cis coupling constant being 6–7 Hz and the trans coupling constant 12–14 Hz.[26] The configurations of the geometric isomers of **9** were assigned as follows. The first step in the synthesis of **9** involves a reaction between the dimethyl acetal of methyl isobutyl ketone and 2-bromoethanol under acid conditions, which leads to a formation of the isomeric species $i\text{-BuC(OCH}_2\text{CH}_2\text{Br)}{=}\text{CH}_2$ and (*E*)- and (*Z*)-$\text{MeC(OCH}_2\text{CH}_2\text{Br)}{=}\text{CHPr-}i$. From previous thermodynamic studies[12,17,19] it can be inferred that the more stable geometric isomer has the *E* configuration. In the second step, HBr is eliminated from the product of the first stage, and since this process is carried out under basic conditions, no (significant) isomerization occurs during this step. Hence the predominating geometric isomer of the final synthetic mixture must have the *E* configuration. The same arguments were applied for the identification of the geometric isomers of **10**.

Determination of Normal Boiling Points. The standard enthalpies and entropies of vaporization at 298.15 K were estimated from the values of the normal boiling points of the compounds studied. The boiling points were determined by the gas chromatographic method described previously.[12] The values obtained follow (in °C): **4a,** 67.0; **4b,** 62.0; **5a,** 121.3; **5b,** 117.0; **6a,** 101.9; **6b,** 98.5; **6d,** 93.5; **7a,** 125.8; **7b,** 121.8; **7c,** 120.0; **7d,** 113.8; **8a,** 138.5; **8b,** 135.3; **8c,** 131.0; **8d,** 125.0; **9a,** 114.8; **9b,** 120.4; **9c,** 114.8; **10a,** 135.8; **10b,** 138.1; **10c,** 130.8; **11a,** 95.7; **11b,** 107.9; **12a,** 72.6; **12b,** 62.6; **13a,** 86.3; **13b,** 80.0.

Equilibrations. The equilibration experiments on **4–8** and **12–13** were carried out in the neat liquid with $Hg(OAc)_2$ as catalyst, and those on **9–11** in cyclohexane solution with I_2 as catalyst. Whenever available, pure isomers were used as starting materials for the equilibrations. In all cases the position of equilibrium was approached from at least two starting mixtures with sufficiently different isomer compositions to be sure that the true thermodynamic equilibrium had been achieved. The equilibrations were carried out at at least four temperatures between 273 and 423 K. The equilibrated samples were analyzed by GLC using an 8-m Carbowax column. The gas chromatograph was equipped with a HP 3370 B electronic integrator for determining the peak areas. For more details of the equilibration procedure see ref 10 and the previous papers of this series.

Acknowledgment. The authors thank Miss Hannele Kalva, M.S., for some experimental aid.

Registry No.—**4a,** 24268-10-8; **4b,** 24268-09-5; **5a,** 40716-31-2; **5b,** 40716-32-3; **6a,** 4696-28-0; **6b,** 4696-29-1; **6c,** 4696-27-9; **7a,** 61463-28-3; **7b,** 61463-29-4; **7c,** 61463-30-7; **7d,** 61463-31-8; **8a,** 61463-32-9; **8b,** 61463-33-0; **8c,** 61463-34-1; **8d,** 61463-35-2; **9a,** 61463-36-3; **9b,** 61463-37-4; **9c,** 61463-38-5; **10a,** 61463-39-6; **10b,** 61463-40-9; **10c,** 61463-41-0; **11a,** 61463-42-1; **11b,** 61463-43-2; **12a,** 10034-13-6; **12b,** 10034-12-5; **13a,** 31915-76-1; **13b,** 31915-77-2; allyl alcohol, 107-18-6; ethyl vinyl ether, 109-92-2; isobutyraldehyde diallyl acetal, 37406-14-7; isobutyraldehyde, 78-84-2; isobutyraldehyde dipropenyl acetal, 39801-12-2; diallyl ether, 557-40-4; butyraldehyde diallyl acetal, 35020-94-1; butyraldehyde, 123-72-8; isovaleraldehyde, 590-86-3; methyl isobutyl ketone dimethyl acetal, 1112-78-3; 2-bromoethanol, 540-51-2; 1-chloro-2-propanol, 127-00-4; methyl isopropyl ketone dimethyl acetal, 59554-08-4; butyraldehyde dimethyl acetal, 4461-87-4; isovaleraldehyde dimethyl acetal, 57094-35-6.

