$S_{RN}1$ REACTIONS OF NUCLEOPHILES WITH RADICAL CLOCKS: RATE CONSTANTS FOR SOME RADICAL–NUCLEOPHILE REACTIONS

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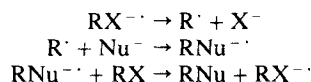*Research School of Chemistry, Australian National University, Canberra, A.C.T., 2601, Australia*

Treatment of o-3-(but-3-enyloxy)benzene (1) with anions ^-SPh, $^-PPh_2$ and $^-PO(OEt)_2$ in ammonia, acetonitrile or dimethyl sulphoxide gives both direct substitution and cyclized products. The formation of the latter confirms the intermediacy of the o-3-(but-3-enyloxy)phenyl radical (2) and confirms that the reactions follow the $S_{RN}1$ pathway. The kinetics of the coupling of the aryl radical 2 were determined by comparison with the known rate of cyclization of 2. Similar experiments with the neopentyl bromide, 6-bromo-5,5-dimethylhex-1-ene, and its 3-oxa derivative also gave cyclized and uncyclized products, thus confirming that the $S_{RN}1$ mechanism applies to the reactions. Approximate rate constants for the coupling of a neopentyl radical with the nucleophiles ^-SPh and $^-PPh_2$ have thus been determined.
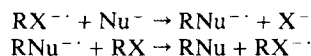
INTRODUCTION

Since they were first described more than 20 years ago,[1] nucleophilic substitutions proceeding via free radical chains have continued to attract considerable attention.[2] Experimental data such as product distribution and the effect of the nature of the leaving group on nucleophilic selectivity firmly indicate that many of these reactions follow the $S_{RN}1$ pathway (Scheme 1; R = aryl or alkyl). However, in some cases the data are consistent with the $S_{RN}2$ mechanism (Scheme 1).[3,4] The feature which most clearly differentiates the two mechanisms is the intermediacy of *free* alkyl or aryl radicals in the former but not in the latter. Consequently, an experimental test of mechanism can be made by employing substrates potentially capable of affording radicals that undergo characteristic rearrangements with known rate constants (radical 'clocks').[5] In the case of $S_{RN}1$ reactions, the use of such a diagnostic probe carries with it the advantage of affording kinetic information about the radical/nucleophile addition step by a method which is both more simple experimentally and more easily interpreted than other physical techniques. A few examples of reactions involving such intermediates have already been recorded.[2,6,7] However, in some cases no rearranged product was observed, either because the expected radical intermediates were not formed or, more probably, because the intermediates underwent subsequent *intermolecular* reactions more rapidly than rearrangement.[7]

$S_{RN}1$:

$$RX^{-\cdot} \rightarrow R^{\cdot} + X^-$$
$$R^{\cdot} + Nu^- \rightarrow RNu^{-\cdot}$$
$$RNu^{-\cdot} + RX \rightarrow RNu + RX^{-\cdot}$$

$S_{RN}2$:

$$RX^{-\cdot} + Nu^- \rightarrow RNu^{-\cdot} + X^-$$
$$RNu^{-\cdot} + RX \rightarrow RNu + RX^{-\cdot}$$

Scheme 1

Ring closure of the o-(but-3-enyloxy)phenyl radical (2) should be a suitable tool for the study of aromatic S_{RN} reactions since it has already been successfully employed to elucidate the kinetics and mechanism of the reactions of arenediazonium salts with thiophenoxide ion.[8] In the present work it was used as a kinetic and mechanistic probe of the photostimulated reactions of iodoarenes with diphenylphosphide, thiophenoxide and diethyl phosphite anions, and the results are compared, where appropriate, with those previously obtained by electrochemical methods.[9] Also, we describe the use of the two alkyl radical clocks, 12a and 12c, to study

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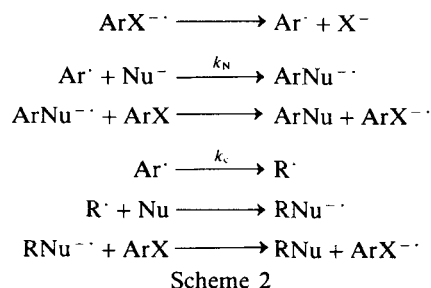photostimulated reactions of substituted neopentyl halides with thiophenoxide and diphenylphosphide anions and to obtain approximate kinetic data. In all cases the data are consistent with the $S_{RN}1$ mechanism.

RESULTS AND DISCUSSION

Aromatic substitution

When o-(but-3-enyloxy)iodobenzene (1) in liquid ammonia or acetonitrile was treated with potassium diphenylphosphide and irradiated with UV light, the only products isolated (Table 1) were 5a, resulting from direct substitution, and 7a, arising via cyclization followed by substitution. Formation of the latter must involve the intermediacy of the aryl radical 2 and its ring closure to give 4. Hence we conclude that the mechanism of formation of 5a must be of the general $S_{RN}1$ type, and that the $S_{RN}2$ process can be precluded from further consideration. Further, it appears that the cyclized radical 4, like 2, is also able to combine directly with the nucleophile to afford a radical anion, $RPPh_2^{-}$ (6a), capable of reducing the iodoarene (1). The complete chain process is depicted in Scheme 2, where ArX represents the iodoarene 1, R· represents the alkyl radical, 4, Nu⁻ represents the nucleophile (⁻PPh₂ in this case), k_N is the rate constant for addition of the nucleophile to 2 and k_c is the rate constant for cyclization of 2.

