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Quantum Yields of the Initiation Step and Chain Propagation Turnovers in $S_{RN}1$ Reactions: Photostimulated Reaction of 1-Iodo-2-methyl-2-phenyl Propane with Carbanions in DMSO

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Neophyl radicals were generated by photoinduced electron transfer (PET) from a suitable donor to the neophyl iodide (**1**, 1-iodo-2-methyl-2-phenylpropane). The PET reaction of **1** with the enolate anion of cyclohexenone (**2**) afforded mainly the reduction products *tert*-butylbenzene (**5**) and the rearranged isobutylbenzene (**6**), arising from hydrogen abstraction of the neophyl radical (**15**) and the rearranged radical **16** intermediates, respectively. The photostimulated reaction of **1** with **2** in the presence of di-*tert*-butylnitroxide, as a radical trap, afforded adduct **10** in 57% yield. The photoinduced reaction of the enolate anion of acetophenone (**3**) with **1** gave the substitution products **11** (50%) and **12** (16%), which arise from the coupling of **3** with radicals **15** and **16**, respectively. The rate constant obtained for the addition of anion **3** to radical **15** was $1.2 \times 10^5\ M^{-1}\ s^{-1}$, by the use of the rearrangement of this radical as a clock reaction. The anion of nitromethane (**4**) was almost unreactive at the initiation step, but in the presence of **2** under irradiation, it gave high yields (67%) of the substitution product **13** and only 2% of the rearranged product **14**. When the ratio of **4** to **1** was diminished, it was possible to observe both substitution products **13** and **14** in 16% and 6.4% yields, respectively. These last results allowed us to estimate the coupling rate constant of neophyl radicals **15** with anion **4** to be at least of the order of $10^6\ M^{-1}\ s^{-1}$. Although the overall quantum yield determined ($\lambda = 350$ nm) for the studied reactions is below 1, the chain lengths ($\Phi_{propagation}$) for the reaction of **1** with anions **3** and **4** are 127 and 2, respectively.

The radical nucleophilic substitution reaction or $S_{RN}1$ is a well-documented process,[1,2] which is proposed to include an initiation, a propagation, and a termination step in a chain process. The propagation cycle is depicted in eqs 1−3.

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

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

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

When RX is an alkyl halide without electron-withdrawing groups,[1c,d] the electron transfer (ET) from $(RNu)^{\bullet-}$ to RX is dissociative,[2] giving the substitution product and the alkyl radical $R^{\bullet}$ that propagates the chain cycle (eq 4).

$$(RNu)^{-\bullet} + RX \longrightarrow RNu + R^{\bullet} + X^{-} \qquad (4)$$

In the thermal $S_{RN}1$ reaction of 4-nitrocumyl chloride and the 2-nitropropane ion, a dissociative ET as in eq 4 has also been suggested.[3]

Because the $S_{RN}1$ is a chain mechanism, the overall reactivity depends on the efficiency of the initiation, propagation, and termination steps. For the process to work efficiently, the initiation step may be slow; however, the chain propagation must be fast and efficient to allow for long chains to build up.

Few systems are known to react through a thermal (or spontaneous) $S_{RN}1$ reaction.[1,3,4] Most systems need to be initiated by other means. The most widely used method to initiate the chain process is photostimulation in aromatic as well as in aliphatic $S_{RN}1$ reactions.[1] Other methods that have been used in aromatic $S_{RN}1$ reactions are solvated electrons[5] or sodium amalgam in liquid ammonia,[6] reactions induced electrochemically,[2] and

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10.1021/jo001141m CCC: $19.00

inorganic salts such as SmI_2.[7] Aromatic and aliphatic halides also can be initiated by Fe^{2+} salts.[8] Data are now available which characterize both the propagation cycle and the termination steps of this reaction.[1,2]

A photostimulated reaction between a nucleophile and a substrate may be rather unreactive at initiation but quite reactive at propagation. The addition of minute amounts of another nucleophile that is more reactive at initiation increases the generation of the reactive intermediates and allows the less reactive initiation nucleophile to start its own propagation. The process, thus, can afford the substitution of an unreactive nucleophile through an *entrainment* reaction, which is also a support for the chain mechanism.[1]

Even though photostimulation is a widely used initiation method (eq 5) there are not many studies on the mechanism involved.

$$\mathrm{ArX} + \mathrm{Nu}^- \xrightarrow{h\nu} (\mathrm{ArX})^{-\bullet} + \mathrm{Nu}^{\bullet} \qquad (5)$$

These photoinduced electron transfers (PET) can conceivably be accomplished in one of the followings ways: (1) homolytic cleavage of the C−X bond; (2) ET from the Nu^- to the excited ArX, generating a radical anion that enters the cycle; (3) ET within an excited charge-transfer complex (CTC); and (4) photoejection of an electron from the excited Nu^-. Depending on the nature of the RX, the Nu^-, and the experimental conditions, any of these mechanisms could probably be the initiation step.

The proposal that initiation occurs by photoexcitation of a CTC formed between the Nu^- and the substrate is reinforced by studies of the wavelength dependence of the quantum yield. This type of initiation has been proposed for the reaction of acetone enolate anions with PhI and PhBr in DMSO,[9] whereas when potassium diethyl phosphite is used as a nucleophile, homolysis of PhI and PET within the CTC is competitive.[9,10] Furthermore, the CTC initiation has been postulated in the reaction of nitrile carbanions with haloarenes such as 2-bromonaphthalene or *p*-bromobiphenyl in liquid ammonia. The quantum yields of these reactions ($\lambda > 313$ nm) range from 7 to 31.[11] Formation of a CTC has also been proposed in the reaction of ethyl phenyl sulfide with diethyl phosphite ions.[12]

The quantum yields for the $S_{RN}1$ substitution reactions of *p*-nitrocumyl chloride with quinuclidine (3.5) and azide ions (6000) have been determined.[13] Furthermore, by studying the wavelength dependence on the quantum yields, evidence has been obtained that the photochemical initiation proceeds by means of a CTC.

