatic and aliphatic substrates with suitable leaving groups. Even aliphatic substrates without electron-withdrawing groups, such as cycloalkyl, bicycloalkyl, and neopentyl halides, react by this mechanism.[1] The reaction proceeds by a chain process, and the propagation steps are shown in eqs 1 and 2. In aliphatic systems that do not have a π^* MO that stabilizes the radical anion $(RX)^{\bullet -}$, there is no intermediate (dissociative electron transfer).[2]

$$R^{\bullet} + Nu^{-} \longrightarrow (RNu)^{\bullet -} \qquad (1)$$

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

This chain process requires an initiation step. In a few systems, spontaneous electron transfer (ET) from the nucleophile to an aromatic substrate has been observed.[3] When the ET does not occur spontaneously, it can be induced by light in aromatic and in aliphatic systems.[4] In aromatic and in aliphatic substrates with electron-withdrawing groups, $S_{RN}1$ reactions have also been initiated by sonication.[5] In aromatic systems this has been initiated by solvated electrons[6] or sodium amalgam[7] in liquid ammonia, by electrochemically induced reactions,[8] or by certain inorganic salts, such as Fe^{+2} in aromatic[9] or vinylic[10] $S_{RN}1$ reactions. Recently we found that a solution of SmI_2 in THF induced the reaction of aryl iodides with carbanions in DMSO, so it, too, is a suitable reagent to initiate these $S_{RN}1$ reactions.[11]

All the $S_{RN}1$ reactions of alkyl halides with nucleophiles without an electron-withdrawing group, such as cycloalkyl, bicycloalkyl and neopentyl halides, have been either thermal reactions or reactions under irradiation, but there are no reports of initiating these reactions by chemical or other methods. Light is the most common initiator in $S_{RN}1$ reactions of these alkyl halides, but irradiation is effective only in dilute solutions. We are therefore in search of new procedures for accomplishing $S_{RN}1$ reactions on a synthetic scale, avoiding the disadvantages of light initiation.

If reactions induced by inorganic salts were to give the same selectivity as those induced by photostimulation, it would seem that the intermediates involved are the same; in other words, the reactions occur via the same mechanism.

This report describes reactions of 7-iodobicyclo[4.1.0]heptane (7-iodonorcarane) with carbanions induced by

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Table 1. Reaction of 7-Iodonorcarane (1) with Carbanions in DMSO Catalyzed by Inorganic Salts[a]

expt	**1**, mmol	carbanion, mmol	catalysts, mmol %[b]	temp, °C	products, (yield %)	exo isomer[c]
1[d]	1.0	**2**, 10.0	–	25	**3** (0)	–
2	0.5	**2**, 5.0	SmI_2,[e] 107	25	**3** (9)	80
3	0.5	**2**, 5.0	SmI_2,[f] 104	25	**3** (8)	95
4	0.6	**2**, 5.0	$FeBr_2$, 21	25	**3** (41)	95
5	0.6	**2**, 10	$FeBr_2$, 71	25	**3** (72)	97
6	0.9	**2**, 2.6	$FeBr_2$, 48	60	**3** (42)	94
7	0.5	**2**, 5.0	$FeBr_2$, 52	60	**3** (69)	96
8	1.0	**2**, 10.0	$FeBr_2$, 103	60	**3** (90)	93
9	0.5	**4**, 3.0	SmI_2,[e] 107	25	**5** (6)	g
10	0.5	**4**, 5.0	SmI_2,[e] 214	25	**5** (8)	93
11	0.5	**4**, 3.0	$FeBr_2$, 107	25	**5** (38)	96
12	0.5	**4**, 5.0	$FeBr_2$, 60	25	**5** (54)	91
13	0.5	**4**, 5.0	$FeBr_2$, 60	60	**5** (60)	96

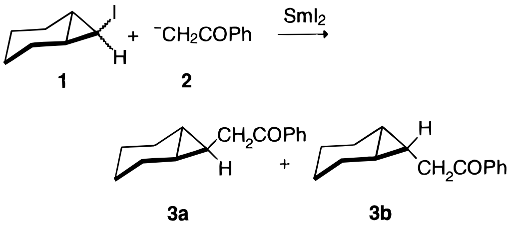
[a] Reactions carried out in 25 mL of DMSO during 30 min, unless otherwise stated. [b] Based on substrate **1**. [c] Yield (%) of the total amount of substitution products. [d] Reference 12. [e] Added as 0.1 N solution in THF. [f] Added as 0.1 N solution in THF with 6% (v/v) of HMPA. Reaction time 15 min. [g] Not quantified.