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Dark Reactions of Halobenzenes with Pinacolone Enolate Ion. Evidence for a Thermally Induced Aromatic $S_{RN}1$ Reaction[1a]

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Iodo- and bromobenzene react with potassium pinacolone enolate in dimethyl sulfoxide at 25 °C in the dark to form the substitution product, $PhCH_2COC(CH_3)_3$. The reaction behaves in fashion consistent with the $S_{RN}1$ radical chain mechanism but inconsistent with nonchain mechanisms. It is inhibited by the electron scavengers *p*-dinitrobenzene and benzophenone and by the radical scavenger di(*tert*-butyl) nitroxide. It is accelerated by light, and the iodobenzene/bromobenzene reactivity ratio, about 6, is the same in the dark and the photostimulated reactions. Some features of it are not understood: a strange rate law and extraordinary accelerations by O_2, nitrobenzene, and ferric nitrate. Several observations serve to rule out an aryne mechanism, but in the case of *m*-iodoanisole an aryne side reaction was encountered.

In recent years it has been found that halobenzenes, unsubstituted or provided even with electron-releasing substituents, will react with certain nucleophiles under stimulation by electrons or photons to form products of substitution. The behavior of these reactions is consistent with the $S_{RN}1$ mechanism,[2] a radical chain mechanism, but not with the longer known S_NAr or benzyne mechanisms. A representative aromatic $S_{RN}1$ reaction is that of phenyl halides with ketone enolate ions[3–6] of which the sort shown in eq 1 will be our present interest.

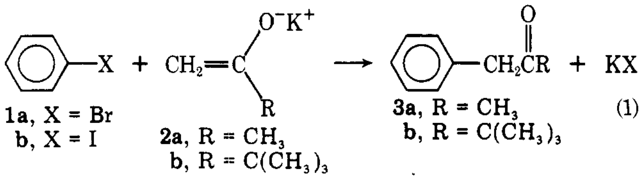
A radical chain mechanism comprises initiation, propagation, and termination steps. Of these, the steps in the propa-

Table I. Reactions of *m*-Iodoanisole with Potassium Pinacolone Enolate (2b) and/or *t*-BuOK in Me$_2$SO at 25 °C

Expt no.	$[\mathrm{ArI}]_0$,[a] M	$[\mathbf{2b}]_0$, M	$[t\text{-BuOK}]_0$, M	$[\mathrm{DNB}]_0$,[b] M	Time, min	Product yields, % I$^-$	**5b**	**6**	Ratio, **6**/**5b**
1	0.082	0.288	0.038		180	89	58	11	0.19
2	0.0073	0.288	0.038		60	84	51	15	0.29
3	0.0074	0.288	0		60	*c*	58	13	0.22
4	0.0068	0.288	0.038		1	27	26	1	0.05
5	0.0076	0	0.18		45	96		44	
6	0.0066	0.288	0.038	0.0011	10	27	*c*	*c*	
					21	43	16	13	0.84
7	0.0081	0.288	0.038	0.0031	60	*c*	*d*	*d*	1.03

[a] ArI is *m*-iodoanisole. [b] DNB is *p*-dinitrobenzene. [c] Not determined. [d] Because no internal standard was used, only the **6**/**5b** product ratio could be determined.

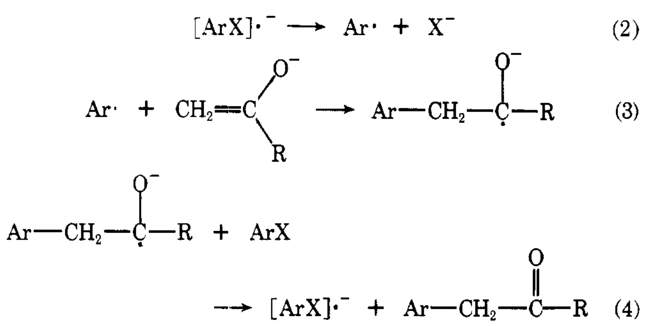
gation cycle are the most characteristic of a given reaction, for various methods of initiation of the same reaction can often be employed and the addition of appropriate substances can often change the termination events. The postulated propagation cycle for the reactions of eq 1 is shown in Scheme I.