Acceleration of the substitution reaction of functionalized aryl bromides with potassium diethyl phosphite or with 2-naphthoxide ions by KI has been explained on the basis of an ET through the exciplex formed between the aryl halide and the I^- ions.[14] Catalysis by I^- ions was observed in the photoinduced reaction of bromoarenes with diethyl phosphite ions in the acetonitrile−tetrahydrofuran mixture.[15]

ET from an excited Nu^- is another possibility for initiation. This is highly probable because nucleophiles are the best candidates for absorption in the usual reaction conditions ($\lambda > 350$ nm). An example of the involvement of the anion in its excited state is the reaction of organic sulfides under laboratory light with Ph_2P^- ions, which absorb strongly in the visible region ($\lambda = 475$ nm).[12] Other evidence for this type of initiation is the fluorescence quenching of the diphenylindenyl anion by PhBr.[16]

Initiation of the reaction of the 1-chloro-2-naphthoxide anion with sodium sulfite has been proposed to occur by ET between the excited triplet state of the substrate and its ground state, with a quantum yield of about 50.[17] For the 1-bromo derivative, photohomolytic C−Br dissociation is proposed, with a quantum yield of about 20.[17] The substitution of 1-chloro-2-naphthoxide ions with sodium sulfite can be dye photoinitiated[18] or initiated by visible light with a Ru complex as sensitizer and a Co complex as the intermediate electron carrier.[19]

In the photostimulated reaction of 1-iodoadamantane with PhS^- ions in acetonitrile, the mechanism of photoinitiation involves excitation of PhS^- ions with concomitant photoejection of electrons to the solvent, with a quantum yield for photoejection of 0.43−0.75 at $\lambda = 308$ nm. The reaction does not follow a chain mechanism.[20]

Varying the experimental conditions, we can change the reactivity of the pair substrate−nucleophile from an unreactive system to a reactive one. For instance, PhI did not react under irradiation (Pyrex-filtered flask) with acetophenone enolate anion in liquid ammonia,[21] but it does react in DMSO.[22] However, a reaction was observed in liquid ammonia when irradiation was conducted in an immersion well.[23]

The photoinduced initiation reaction may have a low quantum yield, because of a fast backward ET which annihilates the ion pair before cage separation occurs. This will result in a poorly efficient source of radicals. The measured quantum yield depends on the efficiency of both initiation and turnover in the propagation steps.

The magnitude of the chain length of any $S_{RN}1$ process can easily be derived from a comparison of the quantum yield of the initiation step and an overall reaction quantum yield. It would therefore be possible to obtain quantum yields for the initiation step, provided that the propagation process is eliminated or reduced significantly in comparison with the initiation step.

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Table 1. Reactions of Neophyl Iodide (1) with Carbanions in DMSO[a]

entry	carbanion	conditions, added compound (M)	I^- (%)[c]	product distributions (%)[b]	
				reduction (**5** + **6**)	other products
1	**2**	dark	9.3	**5** (1.8), **6** (0.3)	
2	**2**	$h\nu$	84	**5** + **6** (49)	
3[d]	**2**	$h\nu$	80	**5** (21), **6** (10)	**7** (6.0), **8** (9.0), **9** (10.4), phenol (1.2)
4[e]	**2**	$h\nu$	77	**5** (36), **6** (7.3)	**7** (2.9), **8** (4.6), **9** (7.7), phenol (2.5)
5[f]	**2**	$h\nu$	74	**5** (27), **6** (6.7)[g]	**9** (9.1), phenol (11.5)
6	**2**	$h\nu$, DTBN (0.004)	74	**5** (10)	**10** (57)
7	**3**	dark	7.2		**11** (5.7)
8	**3**	dark, DTBN (0.008)	6.7		**11** (6.5)
9	**3**	$h\nu$	73	**5** + **6** (3.6)	**11** (45)[h], **12** (16)[h]
10	**3**	$h\nu$	74	*i*	**11** (55), **12** (16)
11	**3**	DTBN (0.008)	13	*i*	**11** (5.5), **10** (2.5)
12	**4**	dark	<1		
13	**4**	$h\nu$	4.5		**13** (3.1)
14[j]	**4**	$h\nu$, 2 (0.04)	79	**5** + **6** (3.9)	**13** (67), **14** (2.0)
15	**4**	$h\nu$, 2 (0.12)	44	**5** + **6** (2.7)	**13** (35), **14** (1.3)
16	**4**[k]	$h\nu$, 2 (0.12)	69	**5** (26), **6** (2.9)	**13** (16), **14** (6.4), **7** (0.8), **8** (2.2)

[a] **1**, 0.04 M; carbanions, 0.12 M. irradiation for 1 h under nitrogen atmosphere, unless otherwise indicated. [b] Determined by GC using the internal standard method, error 5%; **5** and **6** were quantified together in a ca. 3:1 ratio, unless otherwise indicated. [c] Determined potentiometrically. [d] **2**, 0.04 M; reaction time 2 h. [e] The reaction was conducted under a nitrogen atmosphere in a closed system, and the internal standard was added before irradiation. [f] The reaction was performed in 4.0 mL of DMSO-d_6. [g] In the reduction products **5** and **6**, 12.7% of incorporation of deuterium was detected by GC−MS. [h] Isolated product. [i] Not quantified. [j] Reaction time 2 h. [k] **4**, 0.012 M.

It has been reported that 1-iodo-2,2-dimethylpropane (neopentyl iodide) reacts under irradiation with carbanions in DMSO to give the substitution product by the $S_{RN}1$ mechanism[24] and that 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) is more reactive than neopentyl iodide toward Ph_2P^- ions in photostimulated competition experiments run in liquid ammonia.[25] In this context, we decided to study the photoinduced reaction of neophyl iodide with different carbanions in DMSO. In this system, we could measure the quantum yield of the photoinitiation, the rate of coupling of the neophyl radical with acetophenone enolate anion, and the turnover of the propagation cycle of these $S_{RN}1$ reactions.

