

S_{RN}1 Photostimulated Reaction of Triphenylvinyl Bromide with Carbanions in DMSO

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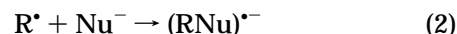
The radical nucleophilic substitution, or S_{RN}1, has been found to be suitable to affect the nucleophilic substitution of aromatic and aliphatic substrates substituted by electron-withdrawing groups which carry suitable leaving groups. It has also been reported that aliphatic substrates having no electron-withdrawing groups such as cycloalkyl, bicycloalkyl, and neopentyl halides react by this mechanism.¹

Vinyl halides react with nucleophiles through different polar mechanisms,^{2,3} but there are few reports on substitution of vinyl halides by the S_{RN}1 mechanism. Bunnett and co-workers investigated the photostimulated reaction of several vinyl halides with ketone enolate and thiophenoxide ions in liquid ammonia.⁴ The photostimulated cobalt carbonylation reaction of aryl and vinyl halides under phase transfer conditions has been suggested to give the carbonylation products through an S_{RN}1 mechanism.⁵ The vinylation of iron porphyrins under electrochemical conditions has been reported,⁶ and the reaction of a vinyl halide moiety of a cyanine dye with different nucleophiles has been suggested to occur by an S_{RN}1-type mechanism.⁷ The reaction of *trans*-1,2-dichloroethene with thiolate ions which gave the *trans* disubstitution product in HMPT was also thought to occur by the S_{RN}1 mechanism.⁸

It has been shown more recently that vinyl halides having a β-vinyl hydrogen undergo substitution by the elimination–addition route involving an acetylenic intermediate, whereas vinylic halides carrying an allylic

rather than vinylic hydrogen(s) give substituted allene.^{9,10} When the vinylic halides, e.g., triphenylvinyl bromide (Ph₂C=C(Ph)Br, **1**) lack either a vinylic or allylic hydrogen they react with nucleophiles exclusively by the S_{RN}1 mechanism.¹⁰ This is a chain process whose propagation steps are shown in Scheme 1.

Scheme 1



Scheme 1 illustrates a nucleophilic substitution in which radicals and radical anions are involved as intermediates. This chain process requires an initiation step, and in a few systems spontaneous electron transfer (ET) from the nucleophile to the substrate has been observed.¹¹ When the ET does not occur spontaneously, it can be induced by light in aromatic as well as in aliphatic systems.^{1,12} In aromatic systems it has also been initiated by solvated electrons¹³ or sodium amalgam in liquid ammonia,¹⁴ by cathodically generated electrons,¹⁵ or by certain inorganic ions in aromatic¹⁶ S_{RN}1 reactions. Photostimulation and Fe²⁺ stimulation were recently applied in vinylic S_{RN}1 reactions.^{9,10}

We undertook the investigation of the photostimulated reactions of the vinyl bromide **1** with different carbanions in DMSO in order to extend the scope of the limited research so far reported.

Results and Discussion

Reactions of 1 with Acetone (2) and Pinacolone (3) Enolate Ions. A solution containing **1** and potassium acetone enolate (**2**) was irradiated for 3 h in DMSO to give 52% yield of bromide ion. Only mere traces of the substitution product were found, and several minor unidentified products were formed (experiment 1, Table 1). A slower reaction in the dark under the same experimental conditions also produced bromide ions, but no substitution products were found (experiment 2, Table 1). These results suggest that the triphenylvinyl radical was formed in the initiation step, presumably by ET from **2** to **1**, but that the radical, reminiscent of the behavior

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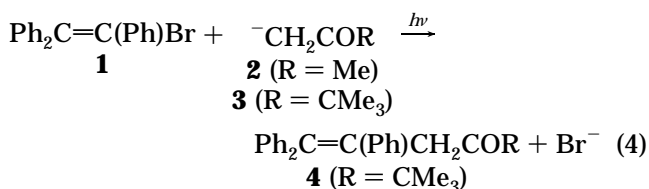
Table 1. Reactions of Triphenylvinyl Bromide (1) with Carbanions in DMSO^a

expt	1 (10 ³ M)	carbanion (10 ³ M)	conds	Br ⁻ (yield, %)	product, (yield, %)
1	20	2 (54)	<i>hν</i>	52	traces
2	20	2 (54)	dark	12	
3	20	3 (60)	<i>hν</i>	95	4 (93)
4	20	3 (60)	<i>hν</i> , <i>p</i> -DNB	48	4 (25)
5	20	3 (60)	dark	16	4 (15)
6	20	3 (60)	dark, <i>p</i> -DNB	6	
7	20	5 (39)	<i>hν</i>	32	6^b
8	17	5 (39) + 2 (20)	<i>hν</i>	95	6 (90)
9	17	5 (39) + 2 (20)	dark	33	6 (31)
10	17	5 (39) + 2 (20)	dark, <i>p</i> -DNB	<5	
11	17	5 (39) + 2 (20)	<i>hν</i> , <i>p</i> -DNB	43	6 (40)
12	17	7 (60)	<i>hν</i>	35	8^b
13	17	7 (84) + 2 (80)	<i>hν</i>	93	8 (89)
14	17	7 (74) + 2 (64)	dark	<10	
15	17	7 (74) + 2 (64)	dark, <i>p</i> -DNB	<10	