1a, X = Br
b, X = I
2a, R = CH$_3$
b, R = C(CH$_3$)$_3$
3a, R = CH$_3$
b, R = C(CH$_3$)$_3$

(1)

Scheme I



$$[\mathrm{ArX}]\cdot^- \longrightarrow \mathrm{Ar}\cdot + \mathrm{X}^- \quad (2)$$

$$\mathrm{Ar}\cdot + \mathrm{CH_2{=}C(O^-)R} \longrightarrow \mathrm{Ar{-}CH_2{-}\dot{C}(O^-){-}R} \quad (3)$$

$$\mathrm{Ar{-}CH_2{-}\dot{C}(O^-){-}R} + \mathrm{ArX} \longrightarrow [\mathrm{ArX}]\cdot^- + \mathrm{Ar{-}CH_2{-}C({=}O){-}R} \quad (4)$$

In Scheme I, the first propagation step shown is scission of the radical anion of the reacting aryl halide to give an aryl radical and halide ion. The next is combination of the aryl radical with an enolate ion to give a radical anion of the sort sometimes called a ketyl. The last (step 4) is an electron transfer from the ketyl to another aryl halide molecule, furnishing the arylated ketone product as well as the aryl halide radical anion which is the reactant in step 2. Other modes of reaction of the ketyl are also conceivable.

It is plain why solvated electrons in liquid ammonia act to stimulate aromatic S$_{\mathrm{RN}}$1 reactions: they convert aryl halides or other substrates to their radical anions, $[\mathrm{ArX}]\cdot^-$, which enter the propagation sequence at step 2. Stimulation of these reactions by photons may involve photolysis of the C–X bond[7] or photostimulation of electron transfer from the nucleophile to the substrate.

The initial recognition of aromatic substitution by the S$_{\mathrm{RN}}$1 mechanism concerned a reaction, that of some iodopseudocumenes with amide ion in ammonia,[2] that did not depend on stimulation by electrons or photons (unless from the diffuse light of the laboratory). There has, however, been little other evidence of thermally induced aromatic substitution by this mechanism.[8] We recently encountered such a reaction,[9] and now report some of its characteristics.

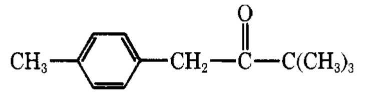
Results

In the course of a brief investigation of photostimulated reactions of bromo- and iodobenzene with ketone enolate ions in dimethyl sulfoxide (Me$_2$SO) solution, which occur according to eq 1 except that there is also some diphenylation, we observed that substantial reaction also occurs at room temperature without illumination.[10a] For example, iodobenzene (0.1 M) reacted with potassium acetone enolate (0.4 M) at ca. 23 °C to release 31% of iodide ion in only 12 min in the dark.

In the photochemical studies it was found that potassium pinacolone enolate (**2b**) reacts about as rapidly as the acetone enolate (**2a**) but gives less diphenylation product and less by-products attributable to aldol condensation. Reactions with **2b** were chosen for principal emphasis in the present work. Iodobenzene (0.1 M) with **2b** (0.4 M) reacting 30 min in the dark released iodide ion in 68% yield. In another experiment, 73% of iodide ion and 70% of 1-phenyl-3,3-dimethyl-2-butanone (**3b**) were formed during 60 min in the dark. In still others, **1b** (0.01M) and **2b** (0.3 M) reacted during 105 min to form **3b** in quantitative yield, and **1b** (0.023 M) with **2b** (0.1 M) afforded 81% of **3b** in a 20-h dark reaction.

Bromobenzene is less reactive. During 90 min in the dark, **1a** (0.1 M) and **2b** (0.4 M) released only 9% of bromide ion. The product of reaction of **1a** with **2b** was shown to be **3b**.

Other aryl iodides were found also to react in the dark in the manner of eq 1. Indeed, we shall report separately on substituent effects on reactivity in such reactions.[10b] We mention here only certain observations that bear on the possibility of an aryne mechanism, either for the main reaction or as a subsidiary reaction pathway. *p*-Iodotoluene reacted with **2b** to give the anticipated *p*-tolyl product (**4**) while *m*-iodotoluene gave its meta isomer (**5a**), each of these isomeric products free of contamination by the other. *m*-Iodoanisole afforded **5b** in 58% yield, but also 13% of a wholly different kind of product, namely, phenol **6**.



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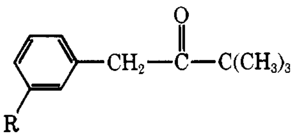
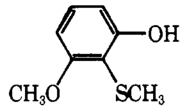


5a, R = CH$_3$
b, R = OCH$_3$



6

Several experiments concerning reactions of *m*-iodoanisole are summarized in Table I. It should be noted (expt 5) that reaction only with *t*-BuOK, **2b** being absent, afforded phenol