Results

Photophysical Properties of Carbanions and Neophyl Iodide (1). CTC Formation. The enolate anion of cyclohexenone (**2**) absorbs maximally at 339 nm, whereas the neophyl iodide (**1**) shows absorption below 300 nm (Figure 1). When increasing amounts of **1** are added to a solution of **2**, an enhancement of the absorption maximum of the anion is observed. However, a new absorption band is not apparent; therefore, this increase can be ascribed to an interaction between **1** and the anion, i.e., the formation of a CTC[26] between both species. The equilibrium constant[27] for the formation of this complex is 15 M^{-1}.

For the enolate anion of acetophenone (**3**), which shows a maximum of the absorption band at 337 nm, a similar phenomenon was observed when increasing amounts of **1** are added (not shown). This can also be ascribed to the formation of a CTC with an equilibrium constant of 51 M^{-1}.

For the nitromethane anion (**4**) which absorbs maximally at 290 nm similar to the absorption of **1**, no interaction between **1** and **4** could be determined.

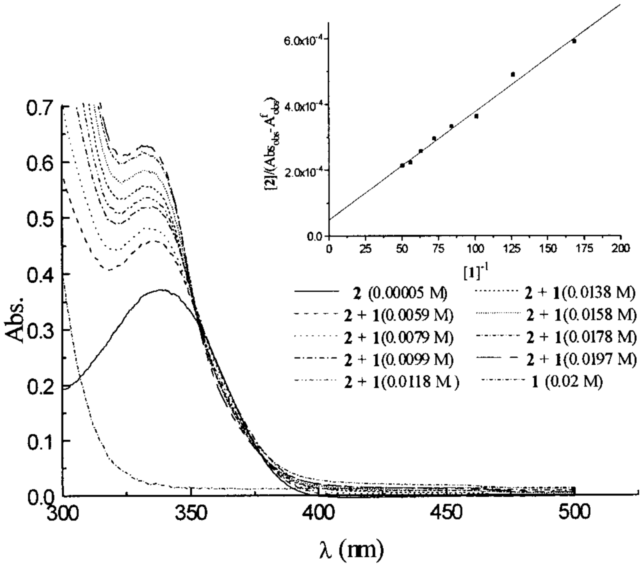

Figure 1. UV−vis spectra of carbanion **2** and iodide **1** and CTC formation (measured at $\lambda = 338.6$ nm).

Reactions of 1 with Enolate Anion 2. There is almost no reaction of **1** with enolate anion **2** after 1 h in the dark in DMSO. When a solution of **1** and **2** is irradiated for 1 h at 365 nm, a mixture of *tert*-butylbenzene (**5**) and isobutylbenzene (**6**) is produced in 49% yield (Table 1, entries 1 and 2). Product **6** is formed through the rearrangement of the neophyl radical. No products from the addition of radicals to **2** were found in the reaction mixture. Both reactions were performed using a **2**:**1** ratio of 1:3. When equimolar amounts of **1** and **2** were employed, the reaction was slower, and 2 h of irradiation were necessary to reach the same conversion. As control experiments, the photoinduced reaction was conducted under nitrogen atmosphere in a closed system and the internal standard for GC-quantification was added before irradiation. It made no difference whether the experiment was conducted in a closed system under nitrogen or with nitrogen circulation. Small amounts of olefins (2-methyl-3-phenylpropene, **7**, and 2-methyl-1-

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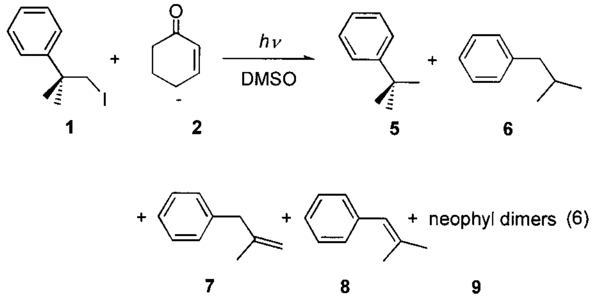
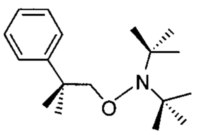
(27) It was obtained from the following equation: $[Nu^-]/(A_{obs} - A^f_{obs}) = 1/\Delta\epsilon + 1/\Delta\epsilon\, K_{ctc}\, [\mathbf{1}]^{-1}$.

propene, **8**) and neophyl dimers (**9**) were also formed (eq 6). Traces of phenol are observed. (Table 1, entries 3 and 4).



When the photochemical reaction was performed in DMSO-d_6, 12.7% of deuterium incorporation was detected in the reduction products **5** and **6** by GC−MS. In this reaction, the amount of phenol increases up to 11.5%, and incorporation of deuterium was also observed. In the presence of a very efficient radical trap like di-*tert*-butylnitroxide (DTBN), the main product is the corresponding adduct **10** in 57% yield and **5** as minor product in 10% yield (Table 1, entries 5 and 6).



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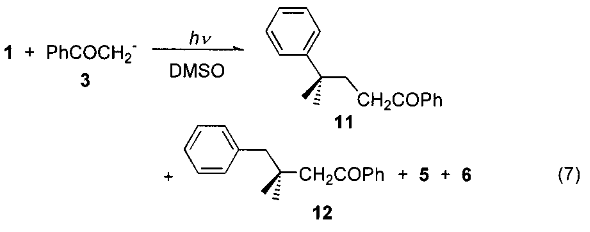
Reaction of 1 with the Enolate Ion of Acetophenone (3). The dark reaction of **1** with enolate anion **3** in DMSO yielded, after 1 h, only 5.7% of the substitution product **11**. This sluggish reaction was not inhibited in the presence of 20 mol % of DTBN. When the reaction was irradiated for 1 h, it afforded the expected substitution product **11** in 55% yield, the rearranged substitution product **12** (16%), and small amounts of **5** and **6** (eq 7; Table 1, entries 7−10).