^a Reaction time 3 h. ^b Not quantified.

of aliphatic radicals, such as 1-adamantyl¹⁷ or 7-norcaranyl¹⁸ formed under similar S_{RN}1 conditions, reacts slower with **2** than other competing reaction routes. We did not study these reactions further.

In contrast, the photostimulation reaction of **1** with the enolate ion of pinacolone (**3**) afforded bromide ion (95% yield) together with an excellent yield (93%) of the substitution product **4** (experiment 3, Table 1) (eq 4).

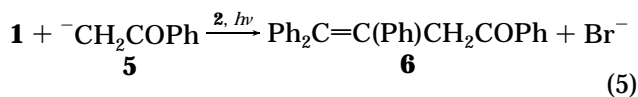


This reaction was inhibited in part by adding *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of S_{RN}1 reaction,¹ to give only 25% yield of the substitution product **4** under the same conditions (experiment 4, Table 1). Also, the use of irradiation accelerates the reaction since in the dark the reaction is sluggish and yields only 15% of the substitution product (experiment 5, Table 1). In the dark and in the presence of *p*-DNB there was no substitution product (experiment 6, Table 1). These results corroborate the recent suggestion of and S_{RN}1 vinylic route for the reaction of **1** and **3**.¹⁰

Reactions of 1 with Acetophenone Enolate Ions

5. When the photostimulation reaction (3 h) was carried out with the enolate ion of acetophenone (**5**) a low yield of bromide ion (32%) and low yield of the substitution product **6** (<5%) were obtained (experiment 7, Table 1). When the reaction was performed in the presence of acetone enolate ion (**2**), we obtained a 95% yield of bromide ion, 90% yield of the substitution product **6** of acetophenone, but no substitution product of acetone (experiment 8, Table 1) (eq 5).

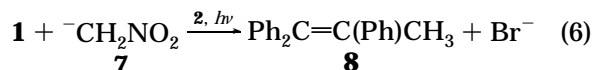
Similar reactions in the dark rendered 33% yield of bromide ion and a 31% yield of **6**, and when they were carried out in the presence of *p*-DNB, only ca. 5% Br⁻ ions were found (experiments 9 and 10, Table 1). These light-catalyzed reactions and the inhibition by *p*-DNB



suggest again that **1** reacts with **5** by the vinylic S_{RN}1 mechanism.

The overall reactivity in the S_{RN}1 mechanism depends on the rate (or efficiency) of the photostimulated initiation step, the individual rates of the propagation steps, and the termination steps. The fact that **5** reacted sluggishly under irradiation with **1**, but gave high yields in the presence of the carbanion **2**, suggests that carbanion **5** has low ET reactivity in the initiation step, but once the vinyl radical is formed, it reacts faster with carbanion **5** than with carbanion **2** (entrainment reaction).¹ On the other hand, carbanion **2** is more effective than carbanion **5**, in the rate determining initiating step ET to **1** under irradiation, thus increasing the rate of the overall reaction. This sequence of irradiation by ET follows roughly the same order of the pK_a of the conjugated acids of the carbanions, as has been previously proposed in the photostimulated reaction with haloarenes¹⁹ and 1-iodoadamantane.^{17b}

Reactions of 1 with Nitromethane Anion (7). The reaction of **1** with the anion of nitromethane (**7**) as the nucleophile takes a different course. No substitution product is formed after 180 min of irradiation (although a 35% yield of Br⁻ ions was formed). However, when **2** was added to the reaction mixture, a reaction took place, but rather than yielding the desirable substitution product, the product isolated was 1,1,2-triphenylpropene **8** (experiment 13, Table 1) (eq 6).



This reaction did not occur in the dark (experiment 15, Table 1), and the photostimulated reaction was inhibited by *p*-DNB (experiments 2 and 3, Table 1).

On the basis of these and previous results, it follows that nucleophiles **5** and **7** are unable to initiate the photostimulated reaction, but once the vinyl radical is formed it is capable of coupling with them, whereas **2** is more effective in starting the photostimulation reaction.