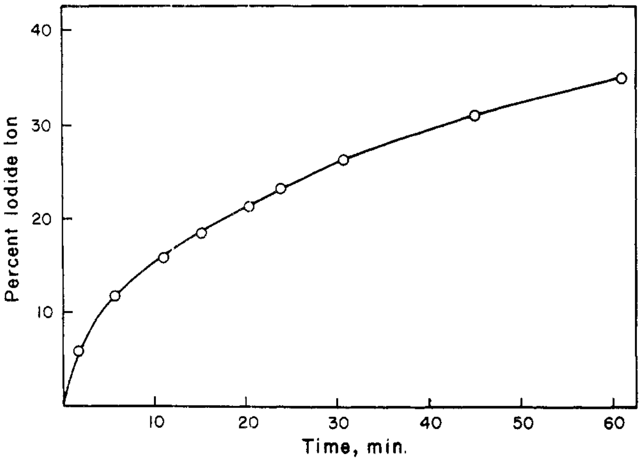


Figure 1. Percent reaction as function of time in dark reaction of iodobenzene (0.0246 M) with **2b** (0.100 M) and *t*-BuOK (0.003 M) in $\mathrm{Me_2SO}$ at 25 °C.

6 in substantial amount together with tars and unidentified minor products. In expt 3, no excess *t*-BuOK was present but the yield and proportion of **6** were about the same as in expt 1 and 2. The initial rate of reaction with **2b** is very high, as shown by expt 4; after only 1 min, 27% of iodide ion had been released. Moreover, the products formed in the first minute were richer in ketone **5b** than the products formed during longer periods of reaction.

p-Dinitrobenzene acts to depress overall reaction rate and to increase the fraction of phenol **6** among the products. In expt 6, 17 mol % of *p*-dinitrobenzene was employed and it took 10 min to obtain 27% release of iodide ion whereas the same amount of iodide ion was liberated in only 1 min in the absence of *p*-dinitrobenzene (expt 4). The product ratio of phenol **6** to ketone **5b** was 0.84 in contrast to ratios about 0.2 in the absence of *p*-dinitrobenzene (expt 1–3). With further increase in the amount of *p*-dinitrobenzene present, to 38 mol % (expt 7), there was a small further increase in the phenol/ketone product ratio, to 1.03.

2-Iodomesitylene also reacted with **2b**, but rather slowly. During 3 h in the dark, 20% of iodide ion was released, 15% of 1-mesityl-3,3-dimethyl-2-butanone and 2% of mesitylene were formed, and 80% of 2-iodomesitylene remained unreacted.

Kinetic Studies. Efforts were made to determine the rate law governing the reaction of iodobenzene with **2b**. Reactions were conducted under a blanket of N_2 at 25 °C in flasks wrapped with an opaque covering, and samples were taken at intervals by pipet.

Figure 1 depicts the results of a typical run. Iodide ion release is initially very fast but it slows down remarkably as the reaction progresses toward completion. The data obtained do not fit the simple rate laws appropriate for first- or second-order kinetics or for reaction zero order in reactants but inverse first order in a product. On the other hand they do conform rather well to rate equation 5 in its integrated form (eq 6).

$$\mathrm{d}x/\mathrm{d}t = k_e[\mathrm{PhI}]/[\mathrm{X}] \tag{5}$$

$$-x + a \ln \frac{a}{a - x} = k_e t \tag{6}$$

In these equations, a represents the initial concentration of **1b** and x the concentration of iodide ion at any time. The data of Figure 1 are replotted in Figure 2 according to eq 6.

We are unsatisfied by eq 5 and 6 because, as reported below, we find it difficult to ascribe chemical significance to them. Nevertheless, we use the slopes and plots according to eq 6 for the purpose of representing reactivity; they constitute empirical rate constants with units of mol $\mathrm{l.^{-1}\,s^{-1}}$, symbolized k_e.

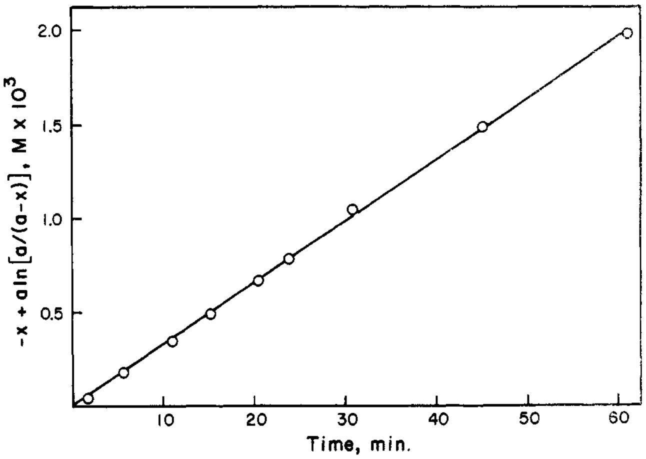


Figure 2. The data of Figure 1 plotted according to eq 6.