This reaction showed a strong inhibition after 1 h upon addition of 20 mol % of DTBN, affording only products derived from the neophyl radical, the substitution product **11 (**5.5%), and the adduct **10** (2.5%).

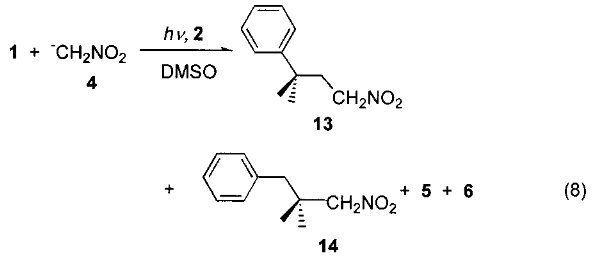
Reaction of 1 with Nitromethane Anion (4). There is no dark reaction of **1** with **4** (1 h). The photoinduced reaction of **1** with **4** yields only 3.1% of the substitution product **13** after 1 h. When the reaction was performed in the presence of **2**, which is a good electron donor (**1**:**4**:**2** ratio of 1:3:1), the substitution product **13** is obtained in 67% yield and only 2% of the rearranged substitution product **14** is observed (eq 8; Table 1, entries 12−14).

When the amount of anion **2** was increased to a 1:3:3 ratio (**1**:**4**:**2**), the conversion of the reaction markedly diminishes after 2 h of irradiation. The photoinduced reaction of **1** with a 10-fold decrease in the concentration of **4** affords the expected **13** and the rearranged **14** substitution products in 16 and 6.4% yields, respectively (Table 1, entries 15 and 16).

Table 2. Quantum Yields and Chain Lengths of the PET Reactions of 1 with Carbanions[a]

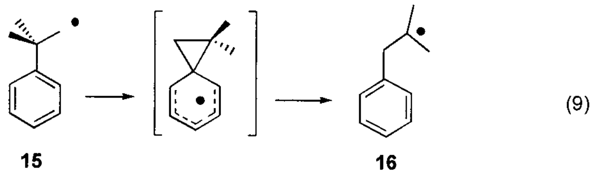
entry	carbanion	ϕ_{products}[b]	chain length[c]
1	**2**	0.17 ± 0.03 (**5** + **6**)	
2[d]	**3**	0.124 ± 0.011 (**11**)	127
		0.0027 ± 0.0005 (**12**)	
3[e]	**3**	0.0010 ± 0.0002 (**10**)	
4[d]	**4** (**2**)	0.33 ± 0.05 (**13**)	2

[a] Performed under nitrogen atmosphere, using 0.04 M solutions of substrate and 0.12 M solutions of the nucleophiles. [b] Determined at $\lambda_{\text{max}} = 350$ nm. [c] Determined by eq 25. [d] Duplicate experiments. [e] In the presence of 20 mol % of DTBN.



Quantum Yield Measurements and Determination of the Rate Constant for Nucleophilic Addition. The quantum yields determined ($\lambda = 350$ nm) for the reactions of carbanions **2** and **3** with iodide **1** were below 1. A quantum yield of ca. 10^{-3} was obtained for the formation of adduct **10** in the reaction with **3** in the presence of DTBN.[28] Product **13** was formed with a quantum yield of 0.33 when **1** is made to react with **4** in the presence of **2** as initiator (Table 2).

The rearrangement of the neophyl radical (**15**) to the tertiary radical **16** is a well-known process, and there is an abundance of evidence that supports phenyl migration by a cyclic transition state.[29] The Arrhenius function for this reaction has recently been determined by ESR methods[30] (eq 9). Therefore, the rate constant for the coupling reaction of radical **15** with a nucleophile may be determined by using its rearrangement as a "radical clock".[31]



The quantum yields for substitution products **11** and **12** were determined ($\lambda = 350$ nm) and were found to be dependent on the concentration of the nucleophile. A plot of the **11**:**12** quantum yield ratio against the concentra-

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[28] Di-*tert*-butylnitroxide (DTBN) absorbs maximally at 440 nm and shows a minimum at 340 nm with a $\epsilon_{350} \approx 2$, whereas the anions **2** and **3** have molar extinction coefficients at the absorption maximums of 4000 and 7700, respectively.

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[31] General references for free radical clocks: (a) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Essay 4. (b) Surzur, J. M. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1981; Vol. 2, Chapter 2. (c) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

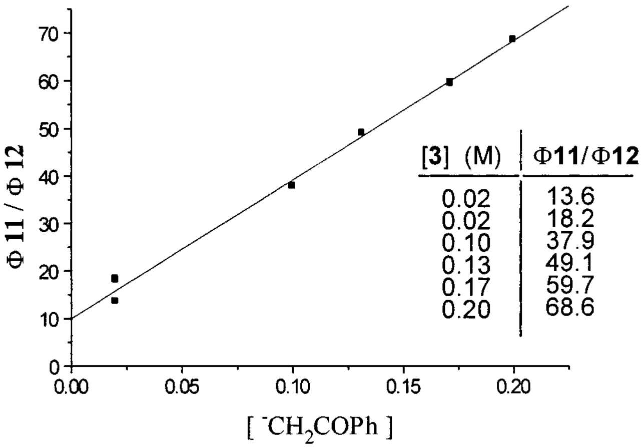


Figure 2. Rate constant for the coupling of carbanions **3** with radical **15**. The reactions were performed under a nitrogen atmosphere, using 0.04 M solutions of substrate, and varying concentrations of anion **3**. The quantum yields were determined at $\lambda_{max} = 350$ nm, and the rate constant was obtained by the equation in ref 32.

tion of anion **3** is linear. From the slope of this plot and taking into account the rearrangement rate of the neophyl radical ($k_r = 402\ s^{-1}$),[30] the rate constant of the coupling of the neophyl radical with **3** was calculated to be $k_c = 1.2 \times 10^5\ M^{-1}\ s^{-1}$ (Figure 2).[32]

Discussion

A detailed mechanistic study of the photochemical reactions of iodide **1** with carbanions **2**−**4** was conducted in DMSO. These three carbanions have distinct reactivity on the different reaction pathways of the $S_{RN}1$ mechanism.