The formation of the substitution product **8** can be explained according to the S_{RN}1 mechanism considering that anion radicals of nitro derivatives can fragment. Consequently, we suggest an initial photostimulated ET from the nucleophile, probably **2** to the substrate to form the radical anion **1^{•-}** which fragments in the usual way (cf. eq 1) to the radical intermediate **9** and bromide ion (eq 7). Radical **9** then couples with **7** faster than with **2** to give the radical anion **10** (eq 8). Radical anion **10** fragments faster to the stabilized allyl radical **11** and NO₂⁻ ions (eq 9) than it transfers electron to neutral **1** to give the expected substitution product in a step similar to eq 3. Finally, radical **11** does not react with **7** or **2** in a step similar to eq 2, but it reacts faster by hydrogen abstraction from the solvent SH to give the reduced

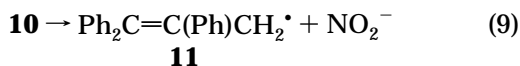
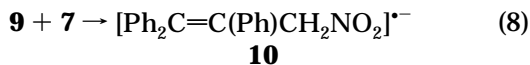
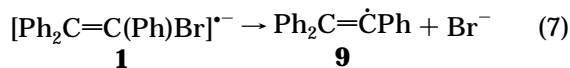
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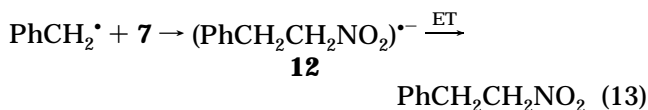
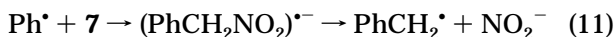
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product **8** (eq 10) (Scheme 2).

Scheme 2



This variant of the vinylic $S_{\text{RN}}1$ route is reminiscent of the results obtained in the photostimulated reaction of iodobenzene with **7** in DMSO,¹⁹ which yielded products derived from benzyl radicals by fragmentation of the radical anion intermediate arising from the coupling of phenyl radicals and **7** (eq 11). The main difference is that benzyl radicals are not exclusively reduced to toluene (eq 12) but are also able to couple partly to the nucleophile **7** to give the radical anion **12**, which gives finally the product 1-phenyl-2-nitroethane (eq 13).¹⁹ We did not find any products from the reaction of the allylic radical **11** and **7**.



Radical anions derived from anions of nitroalkanes are prone to fragment when they give stabilized radicals, such as benzyl, or in our case allyl radicals. Even the electrochemically induced $S_{\text{RN}}1$ reaction of 4-bromobenzophenone with 2-nitropropane anion gave products only derived from the fragmentation of the radical anion intermediate.²⁰ When the fragmentation of the radical anion gives an unstabilized alkyl radical, as is the case for **12** which would lead the primary $\text{PhCH}_2\text{CH}_2^{\cdot}$ radical or for the radical anions formed in the reaction of 1-adamantyl¹⁷ or 7-norcaranyl¹⁸ radicals with **7**, the ET rate to the substrate is faster than the fragmentation rate, and only substituted nitroalkanes are obtained.

Relative Reactivity of Carbanions 3 and 5 toward the Vinyl Radical 9. In order to determine the relative rate constants for the reacting nucleophiles toward the vinyl radicals (step 2), we carried out the competitive photostimulation reactions of **1** with excess of the enolate ions **3** and **5**. The relative reactivities were estimated as in previous work.²¹ Using this procedure, we determined that the k_5/k_3 ratio is 3.7 ± 0.4 in their competitive coupling with the triphenylvinyl radical **9** (Table 2).

These results are consistent with earlier findings where the reactivity of ketone enolate ions toward radicals increased with the increasing stability of the

Table 2. Competition Experiments in the Photostimulated Reaction of Carbanions 3 and 5 toward 1^a

5 (10 ² M)	3 (10 ² M)	reaction time (h)	products (yield, %)		k_5/k_3
			6	4	
5.0	5.0	1	71	22	3.5
3.3	6.7	3	59	37	4.3
3.3	8.3	3	49	49	3.4
					3.7 ± 0.4^b

^a Reactions carried out in 15 mL of DMSO with 0.017 M of substrate **1**. ^b Average value.

radical anion intermediate formed and with the results obtained in competition experiments of acetone enolate ion (**2**) and acetophenone enolate ion (**5**) toward iodobenzene ($k_5/k_2 = 7.5$)¹⁹ and 1-iodoadamantane ($k_5/k_2 = 11$).¹⁷ The fact that structurally different substrates (phenyl, vinyl, and 1-adamantyl halides) show nearly similar selectivity toward carbanions is consistent with their reaction by the same mechanism and indicates that for this limited group of substrates the reactivity of the derived radicals depends less on their structure than on the stability of the radical ion products formed in the coupling process.