$$ArX^{-} \cdot \longrightarrow Ar \cdot + X^{-}$$

$$Ar \cdot + Nu^{-} \xrightarrow{k_N} ArNu^{-} \cdot$$

$$ArNu^{-} \cdot + ArX \longrightarrow ArNu + ArX^{-} \cdot$$

$$Ar \cdot \xrightarrow{k_c} R \cdot$$

$$R \cdot + Nu \longrightarrow RNu^{-} \cdot$$

$$RNu^{-} \cdot + ArX \longrightarrow RNu + ArX^{-} \cdot$$

Scheme 2

Kinetic analysis of the reactions of Scheme 2, when the nucleophile is present in large excess and consequently its concentration is approximately invariant throughout the reaction, gives the integrated rate equation [equation (1)] in which $[ArNu]_f$ and $[RNu]_f$ are the final concentrations of uncyclized and cyclized products respectively, and $[Nu^-]_m$ is the mean concentration of the nucleophile.

$$k_N/k_c = [ArNu]_f/([RNu]_f[Nu^-]_m) \qquad (1)$$

Since liquid ammonia is not a suitable solvent for quantitative work, kinetic experiments were conducted in acetonitrile. The product mixture was first treated with hydrogen peroxide to convert the relatively unstable phosphines 5a and 7a into their more stable phosphine oxides.[10] The yields of products formed at various temperatures were then accurately determined by gas chromatography, and are given in Table 2
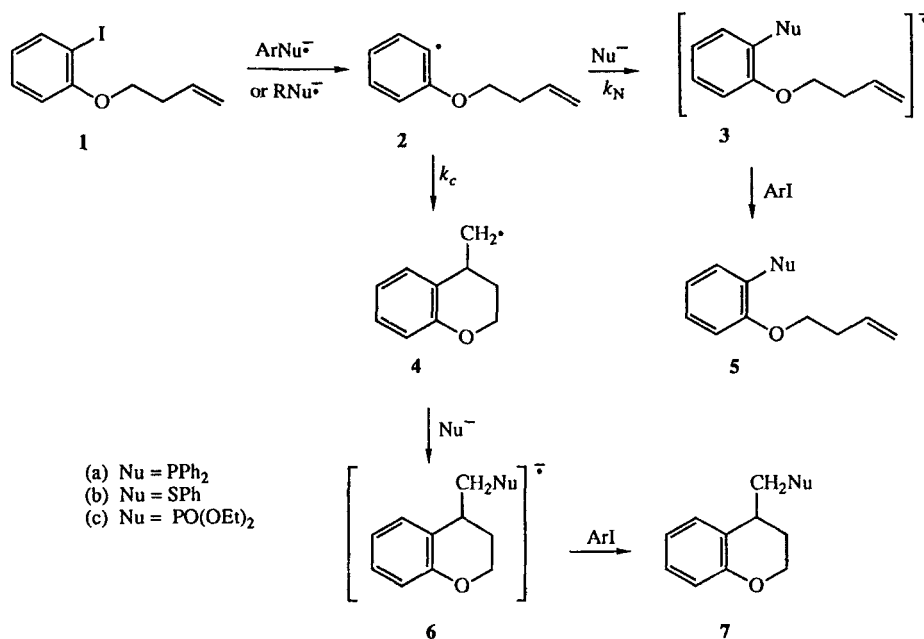

(a) Nu = PPh₂
(b) Nu = SPh
(c) Nu = PO(OEt)₂

Table 1. Photostimulated reactions of 2-(but-3-enyloxy)-1-iodobenzene (1) with various nucleophiles[a]

Reagent	Concentration (M)	Solvent	Time (h)	Products (yields, %)
KPPh$_2$	0·04	NH$_3$	0·1	5a (67), 7a (33)
KPPh$_2$	0·63	ACN	2·0	5a (24), 7a (75)
NaSPh	0·095	NH$_3$	4·0	5b (5·8), 7b (75), 8 (10·2), 9 (9·2)
NaSPh	0·088	ACN	4·7	5b (7·3), 7b (30), 8 (59), 9 (3·8)
LiSPh	0·130	DMSO	5·0	5b (35), 7b (50), 8 (15)
NaSPh	0·390	DMSO	3·0	5b (76), 7b (15), 8 (9)
KPO(OEt)$_2$	0·032	NH$_3$	6·0	5c (15), 7c (15), 8 (9), 9 (10), 10 (5)
KPO(OEt)$_2$	0·040	THF	4·0	5c (3), 8 (23), 10 (21)
KCH$_2$COBu^t	0·224	DMSO	2·0	No reaction
KCH$_2$COCH$_3$	0·004	NH$_3$	2·0	No reaction
KCH$_2$COCH$_3$	0·500	DMSO	3·0	No reaction

[a] Reactions in NH$_3$ at $-33\,^{\circ}$C; others at room temperature (ca 25 $^{\circ}$C).