Most of our rate measurements are summarized in Table II. The first k_e entry (expt 8) is the average from four runs, the k_e's from which were individually 5.4, 7.0, 7.2, and 5.7 M $\mathrm{s^{-1}}$. Reproducibility was thus good, and remained so throughout this work.

Halving the initial concentration of iodobenzene (expt 9) did not change k_e within experimental error. It ought not to if rate equation 6 is correct, for in its derivation (in eq 5) explicit account is taken of the effect of varying iodobenzene concentration. Equation 6 has some of the characteristics of the rate equation for pseudo-first-order kinetics. As in the case of pseudo-first-order kinetics, iodobenzene is in deficiency with respect to **2b** in all the experiments of Table II, and there is relatively little change in the **2b** concentration during any run.

Doubling the concentration of **2b** doubled k_e; compare expt 10 with expt 8. This again is unexceptional in view of the resemblance to pseudo-first-order kinetics. Halving the **2b** concentration (expt 13) cut k_e by a factor of somewhat more than 2.

The presence of excess potassium *tert*-butoxide (*t*-BuOK) had little effect;[11] compare expt 11 with 9, or expt 12 with 8. However, having molecular pinacolone in excess depressed k_e; compare expt 14 with 13.

Raising the temperature increased the reaction rate. The 10 °C increase from 40 to 50 °C (expt 15 and 16) essentially doubled the rate in almost perfect conformance with the familiar rule of thumb. From expt 15 and 16 and an average k_e at 25 °C of 7.0×10^{-7} M $\mathrm{s^{-1}}$, we calculate the activation enthalpy, $\Delta H^{\ddagger}$, to be 13.2 kcal/mol. Because of the strange units of k_e, we do not undertake to reckon $\Delta S^{\ddagger}$.[12b]

Rate Effects of Added Substances. Addition of KI (expt 17) had little effect. There was a slight induction period, and the k_e was slightly depressed, but the effect was scarcely outside experimental error.

Another candidate for species X in the denominator of eq 5 was the potassium salt of product **3b**, which we symbolize **K3b**. Remarkably, the effect of having **K3b** present together with **2b** was not to retard, but rather to accelerate the liberation of iodide ion. There was an initial burst of iodide ion release, and the overall k_e was approximately doubled in expt 18 and tripled in expt 19. The exaltation was thought perhaps to be due to greater reactivity by **K3b** than by **2b**, but analysis of the organic products formed under the conditions of expt 19 showed that only a small amount of 1,1-diphenyl-3,3-dimethyl-2-butanone had been formed. **K3b** separately appeared to have about the same reactivity as **2b**; compare expt 20 with expt 13.

Table II. Kinetics of the Reaction of Iodobenzene with Pinacolone Enolate Ion in Dimethyl Sulfoxide in the Dark

Expt no.	Temp, °C	$[PhI]_0$, M	$[\mathbf{2b}]_0$, M	$[t\text{-BuOK}]_0$, M	Other substance, M	$10^7 k_e$,[a] $M\ s^{-1}$	Comments
8	25	0.023	0.100	0.004		6.3 ± 0.9[b]	
9	25	0.011	0.100	0.004		6.5	
10	25	0.023	0.200	0.006		13.5[c]	
11	25	0.012	0.100	0.106		7.3[c]	
12	25	0.023	0.100	0.060		7.7	
13	25	0.011	0.050	0.054		2.8[c]	
14	25	0.012	0.054		CH_3COCMe_3, 0.046 M	1.3[c]	
15	40	0.024	0.098	0.060		20	
16	50	0.024	0.098	0.060		43	
17	25	0.023	0.100	0.004	KI, 0.12 M	6.3	Slight induction period
18	25	0.023	0.084[d]		**K3b**,[e] 0.02 M	12.5	Initial burst
19	25	0.023	0.100	0.044	**K3b**,,[e] 0.016 M	22	Initial burst
20	25	0.024		0.80	**K3b**,[e] 0.063 M	4.2	Initially faster
21	25	0.023	0.100	0.004	$p\text{-}C_6H_4(NO_2)_2$, 0.0060 M	0	
22	25	0.023	0.100	0.004	$p\text{-}C_6H_4(NO_2)_2$, 0.00024 M	0	
23	25	0.023	0.100	0.004	$p\text{-}C_6H_4(NO_2)_2$, 8×10^{-5} M	0.7	
24	25	0.024	0.100	0.060	Ph_2CO, 0.0052 M	1.8	45-min induction period
25	25	0.024	0.100	0.060	Ph_2CO, 0.024 M	1.1	50-min induction period
26	25	0.024	0.100	0.060	$(t\text{-}Bu)_2NO$, 0.0024 M	0.3	Initially even slower
27	25	0.023	0.100	0.060	O_2, bubbling	130	
28	25	0.023	0.100	0.004	$PhNO_2$, 0.0034 M	17	Induction period
29	25	0.024	0.100	0.060	$PhNO_2$, 0.006 M	43	Induction period
30	25	0.024	0.100	0.060	$Fe(NO_3)_3$, 0.0025 M	770	
31	25	0.024	0.100	0.060	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 0.0025 M	2	
32	25	0.024	0.100	0.060	$Fe_2(SO_4)_3$, 0.0025 M	0.7	
33	25	0.026[g]	0.300	0.037		1.8	