PET Reduction of Iodide 1 by 2. The enolate anion **2** reacts only under photostimulation with **1** to afford mainly the reduction products **5** and **6** together with small amounts of olefins and dimers. The intermediacy of the neophyl radicals in this reaction was confirmed by the observation of product **6** which arises from rearrangement, the efficiency of the DTBN in affording the adduct **10**, and the deuterium incorporation in the reduction products when using labeled DMSO.

A possible mechanism to account for this reductive process involves an initial PET from anion **2** to the substrate **1** to yield radical **15** (eq 10). Three competitive reactions' pathways can take place for the neophyl radical **15** thus formed: (1) reduction to **5** by hydrogen abstraction from the solvent (eq 11); (2) rearrangement to a tertiary radical **16** which affords **6** after hydrogen abstraction (eq 12); or (3) in the presence of DTBN, formation of the corresponding adduct **10** with a rate constant of approximately $10^9\ M^{-1}\ s^{-1}$ (eq 13).[31c]

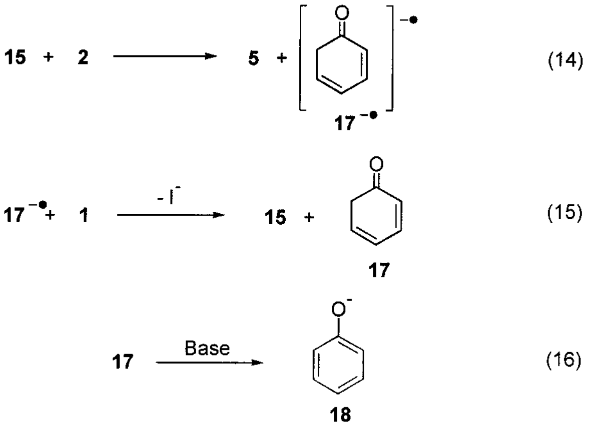
An alternative mechanism for the reduction of **15** could be hydrogen atom abstraction from enolate anion **2**, which yields the cyclohexadienone radical anion (eq 14). This radical anion intermediate ($17^{\bullet-}$), could transfer its odd electron to another molecule of **1** (eq 15) to render **15** and **17** and build a chain mechanism for this reductive process. Under the basic reaction conditions, **17** affords the phenoxide anion **18** (eq 16).

$$\mathbf{1} \xrightarrow{\mathbf{2},\ h\nu} \mathbf{15} + I^- \qquad (10)$$

$$\mathbf{15} \xrightarrow{SH} \mathbf{5} \qquad (11)$$

$$\mathbf{15} \xrightarrow[4\times10^2\ s^{-1}]{\bigcirc} \mathbf{16} \xrightarrow{SH} \mathbf{6} \qquad (12)$$

$$\mathbf{15} \xrightarrow[10^9\ M^{-1}s^{-1}]{DTBN} \mathbf{10} \qquad (13)$$



The lack of inhibition by a radical trap, the presence of only traces of phenol[33] (below 2.5%) in the reaction mixture, and the deuterium incorporation when labeled DMSO is used allow us to rule out this alternative pathway, suggesting that the mechanism for the reduction is hydrogen atom abstraction from the solvent in a nonchain reaction. When the reaction is conducted in DMSO-d_6 the rate for atom abstraction from the solvent slows down, and the reduction process by anion **2** becomes more important with the concomitant increase in the amount of phenol. Small amounts of olefins are formed because of a disproportionation process. Thus, the quantum yield measurement for the formation of the reduction products renders the efficiency of this process ($\Phi_{initiation}$, see below).

Nucleophilic Substitution Reaction of Iodide 1. The slow dark reaction of **1** with enolate anion **3** does not show inhibition in the presence of a radical trap, which indicates that it may proceed by a polar mechanism.[34]

The photoinduced reaction of **1** with **3** gives the expected and the rearranged substitution products **11** and **12** in good yields and minor amounts of the reduction products **5** and **6**. This reaction, strongly inhibited by DTBN, occurs by a radical chain $S_{RN}1$ mechanism and can be rationalized in the terms of PET from nucleophile **3** to **1** (initiation step eq 17). Radical **15,** thus formed, reacts with **3** to give the radical anion intermediate $\mathbf{11}^{\bullet-}$, which by an ET to **1** affords the substitution product **11**

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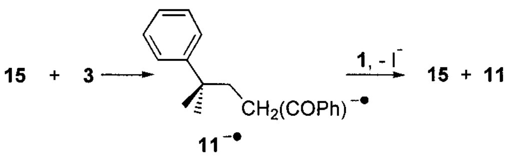
[32] The equation used in the evaluation of the coupling rate constant of ion **3** with radical **15**, assuming that the concentration of Nu^- is constant during the reaction, is the following: $\Phi 11/\Phi 12 = a[Nu^-] + b$, where a is equal to k_c/k_r and b = constant.

[33] In a control experiment, phenol in a concentration of 0.04 M was recovered in ca. 85%.