Table 2. Photostimulated reactions of 1 with KPPh$_2$ in acetonitrile

| Experiment No. | [KPPh$_2$] (M) | Temperature (K) | Product yield (%)[a] | | k_N/k_c (M^{-1}) |
			5a[b]	7a[b]	
1	0·0128	238	19	81	18·5
2	0·0633	253	44	56	12·2
3	0·0633	273	31	69	6·9
4	0·0633	289	24	76	5·0

[a] Relative yields.
[b] Quantified as the phosphine oxide by GC with an internal standard.

together with the derived values of k_N/k_c calculated from them by application of equation (1).

The usual treatment of the values of k_N/k_c gives the temperature dependence: $\log(k_N/k_c)/M^{-1}s^{-1} = -(1\cdot97 \pm 0\cdot17) + (3\cdot53 \pm 0\cdot20)/\theta$, where $\theta = 2\cdot303$ RT kcal/mol^{-1} (1 kcal $= 4\cdot184$ kJ). Previous determinations[11] of k_c give the Arrhenius equation (2) from which the Arrhenius equation for k_N, the rate constant for reaction of 2 with $^-$PPh$_2$, can be derived [equation (3)]. (The value of k_c given in Ref. 11 was based on the value of k_H, the rate constant for hydrogen atom transfer from tributylstannane to phenyl radicals, given in Ref. 12. It is now known that this was in fact the value of k_H for the reaction of benzoate radicals with tributylstannane. The value of k_c given in the text is based on a new value for k_H recently determined in these laboratories.)

$$\log k_c/s^{-1} = (11\cdot26 \pm 0\cdot12) - (4\cdot30 \pm 0\cdot16)/\theta \quad (2)$$

$$\log k_N/M^{-1}s^{-1} = (9\cdot29 \pm 0\cdot21) - (0\cdot77 \pm 0\cdot24)/\theta \quad (3)$$

The value of k_N at 25 $^{\circ}$C calculated from equation (3) is 5.3×10^8 M^{-1}s^{-1}. By comparison with other intermolecular reactions of aryl radicals, the value of $\log A$ seems low; we suggest, therefore, that the true values are probably at the upper end of the range, i.e.
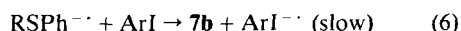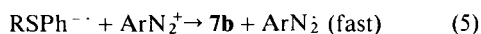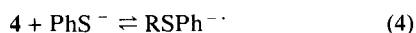
$\log A/M^{-1}s^{-1} \approx 9\cdot5$ and $E \approx 1\cdot0$ kcal mol^{-1}, and the reaction is close to being under diffusion control.

The photostimulated reactions of the iodoarene, 1 with thiophenoxide ion in liquid ammonia, acetonitrile or dimethyl sulphoxide were more complex than those involving diphenylphosphide anion in that they afforded not only the substitution products 5b and 7b but also the reduced cyclized product 8 and, in some cases, the dimer 9. The formation of 5b and 7b indicates that the reaction conforms to the generalized $S_{RN}1$ mechanism of Scheme 1 in which ring closure competes with the Ar$^{\cdot}$/PhS$^-$ addition step.

The most plausible pathway to the product 8 involves reduction of 4 by RSPh$^{-\cdot}$, ArSPh$^{-\cdot}$ or PhS$^-$, followed by protonation, while 9 clearly arises by dimerization of 4. Both of these processes must be in competition with the coupling of 4 with thiophenoxide ion. At first sight the results suggest that the coupling step must be relatively slow, but this cannot be so because when 4 was formed from the appropriate diazonium salt in the presence of PhS$^-$ it was converted quantitatively into 7b.[8] The only plausible conclusion is that coupling of 4 with PhS$^-$ is fast but reversible [equation (4)].[13] In the diazonium salt reactions, the fast reduction of RSPh$^{-\cdot}$ by the diazonium ion [equation (5)] competes effectively with
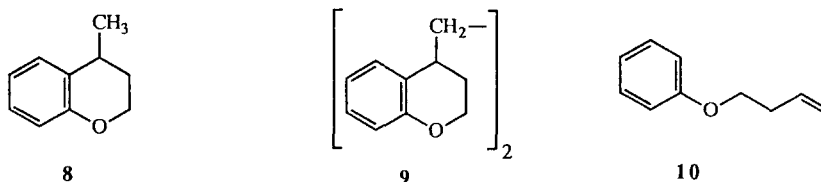
the reverse of the coupling step [equation (4)]. However, we suggest that when the aryl iodide 1 is the substrate, the reduction step [equation (6)] is much slower, the equilibrium of equation (4) is established and the conversion of 4 into 8 and 9 now competes with formation of 7b by the reaction of equation (6). In the light of this hypothesis it is not surprising that the relative yields of 7b, 8 and 9 are highly variable, since the relative rates of their formation will be related to the stationary concentrations of RSPh$^{-\cdot}$, ArSPh$^{-\cdot}$ and 4. These in turn depend on such imponderable factors as initiation and termination rates.

$$4 + PhS^- \rightleftharpoons RSPh^{-\cdot} \qquad (4)$$

$$RSPh^{-\cdot} + ArN_2^+ \rightarrow 7b + ArN_2^\cdot \text{ (fast)} \qquad (5)$$

$$RSPh^{-\cdot} + ArI \rightarrow 7b + ArI^{-\cdot} \text{ (slow)} \qquad (6)$$

Despite the complexity of the product mixtures it is still possible to determine values of k_N since the essential competition is between the reaction of 2 with PhS$^-$ (assumed to be irreversible under the experimental conditions used here) and its cyclization to give 4 from whence all the other products are derived. Hence, the above rate equation [equation (1)] can be applied when $[ArNu]_f = [5b]_f$ and $[RNu]_f = [7b]_f + [8]_f + 2[9]_f$. The experimental results and derived values of k_N/k_c are given in Table 3.