SmI_2 and $FeBr_2$ in DMSO, as well as reactions of 1-iodoadamantane and neopentyl iodide induced by $FeBr_2$ in DMSO.

Results and Discussion

7-Iodonorcarane (1). The photostimulated reaction of 7-iodonorcarane (7-iodobicyclo[4.1.0]heptane) **1** (a mixture of *exo:endo* isomers with a ratio of *ca.* 1:1) with carbanions in DMSO gave the expected substitution products in good yields with a remarkable selectivity, that is, more than 90% of each substitution product mixture was the *exo* isomer, so it was suggested that 7-norcaranyl radicals are intermediates of these reactions.[12]

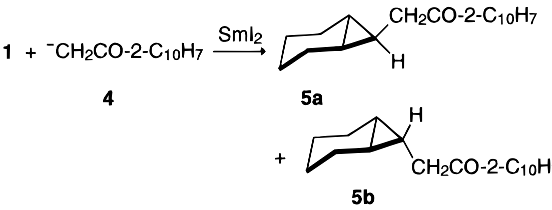
When a solution of SmI_2 in THF was added to a solution of **1** with acetophenone enolate ions **2** in DMSO and reaction was allowed to occur for 30 min at room temperature, a small amount of the substitution product α-(7-norcaranyl)acetophenone (**3**) (9%) was formed, 80% of it being the isomer *exo*-**3a** (eq 3).



(3)

The initiation of these reactions by SmI_2 was not as successful as that of reactions of aryl halides with carbanions in DMSO, where more than 80% yields of substitution products were obtained.[11] It is known that reactions of SmI_2 can be improved by adding HMPA as cosolvent,[13] but in the reaction of **1** with **2** in DMSO with a solution of SmI_2 in THF with 6% of HMPA, 8% yield of **3** was obtained of which *ca.* 95% was *exo* isomer **3a**, a ratio similar to that found in photostimulated reactions[12] (Table 1, experiments 1 and 2).

The reactions of **1** with 2-naphthyl methyl ketone enolate ions **4** with the addition of a solution of SmI_2 also gave low yields of substitution product **5** (6–8%), *ca.* 90% of which was *exo* isomer **5a** (eq 4) (Table 1, experiments 9 and 10).



(4)

Although the yields of substitution products **3** and **5** were low, the fact that almost the same *exo*/*endo* product ratios were observed as in photostimulated reactions suggests that free 7-norcaranyl radicals are intermediates in the reactions induced by SmI_2.

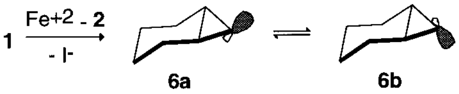
In the reaction of **1** with **2** at room temperature with the addition of 21 mol % of $FeBr_2$ (referred to the substrate concentration), the substitution products **3** were formed in 41% yield. This yield increases to 72% with 71 mol % of $FeBr_2$; 95–97% of the substitution product was *exo* isomer **3a** (eq 5) (Table 1, experiments 3 and 4).

$$\mathbf{1} + \mathbf{2} \xrightarrow{FeBr_2} \mathbf{3a} + \mathbf{3b} \qquad (5)$$

These results may indicate that Fe^{+2} induced the reaction of **1** with **2** and that 7-norcaranyl radicals are intermediates of these reactions, with **2** having the same selectivity as in photostimulated reactions, as well as in reactions induced with SmI_2. The fact that with 21 mol % of $FeBr_2$ the yield of substitution products **3** was only 41% suggests that there is a chain process, though not a very efficient one.

The reaction of **1** with **2** in DMSO at 60 °C with 48 mol % of $FeBr_2$ gave 42% of substitution product **3**; the yield increases to 90% when the substrate **1**/$FeBr_2$ ratio is 1, with 93% of the product being isomer **3a**.