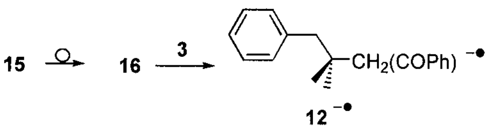
[34] Slow substitution of **1** by t-BuO$^-$ ion by a polar mechanism was previously observed: Argüello, J. E.; Peñéñory, A. B.; Rossi, R. A. *J. Org. Chem.* **1999**, *64*, 6115. This reaction was not observed at very short times, i.e., the employed time for the quantum yield measurements.

and radical **15**, which may continue with the propagation cycle (eq 18) or be reduced to **5** (eq 11). Radical **15** rearranges to give radical **16,** which is also able to react with **3** to render the radical anion intermediate $\mathbf{12}^{\bullet-}$ that yields through an ET to **1** the rearranged product **12** and radical **15** (eqs 19 and 20**)**. Finally, radical **16** affords the reduction product **6** by hydrogen atom abstraction from the solvent (eq 12).

$$\mathbf{1} \xrightarrow{\mathbf{3},\, h\nu} \mathbf{15} + \mathrm{I}^- \qquad (17)$$



(18)



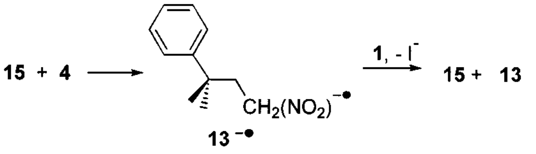
(19)

$$\mathbf{12}^{-\bullet} \xrightarrow{\mathbf{1},\, -\mathrm{I}^-} \mathbf{15} + \mathbf{12} \qquad (20)$$

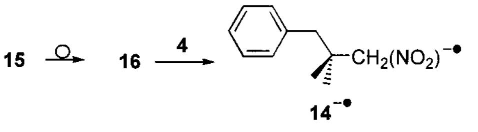
The nitromethane anion **4** does not react with **1** in the dark but upon irradiation affords the substitution product **13** in very low yield (see above).

The nitronate anions are poor electron donors, and they are unable to transfer one electron to nonactivated alkyl halides to initiate an $S_{RN}1$ process.[35] Nevertheless, the photoinduced reaction of **1** with **4** in the presence of the enolate anion **2** (entrainment reagent) renders the substitution product **13** in high yield and the rearranged product **14** only in traces.

Carbanion **2** is able to transfer one electron to **1** under irradiation to yield radical **15** (eq 10), but this anion does not add to the radical (see the above results). Furthermore, **4** is more reactive in the coupling reaction, and the only product formed is the substitution product from the addition of **4** to radicals **15** (eq 21) and **16** (eqs 22 and 23).



(21)



(22)

$$\mathbf{14}^{-\bullet} \xrightarrow{\mathbf{1},\, -\mathrm{I}^-} \mathbf{15} + \mathbf{14} \qquad (23)$$

The three carbanions studied showed different reactivity in the initiation and propagation steps of the $S_{RN}1$ process. The PET from the carbanion to **1** depends on the oxidation potential of the anion, which is related to the HOMO energy, and it increases with an increase in the pK_a of the carbanion[36] (the pK_a in DMSO are as follows: cyclohexenone, undetermined; acetophenone, 24.7; and nitromethane, 17.2).[37] Thus, the enolate anions **2** and **3** are more reactive than anion **4** in the initiation step. Furthermore, it has been previously proposed[22,38] that, in the addition step, the reactivity of the carbanions would depend in part on their HOMO (pK_a) as well as on the SOMO of the radical anion intermediate. Thus, anion **4** is more reactive in the coupling reaction with the radicals than the enolate anions **2** and **3**. For these carbanions, the reactivity increases with a decrease in the pK_a of the conjugated acids (HOMO energy).

The coupling reaction between the nucleophile and the radical is the most important step in determining whether an $S_{RN}1$ process takes place. If this reaction cannot compete efficiently with the termination steps, the chain will be short or even nonexistent. For aromatic radicals, absolute rate constants for the addition of several nucleophiles have been determined by cyclic voltammetry, and a large number of these values are near the diffusion limit.[2] Nevertheless, little is known about the rates of these reactions in aliphatic systems.[39]

The observation of products, which arises from addition of ion **3** to radical **15** and the rearranged radical **16**, allow us to obtain a value of 1.2×10^5 M^{-1} s^{-1} for the rate constant for the coupling reaction of radical **15** with this nucleophile.

The fact that only traces of **14** were detected suggests that the reaction of radical **15** with **4** is faster than its rearrangement to give radical **16** at least by 3 orders of magnitude, so this is not an appropriate clock for determining the addition rate constant. When the concentration of **4** was decreased by 10-fold (to slow the coupling reaction with radical **15**), both products **13** and **14** were formed, so we can estimate the rate constant of the coupling reaction between **15** and **4** to be ca. 10^6 M^{-1} s^{-1}. This is an approximate value, which is about 2 orders of magnitude below the previously reported rate constant for the addition of **4** to methyl radicals determined by pulse radiolysis,[39c] and to achieve a more realistic one it should be necessary to use a faster radical clock. Finally, the results obtained herein for the addition of these carbanions to **15** are in complete agreement with their previously reported relative reactivity toward adamantyl[38] and phenyl radicals.[22]

Efficiency and Chain Length in $S_{RN}1$ Reactions. A photoinduced $S_{RN}1$ mechanism involves, as an initiation step, a PET reaction from the nucleophile to the substrate in the majority of the cases, followed by a propagation cycle and termination steps. For enolate anion **3** which is reactive at both the initiation and the propagation pathways, the quantum yield for the forma-

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(35) Nevertheless, with a better electron acceptor (*p*-nitrobenzyl-halides, α-nitrohalo alkanes, and related compounds), the PET is very efficient. See ref 1d.

(36) Bordwell, F. G.; Clemens, A. H.; Smith, D. E.; Begemann, J. *J. Org. Chem.* **1985**, *50*, 1151.

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

(38) Rossi, R. A.; Pierini, A. B.; Borosky, G. L. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2577.