The experimental data afford the temperature dependence of k_N/k_c as $\log(k_N/k_c)/M = -(1\cdot43 \pm 0\cdot60) + (2\cdot41 \pm 0\cdot79)/\theta$. Substitution of the value for $\log k_c$ [equation (2)] gives the Arrhenius equation [equation (7)] from which the rate constant for reaction of 2 with PhS$^-$ is $k_N = 2\cdot6 \times 10^8$ M^{-1}s^{-1} at 25 °C.

$$\log k_N/M^{-1}s^{-1} = (9\cdot83 \pm 0\cdot61) - (1\cdot89 \pm 0\cdot79)/\theta \quad (7)$$

The relatively large uncertainties in the values of log A and E undoubtedly reflect the experimental errors associated with the difficulty of accurately analysing such complex reaction mixtures. Under these circumstances, the agreement with the data previously obtained by diazonium salt chemistry can be regarded as satisfactory. However, the latter work,[8] which affords Arrhenius equation (8) and gives $k_N = 8\cdot2 \times 10^7$ M^{-1}s^{-1} at 25 °C, should be regarded as the more reliable.

$$\log k_N/M^{-1}s^{-1} = 9\cdot71 - 2\cdot45/\theta \qquad (8)$$

The only other quantitative determinations of the rate constants for reactions of aryl radicals with PhS$^-$ appear to be those of Amatore et al.,[9] who found values of k_N in the range 10^7-10^{10} M^{-1}s^{-1}. For the phenyl radical itself Amatore et al. gave a value of $2\cdot6 \times 10^7$ M^{-1}s^{-1} at -33°C, in excellent agreement with that $(3\cdot0 \times 10^7$ M^{-1}s$^{-1})$ calculated from equation (8).

The relative reactivity of diphenylphosphide anion and PhS$^-$ towards p-anisyl radicals in dimethyl sulphoxide has been measured by Palacios et al.[14] The value obtained at 25 °C in dimethyl sulphoxide (8·4) is in reasonable agreement with that (6·5) calculated from equations (3) and (8).

The photostimulated reaction of 1 with potassium diethylphosphite in liquid ammonia gave reduced products 8 and 10 together with the expected substitution products 5c and 7c. The last two arise, presumably, by the general mechanism of Scheme 2 involving coupling of the diethylphosphite anion with

Table 3. Photostimulated reactions of 1 with NaSPh in dimethyl sulphoxide

Experiment No.	[NaSPh] (M)	Temperature (K)	Product yield (%)[a]				k_N/k_c(M^{-1})
			5b	7b	8	9	
1	0·15	295	20	52	20	7	1·66
2	0·59	301	56	7	38	—	2·10
3	0·59	317	51	1	48	—	1·76
4	0·59	337	47	27	25	—	1·62
5	0·15	355	12	38	49	—	0·93
6	0·59	357	40	32	27	—	1·15
7	0·15	415	8	16	76	—	0·60

[a] Relative yield quantified by GC.

the aryl and alkyl radicals, 2 and 4, respectively. The latter appears to be the first example of this class of reaction since previous attempts to observe $S_{RN}1$ reactions of this anion with alkyl substrates were unsuccessful.[15,16] Since the mode of formation of the reduced products 8 and 10 is not clear, it is not possible to derive accurate kinetic data. However, the ratio of cyclized to uncyclized products suggests that $k_N \approx 10^8$ $M^{-1}s^{-1}$ at $-33\,°C$.

We were unable to bring about the reaction of potassium diethylphosphite with 1 in dimethyl sulphoxide, whereas in tetrahydrofuran the major products were 8 and 10. Presumably, in the latter solvent, direct H⁻ abstraction from the solvent by 2 or 4 is sufficiently fast to compete effectively with coupling with the nucleophile.

Unlike iodobenzene, which gives high yields of substitution product when treated with the enolate of pinacolone in dimethyl sulphoxide,[17] the iodoarene 1 failed to react under similar conditions. It also did not react with acetone enolate in either dimethyl sulphoxide or liquid ammonia. We believe that the coupling of either of these nucleophiles with the aryl radical 2 is insufficiently fast to compete with its cyclization to give 4. However, 4, once formed, like other alkyl radicals (adamantyl and neopentyl),[15,16] reacts with the enolate ion too slowly to maintain chain propagation.

Aliphatic substitution

It has been suggested that various aliphatic substrates, including bridgehead halides,[15] cyclopropyl halides,[18] neopentyl halides,[16,19] and alkylmercury halides,[20] can undergo reaction with nucleophiles by the $S_{RN}1$ mechanism. However, in some cases the experimental evidence is not clear and in others, e.g. the reactions of some alkyl halides with thiolates, it favours the simultaneous occurrence of polar and free radical mechanisms, with the latter involving single electron transfer and cage recombination.[21] In order to clarify further the mechanism of photostimulated nucleophilic substitution at neopentyl centres, we examined reactions of 11a and 11c, each of which is potentially capable of generating a radical expected to undergo fast ring closure.