The fact that the reaction of **1** and **2**, with $FeBr_2$, gave substitution products **3a** and **3b** of which the proportion of the *exo* isomer is about 95%, similar to the product ratio that was found in the photostimulated reaction, suggests that the reaction of **1** with Fe^{+2} ions and carbanion **2** produced σ-type 7-norcaranyl radicals **6a** and **6b**, which reacted with **2** by the $S_{RN}1$ mechanism. It is known that cyclopropyl radicals are σ radicals[14] with a very high rate of interconversion of the *exo*–*endo* isomers.[15] As explained before,[12] **6a** is more reactive and reacts with **2** to give high yields of the *exo* isomer (eq 6).



(6)

The reaction of **1** with the enolate ion of 2-naphthyl methyl ketone (**4**) was also induced by $FeBr_2$. Thus, the reaction at room temperature gave 54% of **5**, increasing slightly at 60 °C (60% yield) (eq 7) (Table 1, experiments 10–12), with more than 90% of the substitution products being the *exo* isomer **5a**; similar results were found in

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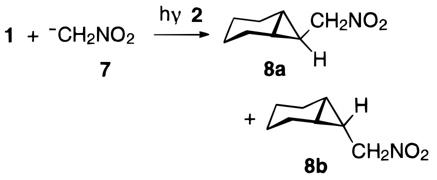
the photostimulated reactions.

$$\mathbf{1} + \mathbf{4} \xrightarrow{Fe^{+2}} \mathbf{5a} + \mathbf{5b} \qquad (7)$$

The anion of nitromethane (**7**) did not give substitution products under irradiation with **1**. However, in the presence of acetophenone enolate ion (**2**) the photostimulated reaction gave substitution products **8** in 41% yield, with *ca.* 90% yield of the substitution products being *exo* isomer **8a** (eq 8).[12] The fact that **7** reacts under irradiation in the presence of **2** but not in its absence to give substitution products **8a** and **8b** indicates that **2** facilitates initiation of the $S_{RN}1$ mechanism. The fact that the **8**/**3** product ratio shows that the 7-norcaranyl radicals thus formed react faster with **7** than with **2** to give finally the products observed (vide infra).



(8)

When a solution of **1** and the anion **7** was prepared in DMSO, and $FeBr_2$ was added to initiate reaction, a precipitate was formed. When the anion of acetophenone (**2**) was formed in DMSO, and $FeBr_2$ was added, the color of the solution changed, probably by interaction of **2** with $FeBr_2$. A solution of **2** (5 mmol) with an excess of *t*-BuOK (6 mmol) and $FeBr_2$ (1.03 mmol) in 25 mL of DMSO at 60 °C was prepared, and then nitromethane (5 mmol) was added and immediately followed by the addition of **1** (1 mmol) after 30 min. In this case, **8** was formed in 71% yield, with 92% of it being *exo* isomer **8a**, and **3** was formed in 19% yield of which 85% was *exo* isomer **3a** (eq 9) (Table 2, experiment 5).

$$\mathbf{1} + \mathbf{2} + \mathbf{7} \xrightarrow{Fe^{+2}} \mathbf{3} + \mathbf{8} \qquad (9)$$

These results show that in these experimental conditions, that carbanions **2** and **7** together with $FeBr_2$ remain soluble and able to initiate the $S_{RN}1$ reaction and that the 7-norcaranyl radicals thus formed react faster with **7** than with **2** (see competition experiments).

The fact that in the $FeBr_2$-induced reactions of **1** with carbanions gave mainly the *exo* substitution products and that the relative reactivity of carbanions are similar to the photostimulated reactions suggests that the $FeBr_2$ associate with enolate ions to produce free 7-norcaranyl radicals by an electron transfer reaction and probably rules out a mechanism that involves an organo−Fe bond as intermediate.[9] Although Fe^{+2} is a modest reductant (0.1 V in DMSO vs SCE)[9b] and the redox potential does not change when the complex with enolate ions is formed, this complex may facilitate the electron transfer to the substrate, as was suggested with the aromatic systems.[9b]

Competition Experiments. The product comparison from reaction of **1** with carbanions **2** and **4** induced with $FeBr_2$ shows that **2** is qualitatively more reactive than **4**.