[a] From application of eq 6. [b] Average of four runs; standard deviation is shown. [c] Average of two runs. [d] Pinacolone, 0.016 M, also present. [e] **K3b** is the potassium salt of **3b**. [f] Addition of $Fe(NH_4)(SO_4)_2$ (0.0038 M) after 32 min did not cause noticeable acceleration. [g] Bromobenzene.

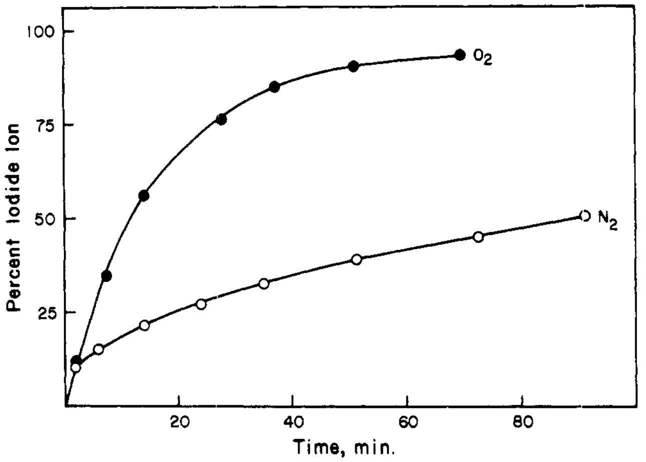


Figure 3. The effect of O_2 on reaction rate. Data of expt 12 and 27, Table II. A plot of the data under O_2 according to eq 6 is linear and steep for the points at 7.4–50.8 min, inclusive.

One would anticipate, on the basis of the mechanism of Scheme I, retardation by reagents that would intercept radicals or act as superior electron acceptors. p-Dinitrobenzene has been found to suppress many aliphatic $S_{RN}1$ reactions.[13] In modest concentrations it absolutely stopped the release of iodide ion (expt 21 and 22). Even at the concentration level of 8×10^{-5} M, which represents 0.3 mol with respect to iodobenzene, it reduced k_e tenfold; compare expt 23 with 8.

Benzophenone also inhibits the reaction. At the level of 21 mol % (expt 24) it causes a long induction period and even the subsequent reaction goes at only a quarter of its usual rate. The reaction was still slower in the presence of 100 mol % of benzophenone (expt 25).

Di(*tert*-butyl) nitroxide (expt 26) at the level of 10 mol % severely depressed the rate.

Dioxygen is another familiar radical scavenger. A reaction (expt 27) continuously bubbled with O_2 behaved spectacularly. During the first 5 min iodide ion release occurred about as rapidly as under N_2. But beyond that point iodide ion release remained rapid, whereas it diminished appreciably under N_2; see Figure 3. In terms of k_e values, the reaction under O_2 after the first 5 min was an order of magnitude faster than under N_2. Product analysis on a reaction run under O_2 revealed no formation of **3b**. When a solution of **K3b** in Me_2SO was bubbled with O_2 for 45 min and an attempt was made to recover **3b**, none could be found. In both cases, after esterification of the product mixtures, small amounts (ca. 13%) of methyl benzoate were detected. Ketones are known to undergo autoxidation in basic media.[14]

Nitrobenzene also had an unusual effect. When present to the extent of 14 or 25 mol % in respect to iodobenzene (expt 28 and 29), it inhibited the liberation of iodide ion for a while, but when reaction once started the rate of iodide ion formation was much greater than usual; see Figure 4 for example. Product analysis on a reaction run in the presence of 27 mol % of nitrobenzene showed that iodide ion and **3b** had been formed in yields of 79 and 74%, respectively, and that most of the nitrobenzene had been consumed.