Treatment of 11a with potassium thiophenoxide in liquid ammonia afforded both uncyclized and cyclized substitution products, 15a and 17a, respectively, albeit in modest yield (Table 4). Formation of the latter must involve the cyclization step 12a → 14a and so provides unambiguous evidence for the intermediacy of the free radical 12a and for the involvement of the $S_{RN}1$ mechanism. When 11a was similarly treated with thiophenoxide in acetonitrile there was no reaction. However, potassium diphenylphosphide, when added

(a) X = CH_2, Nu = SPh
(b) X = CH_2, Nu = PPh_2
(c) X = O, Nu = SPh
(d) X = O, Nu = PPh_2
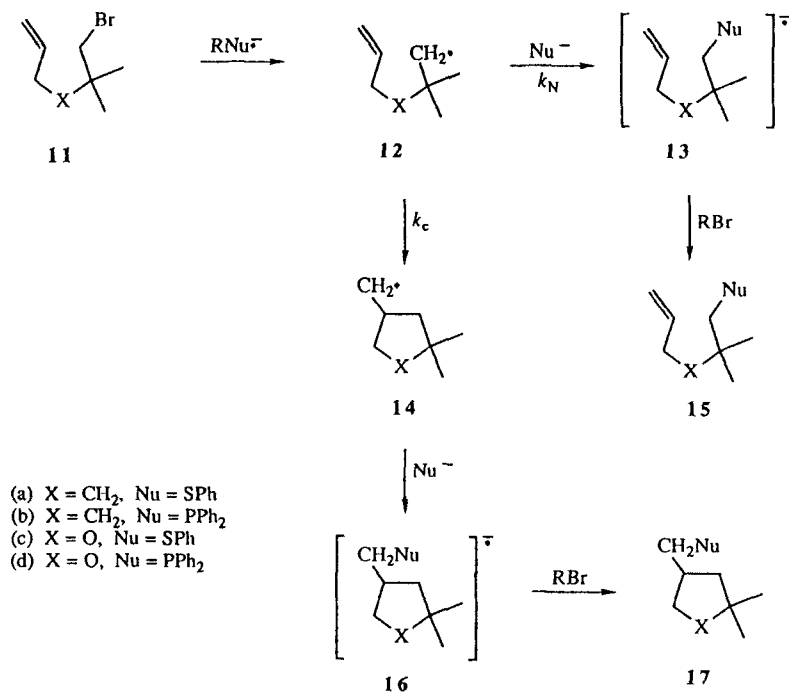
in small amounts (up to 10 mol%), acted as an initiator, and both **15a** and **17a** were then obtained in good combined yield (Table 4). If we assume that a mechanism similar to that of Scheme 2 applies, it is possible to calculate relative and absolute rate constants in the usual way. The data give $k_N/k_c = 42$ M^{-1} at 29 °C and since the rate constant for cyclization of **12a** at this temperature is known[22] to be $k_c = 3 \cdot 0 \times 10^6$ s^{-1}, it follows that the rate constant for the reaction of the alkyl radical **11a** with PhS$^-$ is $k_N = 1 \cdot 2 \times 10^8$ $M^{-1}s^{-1}$.

In dimethyl sulphoxide the reaction proceeded smoothly but the yields were modest and the products included diphenyl sulphide. The most reasonable mechanism for formation of the latter involves interaction of PhS$^-$ with phenyl radicals generated together with the appropriate alkanethiolate anion by decomposition of the radical anions **13a** and **16a**. The formation of diphenyl selenide in reactions of neopentyl bromide with PhSe$^-$ has been similarly rationalized.[16,20] In both cases the generation of Ph· provides evidence for the intermediacy of radical anions and hence for the validity of the $S_{RN}1$ mechanism. Because of the formation of diphenyl sulphide it is not possible to determine rate constants accurately. The usual procedure gives an approximate value of $k_N \approx 2 \times 10^8$ $M^{-1}s^{-1}$.

When **11a** was treated with potassium diphenyl-phosphide in acetonitrile only the uncyclized substitu-

tion produce (**15b**) was obtained, an outcome consistent with either an S_N substitution or an $S_{RN}1$ substitution involving a very fast radical/nucleophile coupling step. Evidence in favour of the latter hypothesis was obtained when the substrate **11c** was employed. Treatment of **11c** in the usual way with potassium thiophenoxide in liquid ammonia gave as the major product the cyclized compound **17c** (Table 5), the formation of which confirms the intermediacy of the radical **12c** in the reaction. When the experiment was repeated in dimethyl sulphoxide both cyclized (**17c**) and uncyclized (**15c**) products were obtained (Table 5). The usual calculations when applied to these results give $k_N/k_c \approx 1 \cdot 1$ M^{-1}. Unfortunately, a reliable value of k_c for the radical **12c** is not yet available. However, it is known that substitution of an oxygen atom into the 3-position of the hexenyl radical increases the value of k_c by a factor of 42 at 25 °C.[23] If the oxygen atom in **12c** has a similar effect, it follows that k_c (**12c**) $\approx 40k_c$ (**12a**), i.e. k_c for **12c** at 25 °C is about $1 \cdot 2 \times 10^8$ s^{-1}. The assumption that k_N for the reaction of PhS$^-$ with **12a** is about the same as that for the reaction with **12c** leads to a similar conclusion, since k_N/k_c (**12a**) $\approx 40k_N/k_c$ (**12c**).