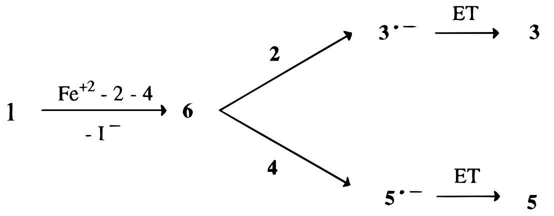
As the $S_{RN}1$ mechanism is a chain process with initiation, propagation, and termination steps, overall reactivity depends on the efficiency of the initiation step, the individual rates of the propagation steps, and the termination steps. To compare the reactivity of different carbanions, the *relative* reactivity was studied by competition experiments with **1**. By these competition reactions, the relative rates of the coupling of 7-norcaranyl radicals toward **2** and **4** were determined.

Table 2. Competition of 2 *vs* 4 and 2 *vs* 7 Reacting with 1 in DMSO[a]

				yield, %		
expt	**2**, mmol	**4** or **7**, mmol	$FeBr_2$, mmol %[b]	**3** (% *exo*)[c]	**5** or **8** (% *exo*)[c]	rel reactivity
1[d]	3	**4**, 3	62	21 (95)	24 (96)	1.2
2	4	**4**, 6	96	21 (92)	60 (92)	1.9
3	5	**4**, 5	102	31 (89)	55 (91)	1.8
4	7	**4**, 3	109	51 (92)	39 (91)	1.8
					average	1.7 ± 0.23
5[e]	5	**7**, 3	103	19 (85)	71 (92)	6.5

[a] Reactions carried out in 25 mL of DMSO with 0.572 mmol of **1**. Reaction time 30 min at 60 °C, unless otherwise indicated. [b] Based on the concentration of **1**. [c] Yields based on the total substitution products. [d] Reaction time 40 min, at 30 °C. [e] 1 mmol of substrate **1**.

When a solution containing carbanions **2** and **4** in excess is allowed to compete toward **1** in the presence of $FeBr_2$, the radical **6** is formed and reacts with **2** and **4** to yield the radical anion intermediates $\mathbf{3}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ along the propagation cycle of the $S_{RN}1$ mechanism (eqs 10a and 10b).



(10a)

(10b)

If there is no other competing reaction,[16] all the radicals will give the substitution products **3** and **5**, and it is possible to estimate the relative rates from the amount of products obtained. The relative reactivities were calculated as in previous works.[17]

In the reaction of **2** and **4** in excess over **1** it was possible to estimate the relative reactivity, and it was found that **4** reacts *ca.* 1.7 faster than **2** (Table 2).

In the competition experiment of **2** and **7** toward **1** it was found that **7** reacts 6.5 times faster than **2**, similarly to the value reported in the photostimulated reaction (6.4),[12] which suggests the same mechanism reaction in both systems. In competition experiments of **2** and **7** toward 1-iodoadamantane, it was reported that **7** reacts 3.0 times faster than **2**.[18]

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(16) Although there is some reduction of the radicals to the hydrocarbons, the amount is small and we consider that the reduction rate of the radicals is similar.

(17) The equation used in the relative reactivity determination of nucleophiles **2** and **4** in excess *vs* substrate **1** is:

$$\frac{k_4}{k_2} = \frac{\ln [\mathbf{4}]_0/[\mathbf{4}]_t}{\ln [\mathbf{2}]_0/[\mathbf{2}]_t}$$

where $[\mathbf{4}]_0$ and $[\mathbf{2}]_0$ are initial concentrations, and $[\mathbf{4}]_t$ and $[\mathbf{2}]_t$ are concentrations at time t of both nucleophiles. This equation is based on a first-order reaction of the radicals with both nucleophiles **2** and **4**; see Bunnett, J. F. *Investigation of Rates and Mechanisms of Reactions*, 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part 1, p 159.