Inasmuch as ferric salts inhibit many radical reactions,[15] the effect of adding various iron salts was investigated. Ferric nitrate (expt 30) strongly stimulated both iodide ion release and the formation of **3b**. However, ferric sulfate and ferric ammonium sulfate (expt 32) as well as ferrous ammonium sulfate (expt 31) mildly inhibited the reaction.

Halogen Mobility. We compared the reactivities of bromo- and iodobenzene by means of competition experiments, several of which are summarized in Table III. The first five concern dark reactions, and among them the **2b** concentration

Table III. Competition between Iodobenzene and Bromobenzene in Reaction with Potassium Pinacolone Enolate (2b) in Me_2SO at 25 °C

Expt no.	$[PhI]_0$, M	$[PhBr]_0$, M	$[\mathbf{2b}]_0$, M	$[t\text{-BuOK}]_0$, M	No. of observations	Lighting condition	k_I/k_{Br}
34	0.0050	0.0259	0.288	0.038	4	Dark	7.2
35	0.0051	0.0215	0.288	0.038	3	Dark	7.4
36	0.0075	0.0242	0.098	0.060	4	Dark	6.9
37[a]	0.0080	0.0289	0.049	0.021	6	Dark	6.1
38	0.0072	0.0214	0.049	0.021	4	Dark	5.9
39	0.0075	0.0238	0.049	0.021	4	$h\nu$	5.9
40	0.0094	0.0236	0.049	0.021	3	$h\nu$	5.7

[a] For illustrative detail on expt 37, see Experimental Section and Table IV.

Table IV. Competitive Reactions of 1a and 1b with 2b in Me_2SO at 25 °C;[a] Detail on Expt 37, Table III

Time, min	$[I^-]$, M	$[Br^-]$, M	$\frac{\ln a/(a-x)}{\ln b/(b-y)}$	$\frac{-x + a \ln a/(a-x)}{t}$, $M\ s^{-1} \times 10^8$	$\frac{-y + b \ln b/(b-y)}{t}$, $M\ s^{-1} \times 10^8$
10.0	0.00121	0.00085	5.5	16.2	2.02
20.3	0.00190	0.00121	6.4	20.8	2.03
29.8	0.00206	0.00137	6.2	17.0	1.78
40.0	0.00234	0.00166	5.9	16.8	1.97
60.0	0.00283	0.00194	6.3	17.3	1.80
71.0	0.00303	0.00214	6.2	17.2	1.85
Av			6.1	17.5	1.90

[a] Initial concentration of **1b**, symbolized a, 0.0084 M; initial concentration of **1a**, symbolized b, 0.0304 M; $[I^-]$ and $[Br^-]$ at any time are symbolized x and y, respectively.

varies more than fivefold. Each experiment involved multiple observations; detail on expt 37 is given in Table IV in the Experimental Section. The data suggest a slight dependence of the iodobenzene/bromobenzene rate ratio on **2b** concentration, in the sense that it is higher at higher **2b** concentrations, but the effect is scarcely outside the bounds of experimental error. The average iodobenzene/bromobenzene reactivity ratio from the five experiments under dark conditions is 6.7.

The last two experiments in Table III concern photostimulated reactions conducted in such a way that the dark components of them represent less than 10% of the total. The average iodobenzene/bromobenzene reactivity ratio for the last two, 5.8, is within experimental error identical with that for the preceding two dark experiments (expt 37 and 38) which involved identical concentrations of **2b** and t-BuOK. Thus in competition experiments the reactivity ratio is the same for the dark reaction as for the photostimulated reaction.

Relative reactivity in the foregoing experiments was reckoned by means of eq 7

$$\frac{k_I}{k_{Br}} = \frac{\ln([PhI]_0/[PhI]_t)}{\ln([PhBr]_0/[PhBr]_t)} \qquad (7)$$

which is appropriate if some reactive intermediate reacts bimolecularly and competitively with iodo- and bromobenzene.[12a] However, if one evaluates data from a competition experiment by means of eq 6, the data for iodo- and bromobenzene being treated separately, one obtains a different estimate of relative reactivity. Specifically, the data of expt 37 (Table III) give k_I/k_{Br} of 6.1 when reckoned by the standard formula (eq 7), but k_e^I/k_e^{Br} obtained via use of eq 6 was 9.2.

We believe it better to reckon relative reactivity in competition experiments by means of eq 7, despite the fact that eq 6 serves well to represent events in particular runs and even the behavior of iodo- and bromobenzene when reacting admixed (see Table IV, Experimental Section). The basis of this judgment is our belief that step 4 (Scheme I) is the one in which the involvement of iodo- or bromobenzene in the propagation sequence is determined.