Only one experiment was conducted in which **11c** was treated with diphenylphosphide anion in acetonitrile (Table 5). The formation of both cyclized (**17d**) and uncyclized (**15d**) products clearly indicates the

Table 4. Photostimulated reactions of **11a** with nucleophiles[a]

| Experiment No. | Reagent | [Nu$^-$] (M) | Solvent | Product yield (%)[b] | | | |
				15a	17a	15b	Ph$_2$S
1	KSPh	0·049	NH$_3$	13	12	—	—
2	KSPh	0·020	DMSO	29	21	—	28
3	KSPh	0·050	ACN	No reaction			
4	KSPh[c]	0·050	ACN	62	26	—	—
5	KPPh$_2$	0·057	ACN	—	—	95	—

[a] Reaction in NH$_3$ at −33 °C; others at room temperature (ca 25 °C).
[b] Relative yield quantified by GC.
[c] KPPh$_2$ (10 mol%) was added.

Table 5. Photostimulated reactions of **11c** with nucleophiles[a]

| Experiment No. | Reagent | [Nu$^-$] (M) | Solvent | Product yield (%)[b] | | | |
				15c	17c	15d	17d
1	KSPh	0·15	NH$_3$	0·8	52	—	—
2	KSPh	0·73	DMSO	33	41	—	—
3	KSPh	1·95	DMSO	26	—	—	—
4	KPPh$_2$	0·05	ACN	—	—	36	64

[a] Reactions conducted at room temperature (ca 25 °C).
[b] Relative yield quantified by GC.

intermediacy of the radical **12c** and confirms the $S_{RN}1$ nature of the reaction. The usual calculations give $k_N/k_c \approx 11 \cdot 0$. It follows that $k_N \approx 1 \cdot 3 \times 10^9 \, M^{-1} s^{-1}$. However, the fact that this is greater than the value of k_N for the reaction of $^-PPh_2$ with the aryl radical **2** raises doubts about its validity; clearly, further experiments are required to determine reliable values of k_c and k_N/k_c for the radical **12c**.

CONCLUSIONS

This work demonstrates the utility of radical clocks as mechanistic probes and kinetic yardsticks. In this case their use has led to the following conclusions:

(i) Photostimulated reactions of the iodoarene **1** with the PhS^-, Ph_2P^-, and $^-PO(OEt)_2$ anions involve the intermediacy of the aryl radical **2**, and proceed by the $S_{RN}1$ mechanism.

(ii) The reaction of ^-SPh with the aryl radical **2** had $\log A/M^{-1}s^{-1} = 9 \cdot 83 \pm 0 \cdot 61$, $E = 1 \cdot 89 \pm 0 \cdot 79$ kcal mol^{-1} and $k_N = 8 \cdot 2 \times 10^7 \, M^{-1} s^{-1}$ at 25 °C in dimethyl sulphoxide, in reasonable agreement with previous estimates.

(iii) The reaction of Ph_2P^- with the aryl radical **2** in acetonitrile has $\log A/M^{-1}s^{-1} = 9 \cdot 29 \pm 0 \cdot 21$, $E = 0 \cdot 77 \pm 0 \cdot 24$ kcal mol^{-1} and $k_N = 5 \cdot 3 \times 10^8 \, M^{-1} s^{-1}$.

(iv) The formation of the products **7a**, **7b** and **7c** indicates that the primary alkyl radical **4** reacts with the nucleophiles $^-PPh_2$, ^-SPh and $^-PO(OET)_2$ to maintain the radical chain.

(v) Photostimulated reactions of the bromides **11a** and **11c** with ^-SPh and $^-PPh_2$ involve the intermediacy of the neopentyl radicals **12a** and **12c** and proceed by the $S_{RN}1$ mechanisms.

(vi) The reaction of **12a** with ^-SPh has a value of k_N of about $1 \cdot 2 \times 10^8 \, M^{-1} s^{-1}$ at 25 °C. However, the value of k_N for the reaction of **12a** with $^-PPh_2$ (ca $1 \cdot 3 \times 10^9 \, M^{-1} s^{-1}$ at 25 °C) determined here appears to be too high in comparison with the value of the rate constant for the reaction of $^-PPh_2$ with the aryl radical **2**.

EXPERIMENTAL

General methods. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX200 spectrometer operating at 199·5 or 50·1 MHz; chemical shifts are given in parts per million (ppm) relative to tetramethylsilane. Gas chromatography (GC) was conducted on Varian 3400 and 6000 chromatographs fitted with flame ionization detectors and Hewlett-Packard 3390A recorders/integrators. Glass columns packed with 3% SE-30 on Chromosorb W or with OV-17 on Gas-Chrom Q were employed with helium as the carrier gas.