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Table 3. Reaction of 1-Iodoadamantane (9) with 2 in DMSO Catalyzed by $FeBr_2$[a]

expt	**9**, mmol	**2**, mmol	$FeBr_2$, mol %[b]	product **10**, yield (%)
1	1	10	32	79
2	0.52	5	51	85
3	0.57	5	0	3
4[c]	1	10	103	35
5[c]	0.54	5	156	47

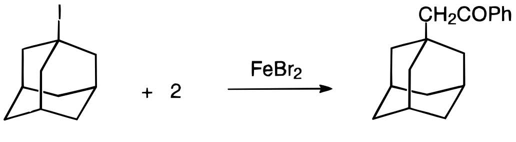
[a] Reactions carried out in 25 mL of DMSO at 60 °C. Reaction time 30 min. [b] Based on substrate **9**. [c] 1-Bromoadamantane.

As it has been shown in the relative reactivity of carbanions toward phenyl radicals[19] and 1-adamantyl radicals,[18] the reactivity is higher when the more stable radical anion intermediate is formed (lower SOMO) in the coupling of the radical and the carbanion (lower pK_a of the conjugated acid), if the $\Delta E\pi$ is similar in this process. In the competition reaction of **2** and **4**, the latter is sligthly more reactive because the SOMO of the radical anion intermediate $\mathbf{5}^{\bullet-}$ is lower in energy than the SOMO of the radical anion $\mathbf{3}^{\bullet-}$.

The fact that **7** is 6.5 times more reactive than **2** agrees with the pK_a of acetophenone (24.7) reported to be higher than the nitromethane (17.2) in DMSO,[20] so that the coupling process of radicals with nitromethane anions would give the more stable radical anion intermediates. Besides, these results suggest that 7-norcaranyl radicals are slightly more selective than 1-adamantyl radicals toward carbanions.

1-Iodoadamantane (9). 1-Substituted bridgehead compounds react slowly by an S_N1 mechanism of nucleophilic substitution, and the reactivity decreases with increasing strain in the substrate.[21] The reactivity of bridgehead halides by the $S_{RN}1$ mechanism depends not only on the nature of the leaving group (Cl < Br < I), but also on the strain of the bicyclic moiety[22] and on the presence of substituents.

It has been reported that the photostimulated reaction of 1-iodoadamantane (**9**) with **2** in DMSO gives the substitution product **10** in 65% yield after 240 min of irradiation.[18] The reaction of **9** with **2** and with the addition of $FeBr_2$ (32 mol % based on **9**) rendered the substitution product **10** in 79% yield, in 30 min of reaction at 60 °C (eq 11) (Table 3, experiment 1).



9 **10** (11)

With 51 mol % of $FeBr_2$ the yield of **10** was 85%. In the same experimental condition, but without adding $FeBr_2$, the yield of **10** was only 3% (Table 3, experiments 2 and 3). The fact that the yields of **10** are higher than the equivalents of $FeBr_2$ indicates that there is a chain propagation step, although the chain is rather short.

1-Bromoadamantane reacts very sluggishly with **2** under irradiation in DMSO.[18a] The reaction induced with $FeBr_2$ (103 mol %) gives, however, 35% yield of **10**, which increases to 47% yield with an excess of $FeBr_2$ (156 mol %) (Table 3, experiments 4 and 5).

Table 4. Reaction of Neopentyl Iodide (11) with 2 in DMSO[a]

expt	$FeBr_2$, mol %	temp, °C	time (min)	I^-, yield (%)	product **12**, yield (%)
1	–	25	60	24	22
2[b]	–	25	240	*c*	7
3	–	55	40	59	45
4[d]	–	55	40	41	31
5	22	25	20	*c*	20
6	69	25	60	*c*	74
7[e]	70	25	60	*c*	7
8	100	25	60	*c*	61
9	81	55	40	*c*	92

[a] **11**: 1.13 mmol, **2**, 5.0 mmol in *ca.* 25 mL of DMSO. [b] 17 mol % of *p*-DNB, see ref 25. [c] Not quantified. [d] 21 mol % of *p*-DNB. [e] 32 mol % of *p*-DNB.