Experimental Section

Photostimulated Reaction of Triphenylvinyl Bromide (1) with Different Carbanions in DMSO. The following procedure is representative of all the reactions. Into a three-necked, 50-mL, round-bottomed flask equipped with a cold finger condenser and a magnetic stirrer was added 25 mL of dry, degassed DMSO under nitrogen. Then, pinacolone (300 mg, 3.0 mmol) and *t*-BuOK (350 mg, 3.1 mmol) were introduced in order to form potassium pinacolone enolate. To this solution was added substrate **1** (338 mg, 1.0 mmol), and then the solution was irradiated for 180 min. The reaction was quenched by adding ammonium nitrate in excess. The DMSO was dissolved with 3-fold excess v/v of water and then extracted with methylene chloride. The bromide ion in the aqueous solution was determined potentiometrically. The methylene chloride extract was washed twice with water and dried, and the products were quantified by GLC using tetraphenyltin as internal standard. In another experiment, the dry organic solvent was removed under reduced pressure after the extraction and the product 2,2-dimethyl-5,6,6-triphenyl-5-hexen-3-one (**4**) was isolated as a white solid after recrystallization from hexane: mp 167–170 °C (lit.¹⁰ 165–168 °C); ¹H NMR (CDCl₃) δ 7.3–7.2 (m, 5H_{Ar}), 7.2–7.1 (m, 5H_{Ar}), 7.0–6.9 (m, 5H_{Ar}), 3.7 (s, 2H_{CH₂}); 0.9 (s, 9H_{CH₃}).¹⁰

1,3,4-Tetraphenyl-3-buten-1-one (6). The general procedure above was used, except that acetophenone and *t*-BuOK were used to form potassium acetophenone enolate ions. Product **6** was isolated as a white solid after recrystallization from hexane–acetone: mp 190–194 °C;

(21) The equation used for determining the relative reactivity of pairs of nucleophiles **I** and **II** vs. a radical is

$$\frac{k_{\text{Nu I}}}{k_{\text{Nu II}}} = \frac{\ln [\text{Nu I}]_0 / [\text{Nu I}]_t}{\ln [\text{Nu II}]_0 / [\text{Nu II}]_t}$$

where $[\text{Nu}]_0$ and $[\text{Nu}]_t$ are initial concentrations and $[\text{Nu}]_t$ are concentrations at time *t* of both nucleophiles. This equation is based on a second-order reaction, first order in each one of the nucleophiles with vinyl radicals. See: Bunnett, J. F. In *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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^1H NMR (CDCl_3) δ 7.4–7.0 (m, 15 H_{Ar}), 8.0–7.8 (m, 5 H_{Ar}), 4.2–4.1 (s, 2 H_{CH_2}); ^{13}C NMR (DCCl_3 relative to TMS) δ 46.3 (CH_2), δ 126.2, 126.4, 127.1, 127.5, 127.8, 128.0, 128.3, 128.4, 129.2, 129.7, 130.7, 132.9, 133.3, 137.0, 142.3, 142.9, 143.3 (C_{Ar} and C_{v}), δ 197.6 ($\text{C}=\text{O}$); mass spectrum, m/z (relative intensity, assignment) 374 (36), 269 (65), 252 (6), 191 (70), 105 (100), 91 (49), 77 (31); HRMS calcd 374.167 065, found 374.166 933.

1,1,2-Triphenylpropene (8). The general procedure was followed except that nitromethane was added instead of the ketone. Product **8** was isolated as a solid: mp 87–90 °C (lit.²² 93 °C); ^1H NMR (CDCl_3) δ 7.4–7.0 (m, 15 H_{Ar}); 2.0–1.6 (s, 3 H_{CH_3}); ^{13}C NMR (DCCl_3 relative to TMS) δ 23.309 (CH_3), δ 125.8, 126.2, 126.5, 127.0, 127.4, 127.5, 127.8, 127.9, 128.0, 128.1, 128.2, 129.3, 129.5, 130.0, 130.3, 130.6 (C_{Ar} and C_{v}); mass spectrum, m/z (relative intensity, assignment): 270 (20), 255 (5), 191 (66), 178

(7), 165 (15), 91 (70), 57 (100). HRMS calcd 270.140 850, found 270.141 658.

1,1,2-Triphenylethene (13). In order to ensure that **8** was not the reduction product (**13**),¹⁰ we synthesized the latter. To the substrate **1** in anhydrous ethanol under nitrogen was added sodium with stirrer, and the product found was different from **8** by cgl.

Photostimulated Reaction of Triphenylvinyl Bromide with Different Carbanions in the Presence of *p*-DNB. The general procedure was followed, except that 20 mol % of *p*-DNB was added prior to addition of the substrate.

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