Materials. Dimethyl sulphoxide (DMSO) was dis-

tilled twice under vacuum from calcium hydride and stored under nitrogen in a bottle fitted with a septum. Acetonitrile (ACN) was dried over calcium hydride, distilled twice under nitrogen from phosphorus pentoxide and stored under nitrogen. Thiophenol was distilled twice under vacuum from sodium hydroxide pellets and stored under nitrogen. Standard sodium thiophenoxide solutions were prepared by careful addition of sodium hydride (1·2 molar equivalents) to thiophenol in DMSO, and the mixture was then diluted appropriately with a further amount of solvent. Diphenylphosphine was used as received from Ega Chemie. Solutions of potassium diphenylphosphide were prepared by addition of freshly sublimed potassium *tert*-butoxide to diphenylphosphine in the appropriate solvent.

o-(But-3-enyloxy)iodobenzene was prepared as described previously[24] by treatment of *o*-iodophenol with 4-bromobut-1-ene and sodium hydroxide in water under reflux.

Bromination of 2-methylpropene with bromine in carbon tetrachloride gave a mixture of 1,2-dibromo-2-methylpropane, b.p. 50 °C (10 mmHg); ^1H NMR (CDCl$_3$), δ 1·91 (s, 3H), 3·80 (s, 1H), and 1,2,3-tribromo-2-methylpropane, b.p. 70–80 °C (0·2 mmHg); ^1H NMR (CDCl$_3$), δ 1·90 (s, 3H), 3·90 (s, 4H). Dropwise addition of silver perchlorate (5·2 g) in allyl alcohol (10 ml) to a solution of the former dibromo compound (5·2 g) and DABCO (1·40 g) in allyl alcohol (8 ml) gave crude 1-(2-propenyloxy)-2-bromo-2-methylpropane (4·0 g, 85%), which was purified by column chromatography on silica to give a clear oil, b.p. 50 °C (0·3 mmHg); ^1H NMR (CDCl$_3$), δ 1·33 (s, 6H), 3·35 (s, 2H), 3·81 (d, 2H), 5·0–6·1 (m, 3H).

6-Bromo-5,5-dimethylhex-1-ene was prepared as described previously.[25]

Procedures. Reactions in liquid ammonia were conducted in a flask fitted with a dry-ice condenser, nitrogen inlet and magnetic stirrer. Ammonia (*ca* 250 ml) was distilled into the flask and the conjugate acid of the nucleophile was added followed by a slight excess of the appropriate base (sodium hydride or potassium *tert*-butoxide). The amount of reagent used is given in the tables. The halo compound (10 mol% with respect to the nucleophile) was then added and the mixture was irradiated with a 400-W high-pressure mercury lamp until all of the substrate was consumed. The ammonia was then removed by evaporation, water was added and the products were extracted with diethyl ether–dichloromethane and analysed by GC (OV-17). Yields of products are given in the tables.

Reactions in ACN, DMSO or THF were conducted similarly. In a typical experiment freshly sublimed potassium *tert*-butoxide was dissolved in the solvent (10–20 ml) and degassed. Diphenylphosphine was then added from a syringe followed by the iodo compound

1. The solution was then irradiated for 3 h, ammonium nitrate was added and the solvent was removed by evaporation under reduced pressure. The residue was extracted with dichloromethane and the extract was shaken with 30% hydrogen peroxide to convert the products to their oxides.[10] The mixture was then analysed by GC on an OV-17 capillary column with docosane as an internal standard. Yields of products are given in the tables.

Reactions of 1 with potassium diphenylphosphide. Medium-pressure liquid chromatography (MPLC) on silica with hexane–ethyl acetate (4:1) as solvent of the mixture obtained by oxidation of the crude product with 30% hydrogen peroxide gave (i) 2-(3-butenyloxy)-phenyl diphenylphosphine (5a) as its oxide; ^{1}H NMR (CDCl$_3$), δ 2·2–2·4 (m, 2H), 3·9 (t, 2H), 4·8–5·0 (m, 2H), 5·4–5·6 (m, 1H) 6·7–7·9 (m, 14H); (ii) (3,4-dihydro-2H-1-benzopyran-4-yl)methyldiphenyl-phosphine (7a) as its oxide; ^{1}H NMR (CDCl$_3$), δ 1·9–2·2 (m, 2H), 2·5–2·9 (m, 2H), 3·2–3·5 (m, 1H), 4·1 (m, 2H), 6·7–8·0 (m, 14H); ^{13}C NMR (CDCl$_3$), δ 27·5, 30·8, 36·5, 62·5, 115·6, 118·8, 126·13, 127·8, 128·1, 131·4, 131·9, 132·2, 132·6, 152·6; mass spectrum, m/z (relative intensity, %) 348 (M$^+$, 4), 215 (3), 202 (37), 88 (37), 77 (5), 73 (31), 70 (46), 61 (100).

Reactions of 1 with sodium thiophenoxide. MPLC of the product mixture on silica with hexane–dichloro-methane (1:1) as solvent gave 2-(but-3-enyloxy)phenyl-thiobenzene (5b) and 4-phenylthiomethyl-3,4-dihydro-2H-1-benzopyran (7b), identical with samples previously prepared in these laboratories, and 1,2-di-(3,4-dihydro-2H-1-benzopyran-4-yl)ethane (9), which crystallized from hexane, m.p. 80–81 °C; ^{1}H NMR, δ 1·2–2·2 (m, 8H), 2·7–3·0 (m, 2H), 4·2 (m, 4H), 6·8–7·3 (m, 8H); mass spectrum, m/z (relative intensity, %) 294 (M$^+$, 46), 147 (6), 133 (100), 105 (15).