(39) (a) The coupling rate constant of the PhS^- ion with the 2,2-dimethyl-5-hexenyl radical is $k = 1.2 \times 10^8$ M^{-1} s^{-1} in acetonitrile at 25 °C. See: Beckwith, A. L. J.; Palacios, S. M. *J. Phys. Org. Chem.* **1991**, *4*, 404. (b) The coupling rate constant of the 2-nitropropane anion with the 5-hexenyl radical is $k \approx 1 \times 10^6$ M^{-1} s^{-1} in DMSO at 40 °C. See: Russell, G. A.; Guo, D. *Tetrahedron Lett.* **1984**, *25*, 5239. (c) The coupling rate constants of nitronate ions with methyl radicals in DMSO at room temperature are the following: nitromethane ($k = 1.35 \times 10^8$ M^{-1} s^{-1}), nitroethane ($k = 1.6 \times 10^7$ M^{-1} s^{-1}), 1-nitropropane ($k = 1.35 \times 10^7$ M^{-1} s^{-1}), and 2-nitropropane ($k = 2.35 \times 10^6$ M^{-1} s^{-1}). See: Veltwisch, D.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1143.

tion of the substitution product (Φ_{global}) encompasses both processes (eq 24). From this expression, it is possible to obtain the $\Phi_{propagation}$ (that is, the chain length) by the ratio of the overall quantum yield and the quantum yield of the initiation step (eq 25).

$$\Phi_{global} = \Phi_{initiation} \times \Phi_{propagation} \tag{24}$$

$$\text{Chain Length} = \Phi_{propagation} = \Phi_{global} / \Phi_{initiation} \tag{25}$$

The quantum yield measured for the formation of both substitution products **11** and **12** is 0.127 (Table 2). To evaluate only the quantum yield of the initiation process, it was necessary to carry out the reactions in the presence of a radical trap such as DTBN, which inhibits the propagation steps. This reaction has a quantum yield of 10^{-3}, which represents the photochemical efficiency of the initiation process.

Thus, the chain length or $\Phi_{propagation}$ for the reaction of iodide **1** with enolate anion **3** obtained from eq 25 is ca.127. As far as we know, this reports represents the first measurement for the efficiency of the propagation step of a $S_{RN}1$ process. This result is important not only because it means a very effective chain with more than 100 cycles but also because a reaction having an overall quantum yield below 1 does not necessarily mean a nonchain process. Thus, many reactions that are thought to proceed by a nonchain reaction, e.g., geminate coupling of a pair of radicals, with the only evidence that the overall quantum yields are below one, should now be revised in the light of our results.

The anion **4** does not transfer one electron to iodide **1** in the dark or upon irradiation, but it is reactive in the addition reaction to alkyl radicals generated by PET from **2** (unreactive anion in the coupling reaction). We have measured a quantum yield of 0.33 for the reaction of **1** with nitronate **4** in the presence of **2** as photoinitiator. This allowed us to evaluate the chain length of this reaction, assuming that the $\Phi_{initiation}$ is the same as that of the reaction of anion **2**. Thus, the reaction of **1** with **4** has a chain length of ca. 2.

The chain length for these reactions depends on the efficiency of the propagation steps in relation to the possible termination pathways. For carbanion **3**, the most probable termination step is the reduction of the radical by hydrogen abstraction. In this latter reaction, the coupling pathway is faster than the reduction process, so that the chain length is ca. 127. In the case of anion **4**, although the coupling reaction is faster, the ET from the stable radical anion of the substitution product ($\mathbf{13}^{\bullet-}$) to the substrate is slower, and a competitive ET to other acceptor molecules can take place (for example, ET to radicals **15** or **16** or the radical of the nucleophile formed in the initiation step, which are considered termination steps). This accounts for the short chain length, i.e., 2.

Conclusions

The main results presented herein can be summarized as follows:

The formation of a CTC between the enolate anions **2** and **3** and iodide **1** was confirmed by UV−vis spectroscopy. Taking into account the magnitude of the equilibrium constant for the formation of a CTC, we found that it is probable that the PET occurs within these complexes. Because the nucleophiles and the complexes show the same absorption band, it is not possible to rule out ET from the excited nucleophile by measurements of the quantum yields of the reaction varying the wavelength.

The reaction of **1** with enolate anion **3** gives the expected and the rearranged substitution products, whereas the reaction with anion **4** yields mainly the unrearranged substitution product. The use of the rearrangement rate constant of the neophyl radical as a clock reaction has allowed us to obtain the rate constant for the addition of nucleophile **3** to a primary alkyl radical.

For the first time, the $\Phi_{propagation}$ (that is, the chain length) for a $S_{RN}1$ process was measured, demonstrating that, although the overall quantum yields for these reactions are below 1, they occur by a chain $S_{RN}1$ mechanism.

Experimental Section

General Methods. Irradiation was conducted with a 125-W medium pressure Hg lamp, emitting maximally at 365 nm (Applied Photophysics Limited). The quantum yield for the reactions of **1** with the carbanions was determined using ferrioxalate actinometry at 350 nm with a 125-W Philips HPW lamp, according to the procedure described in the literature.[40] The conversion of the actinometer was monitored by measuring the absorbance of the complex Fe−(*o*-phenanthroline) at 510 nm. A radiant power of ca. 10^{-7} einstein/min was measured (a mean value among 5, 10, 15, and 20 min of irradiation). The sample and the actinometer were placed equidistant to the lamp in a merry-go-round equipment. ^{1}H and ^{13}C NMR spectra were recorded at 200.00 and 50.288 MHz, respectively, on a Brucker AC-200 spectrometer, and all spectra are reported in δ (ppm) relative to Me_4Si, with $CDCl_3$ as the solvent. HR-MS analyses were recorded at the Facultat de Farmacia Universitat de Bercelona, Barcelona, Spain. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II with a flame-ionization detector and the data system Hewlett-Packard 3396 Series II integrator, on a HP-17 10 m capillary column packed with 50% phenyl and 50% methylpolysiloxane gum of a 0.53 mm × 2.00 μm film thickness. GC−MS analyses were carried out on a Shimadzu GC−MS QP 5050 spectrometer, employing a 30 m × 0.12 mm DB-5 MS column. The column chromatography was performed on silica gel (70−230 mesh ASTM). UV−vis spectra were recorded on a UV−vis spectrophotometer Shimadzu UV-260. 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 a Büchi 510 apparatus and were not corrected.