Neopentyl Iodide (11). We have previously reported photostimulated reactions of neopentyl halides by the $S_{RN}1$ mechanism with different organometallic nucleophiles in liquid ammonia obtaining good yields of the substitution products.[23] In reactions with carbanions we found only dehalogenation in poor yields without products coming from the radical-nucleophilic coupling in liquid ammonia.[24] However, when the solvent was changed to DMSO, the photostimulated reaction of neopentyl iodides with carbanions gave the substitution product in 52–69% yield.[25]

The reaction of neopentyl iodide (**11**) with **2** in DMSO in 1 h at 25 °C gave 22% of substitution product **12**, but the yield drops to 6% of **12** in 4 h in the presence of 17 mol % of *p*-DNB,[25] but increases to 45% yield at 55 °C. The reaction at 55 °C was also partially inhibited by *p*-DNB (Table 4, experiments 1–4). These results suggest that **11** reacts with **2** in the dark by a thermal $S_{RN}1$ reaction (eq 12).

$$\underset{\mathbf{11}}{(CH_3)_3CCH_2I} + \mathbf{2} \longrightarrow \underset{\mathbf{12}}{(CH_3)_3CCH_2CH_2COPh} + I^- \qquad (12)$$

The reaction of **11** and **2** at 25 °C and in the presence of $FeBr_2$ gave **12** in excellent yields. The reaction catalyzed by $FeBr_2$ was also inhibited by *p*-DNB (Table 4, experiments 5–7). These results indicate both that $FeBr_2$ is an efficient reagent for induction of reactions of **11** with carbanions in DMSO and that an $S_{RN}1$ mechanism is probable in view of the inhibition by *p*-DNB.

Conclusions. $FeBr_2$ has been shown to be an efficient reagent to induce reactions of 7-iodonorcarane, 1-iodoadamantane, and neopentyl iodide with carbanions in DMSO. No reduction products derived from the ketone functionality were found. Whereas all these substrates and probably numerous other alkyl iodides react slowly with carbanion nucleophiles by polar mechanisms of nucleophilic substitution, they react easily with by the $S_{RN}1$ mechanism when induced by $FeBr_2$ in DMSO. Even 1-bromoadamantane, which is almost unreactive with **2** in photostimulated reactions, gave a moderate yield (47%) of the substitution product when reaction was induced by $FeBr_2$.

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The facts that the yields of the substitution products with these alkyl iodides are higher than 80–90%, that reaction times are short, and that the reactions are easily handled with better yields than the photostimulated reactions indicate that $FeBr_2$-induced reactions could be the method of choice to perform nucleophilic substitutions.

Experimental Section

Materials. Potassium *tert*-butoxide (Fluka) was sublimed and DMSO (Carlo Erba) distilled under vacuum and stored over molecular sieves (4 Å). Nitromethane (Aldrich) was distilled and dried over Na_2SO_4. Acetophenone (Carlo Erba) was distilled under vacuum. 2-Naphthyl methyl ketone (Alfa) was recrystallized from petroleum ether. Commercially available anhydrous $FeBr_2$ (Strem) was used as received and stored in a dry-seal desiccator. 1-Iodoadamantane (Aldrich) was purified by recrystallization from methanol. Samarium diiodide (0.1 N solution in THF) was purchased from Aldrich and stored under nitrogen atmosphere. 1-Bromoadamantane (Aldrich) and *p*-DNB (Fluka) were used as received.

Synthesis of Reactants. 7-Iodonorcarane was synthesized as described.[26] The crude product was purified by reduced-presure distillation. The synthesis gave an isomer-products mixture with an *exo*–*endo* ratio of *ca.* 1. Neopentyl iodide was synthesized by reaction of the corresponding *p*-toluenesulfonate derivative with KI in DMF[27] and purified by distillation. Neopentyl *p*-toluene sulfonate was prepared from neopentyl alcohol and *p*-toluenesulfonyl chloride in pyridine as solvent. The enolate ions of ketones and nitromethane anions were prepared by acid–base reaction of potassium *tert*-butoxide.