Reactions of 1 with potassium diethylphosphite. MPLC of the crude product on silica with ethyl acetate as eluent gave (i) 1-(3-butenyloxy)-2-diethoxyphos-phorylbenzene (5c); ^{1}H NMR (CDCl$_3$), δ 1·3 (t, 6H), 2·2 (m, 2H), 4·1 (m, 6H), 5·0–6·1 (m, 3H), 6·7–7·9 (m, 4H); mass spectrum m/z (relative intensity, %), 284 (6), 254 (13), 230 (100), 174 (62); (ii) 4-diethyoxyphos-phorylmethyl-3,4-dihydro-2H-1-benzopyran (7c); ^{1}H NMR (CDCl$_3$), δ 1·3 (s, 6H), 2·0–2·3 (m, 4H), 3·1–3·4 (m, 1H), 3·9–4·2 (m, 6H), 6·6–7·2 (m, 4H); mass spectrum, m/z (relative intensity, %) 284 (25), 255 (4), 227 (3), 146 (100), 131 (20).

Reactions of 11a with potassium thiophenoxide. Preparative GC (silicone) gave (i) 5,5-dimethyl-6-(phenylthio)hex-1-ene (15a); ^{1}H NMR (CDCl$_3$), δ 1·0 (s, 6H), 1·4 (m, 2H), 2·0 (m, 2H), 2·9 (s, 2H), 4·9–5·1 (m, 2H), 5·7–5·9 (m, 1H) 7·1–7·4 (m, 5H); mass

spectrum, m/z (relative intensity, %) 220 (M$^+$, 26), 165 (41), 123 (62), 110 (63), 69 (22), 55 (100); (ii) 1,1-dimethyl-3-phenylthiomethylcyclopentane (17a); ^{1}H NMR (CDCl$_3$), δ 0·9 (s, 3H), 1·1 (s, 3H; m, 1H), 1·2 (m, 1H), 1·7 (m, 1H), 1·9 (m, 1H), 2·3 (m, 1H), 2·9 (d, 2H), 7·1–7·4 (m, 5H); mass spectrum, m/z (relative intensity, %) 220 (69), 165 (11), 123 (17), 110 (100), 109 (13), 95 (26), 55 (45).

Reaction of 11a with potassium diphenylphosphide. Radial chromatography of the crude oxidized (30% hydrogen peroxide) product on silica with diethyl ether as solvent gave 2,2-dimethylhex-5-enyldiphenyl-phosphine (17c) as its oxide; ^{1}H NMR (CDCl$_3$), δ 1·0 (s, 6H), 1·4 (m, 2H), 2·1 (m, 2H), 2·3 (d 2H), 4·9 (m, 2H), 4·7 (m, 1H), 7·4–7·9 (m, 10H).

Reaction of 11c with potassium thiophenoxide. Radial chromatography of the crude product on silica with diethyl ether as solvent gave (i) 2-allyloxy-2-methyl-1-phenylthiopropane (15c); ^{1}H NMR (CDCl$_3$), δ 1·3 (s, 6H), 3·1 (s, 2H), 3·9 (d, 2H), 5·2 (m, 2H), 5·9 (m, 1H), 7·1–7·4 (m, 5H); ^{13}C NMR (CDCl$_3$), δ 24·8, 29·2, 44·4, 62·4, 114·5, 124·1, 127·1, 127·6, 134·0; mass spectrum, m/z (relative intensity, %) 222 (M$^+$, 100), 207 (13), 166 (23), 149 (43), 112 (62), 110 (75), 97 (65), 56 (45), 55 (74).

Reaction of 11c with potassium diphenylphosphide. Preparative thin-layer chromatography on silica with methanol as solvent of the material obtained by oxidation with 30% hydrogen peroxide of the crude product gave (i) 2-allyloxy-2-methylpropyldiphenyl-phosphine (15d) as its oxide, m.p. 110–112 °C; ^{1}H NMR (CDCl$_3$), δ 1·3 (s, 6H), 2·6 (d, 2H), 3·8 (d, 2H), 5·0 (m, 2H), 5·6 (m, 1H), 7·3–7·8 (m, 10H); mass spectrum, m/z (relative intensity, %) 314 (M$^+$, 0·6), 313 (1·5), 257 (36), 241 (9), 215 (63), 200 (100), 183 (11), 141 (10), 77 (48); (ii) 2,2-dimethyltetrahydrofuran-4-ylmethyldiphenylphosphine (17d) as its oxide; ^{1}H NMR (CDCl$_3$), δ 1·1 (s, 3H), 1·2 (s, 3H), 1·4 (m, 1H), 1·9 (m, 1H), 2·3 (m, 2H), 2·6 (m, 1H), 3·3 (t, 1H), 3·8 (t, 1H), 7·3–7·9 (m, 10H); mass spectrum, m/z (relative intensity, %) 314 (M$^+$, 19), 299 (63), 215 (100), 202 (84), 20 (72), 183 (21), 155 (22), 125 (37), 77 (55).

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