Materials. Iodide **1**[41] was synthesized by a procedure similar to thatdescribed in the literature regardless of the starting material, neophyl alcohol, which was prepared by air oxidation of the corresponding Grignard reactive from neophyl chloride. The product presents the same spectroscopic data as that given in the literature. *t*-BuOK (Aldrich) and *tert*-butylbenzene (Aldrich) were commercially available and used as received. DMSO (Carlo Erba) was distilled under vacuum and stored over molecular sieves (4 Å). Acetophenone (Aldrich), 2-cyclohexen-1-one (Aldrich), and nitromethane (Aldrich) were distilled and dried over molecular sieves (4 Å). The carbanions were generated in situ by acid−base deprotonation using *t*-BuOK.

General Procedures for the Photochemical Reaction of 1 with Carbanions. The reactions were carried out in a 20-mL three-necked Schlenk tube, equipped with a nitrogen gas inlet, a condenser with a cooling jacket, and a magnetic

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[40] (a) Hatchard, C. G.; Parker, C. A. *J. Chem. Soc.* **1956**, 518−536. (b) Murov, S. L.; Carmichael, I.; Hung, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Decker Inc.: New York, 1993.

[41] Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 310.

stirrer. The tube was dried under vacuum and filled with nitrogen and then loaded with 10 mL of dried DMSO. To the degassed solvent under nitrogen was added 1.2 mmol of *t*-BuOK, 1.2 mmol of the nucleophile precursor, and 0.4 mmol of **1**. After 1 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 GLC with the internal standard method.

Phenyl(3-phenyl-3-methyl-1-butyl)ketone (11). Compound **11** was isolated in 44.9% yield by silica gel chromatography with petroleum ether/diethyl ether (90:10) as eluent from the crude product reaction of **1** and **3**: mp 65−66 °C (Table 1, entry 9); ^1H NMR ($CDCl_3$) δ 1.38 (6H, s), 2.04−2.12 (2H, m), 2.65−2.74 (2H, m), 7.1−7.9 (10H, m); ^{13}C NMR ($CDCl_3$) δ 29.00, 34.50, 37.44, 38.38, 125.78, 125.84, 128.02, 128.29, 128.45, 132.82, 136.94, 148.31, 200.57; MS (EI^+) 252 (2.51, M^+), 133 (10.37), 132 (23.98), 120 (34.10), 119 (100.00), 105 (39.56), 92 (14.84), 91 (39.30), 77 (36.63); HRMS (EI^+) calcd 252.1514, obsd 252.1512.

Phenyl(3-phenyl-2,2-dimethyl-1-propyl)ketone (12). Compound **12** was isolated in 15.5% yield by silica gel chromatography with petroleum ether/diethyl ether (90:10) as eluent from the crude product reaction: ^1H NMR ($CDCl_3$) δ 0.98 (6H, s), 2.71 (2H, s), 2.75 (2H, s), 7.06−7.9 (10H, m); ^{13}C NMR ($CDCl_3$) δ 27.70, 34.87, 47.51, 48.00, 126.00, 127.80, 128.02, 128.48, 130.66, 132.68, 138.61, 138.83, 200.33; MS (EI^+) 133 (4.48), 132 (37.26), 117 (13.69), 106 (7.84), 105 (100.00), 91 (37.27), 77 (54.04); HRMS (EI^+) calcd 252.1514, obsd 252.1508.

3-Phenyl-3-methyl-1-nitrobutane (13). Compound **13** was isolated by silica gel chromatography with petroleum ether/diethyl ether (90:10) as eluent from the crude product reaction: ^1H NMR ($CDCl_3$) δ 1.31 (6H, s), 2.28−2.36 (2H, m), 4.00−4.09 (2H, m), 7.11−7.28 (5H, m); ^{13}C NMR ($CDCl_3$) δ 28.70, 36.70, 40.99, 72.79, 125.38, 126.35, 128.58, 146.37; MS (EI^+) 193 (5.40, M^+), 131 (11.42), 119 (100.00), 92 (5.42), 91 (71.72), 77 (12.46); HRMS (EI^+) calcd 193.1103, obsd 193.1099.

3-Phenyl-2,2-dimethyl-1-nitropropane (14). Compound **14** was isolated by silica gel chromatography with petroleum ether/diethyl ether (90:10) as eluent from the crude product reaction: ^1H NMR ($CDCl_3$) δ 1.07 (6H, s), 2.71 (2H, s), 4.21 (2H, s), 7.17−7.35 (5H, m); ^{13}C NMR ($CDCl_3$) δ 25.25, 36.22, 45.73, 84.79, 126.72, 128.18, 130.63, 136.67; MS (EI^+) 132 (9.60, M^+), 117 (6.41), 107 (5.77), 105 (11.12), 91 (100.00), 65 (14.21); HRMS (EI^+) calcd 193.1103, obsd 193.1103.

Coupling Product from Radical 15 and DTBN (10). The product was isolated by silica gel chromatography with petroleum ether/diethyl ether (90:10) as eluent from the crude product reaction mixture of **1** and **2** in the presence of DTBN: ^1H NMR ($CDCl_3$) δ 1.14 (18H, s), 1.39 (6H, s), 3.74 (2H, s), 7.11−7.41 (5H, m); ^{13}C NMR ($CDCl_3$) δ 25.84, 29.97, 39.19, 62.71, 84.76, 125.73, 126.24, 127.72, 147.56; MS (EI^+) 145 (33.85), 91 (100.00), 89 (99.70), 74 (89.48), 57 (99.59). The compound is so unstable at the MS conditions that the molecular ion cannot be observed.

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Supporting Information Available: ^1H and ^{13}C NMR and mass spectra of compounds **10**−**14**. UV−vis spectra of CTC. Figure S1 UV−vis spectra of carbanion **3** and iodide **1** and CTC formation. This material is available free of charge via the Internet at http://pubs.acs.org.

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