General Procedure. Ferrous Ion-Induced Reaction of Alkyl Iodides with Acetophenone Enolate Ion (2). The following procedure is representative of these reactions. They were carried out in a 100 mL three-necked round-bottomed flask equipped with a nitrogen inlet and magnetic stirrer. To 25 mL of dry and degassed DMSO under nitrogen were added 11 mmol of potassium *tert*-butoxide, 10 mmol of acetophenone, and 0.32 mmol of $FeBr_2$. A few minutes later, when the ferrous ion and enolate anion **2** complex had formed, 1 mmol of 1-iodoadamantane (**9**) was added. The mixture was stirred and the flask placed in a 60 °C temperature bath. After 30 min the reaction was quenched by adding ammonium nitrate in excess and water (100 mL) and extracted with diethyl ether (three portions of 50 mL). The ether extract was washed twice with water, and quantified by GLC. 4-Bromobenzophenone was used as internal standard. The solvent was removed under reduced pressure. The residue, after column chromatography on silica gel (eluted with petroleum ether:diethyl ether = 90:10) gave the substitution product α-(1-adamantyl)-acetophenone (**10**), identified by comparison with an authentic sample.[19]

SmI_2-induced Reaction of 2-Naphthyl Methyl Ketone Enolate Ion (4) with 7-Iodonorcarane (1). The following procedure is representative. They were carried out in a 100 mL three-necked round-bottomed flask equipped with a nitrogen inlet and magnetic stirrer. To 25 mL of dry and degassed DMSO under nitrogen were added 6 mmol of potassium *tert*-butoxide, 5 mmol of 2-naphthyl methyl ketone, and 0.5 mmol of 7-iodonorcarane (**1**). To this solution was added 1.07 mmol of SmI_2 (10.7 mL of 0.1 N solution in THF). The aliquot was transferred by syringe to avoid contact with air. After 30 min, the reaction was quenched by adding ammonium nitrate in excess and 100 mL of water and extracted with three portions of diethyl ether. The ether extract was washed twice with water, dried, and quantified by GLC. The reaction products were compared with authentic samples and were identified as the mixture of α-(7-norcaranyl) 2-naphthyl methyl ketone (**5**) *exo* and *endo* isomers,[12] the overall substitution yield being 8%. These products were compared with authentic samples.

Dark Reaction of Acetophenone Enolate Ion (2) with Alkyl Iodides. The following procedure is representative. They were carried out in a 100 mL three-necked round-bottomed flask equipped with a nitrogen inlet and magnetic stirrer. To 25 mL of dry and degassed DMSO under nitrogen were added 6 mmol of potassium *tert*-butoxide and 5 mmol of acetophenone. The system was enclosed in aluminum foil, and 1.13 mmol of neopentyl iodide was added. The mixture was stirred and the flask placed in a 55 °C temperature bath. After 40 min, the reaction was quenched by adding ammonium nitrate in excess and water (100 mL) and extracted with diethyl ether (three portions of 50 mL). The iodide ions in the aqueous solution were determined by potentiometric titration. The ether extract was washed twice with water, and the substitution product **12** was quantified by GLC. Benzophenone was used as internal standard. The reaction yield was 45%, and the product was identified as α-(neopentyl)acetophenone[25,28] by comparison of the NMR spectra with those of an authentic sample.

Competition Experiments of Acetophenone Enolate Ion (2) and Nitromethane Anion (5) toward 7-Iodonorcarane (1). In order to estimate the relative reactivities of these nucleophiles, $FeBr_2$-induced reactions were done in 25 mL of DMSO in an inert atmosphere. After the addition of 9 mmol of potassium *tert*-butoxide and 5 mmol of acetophenone, 0.59 mmol of $FeBr_2$ was added. After a few minutes, enough for the formation of Fe^{2+} and nucleophile **2** complex, 3 mmol of nitromethane were added in order to prepare the nucleophile **7**. Finally, 1 mmol of the the substrate **1** was added. After 40 min, the reaction was quenched by excess ammonium nitrate and 100 mL of water and extracted with three portions of diethyl ether. The ether extract was washed twice with water, dried, and quantified by GLC. The products obtained were compared with authentic samples by GLC and NMR spectra and identified as α-(7-norcaranyl)nitromethane *exo* and *endo* isomers (**8**) and α-(7-norcaranyl)acetophenone *exo* and *endo* isomers (**3**).[12]

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