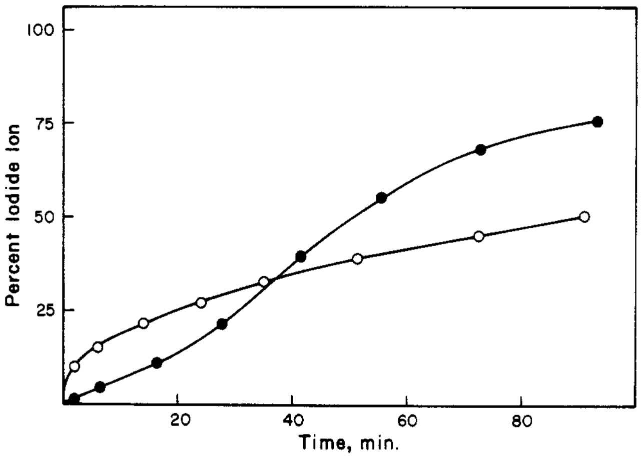


Figure 4. The effect of nitrobenzene on reaction rate. Open circles: without nitrobenzene (expt 12, Table II). Filled circles: with nitrobenzene (expt 29, Table II); a plot of these data according to eq 6 is linear and steep for the points at 41.5–93.0 min, inclusive.

One might anticipate that initiation would be somewhat faster for iodo- than for bromobenzene, and therefore that bromobenzene would react faster in the presence of iodobenzene than in its absence. We have observed that to be the case, as shown in Figure 5. The effect is clear but not spectacular.

In another experiment, iodobenzene was allowed to react completely with excess **2b**, and then bromobenzene was added to the system. The reactivity of bromobenzene under these conditions was the same as in a freshly mixed solution of the same **2b** concentration. Clearly the beneficial effect of iodobenzene is bestowed as iodobenzene reacts; it is not a matter of the iodobenzene reaction destroying some deleterious im-

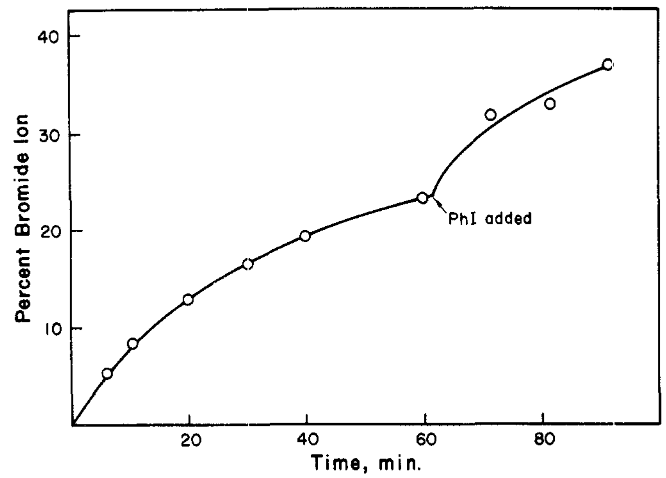


Figure 5. The effect of adding iodobenzene (0.0055 M) on the rate of release of bromide ion in the reaction of bromobenzene with **2b**. Data prior to the time iodobenzene added are treated as expt 33, Table II.

purity or generating some long-lived species that assists the bromobenzene reaction.

Discussion

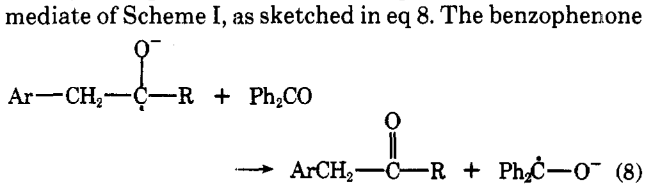
We have found that iodobenzene (**1b**) reacts readily in Me_2SO solution at room temperature with potassium pinacolone enolate (**2b**) to form substitution product **3b**, according to eq 1. Other salient observations are that the reaction appears to obey the peculiar rate law of eq 5 and 6, that it is inhibited by *p*-dinitrobenzene, benzophenone, or di(*tert*-butyl) nitroxide and accelerated by light, and that nitrobenzene, dioxygen, and ferric nitrate have strange kinetic effects. Also, in competition experiments the reactivity of bromobenzene is about one-sixth that of iodobenzene.

These facts constitute compelling evidence that the dark reaction of **1b** with **2b** to form **3b** has a radical chain mechanism. The data are not compatible with a nonchain mechanism.

An important item of evidence toward that conclusion is that the reaction is inhibited by the electron scavenger *p*-dinitrobenzene, being totally stalled even by 1 mol % of this inhibitor in respect to iodobenzene. Inhibition by *p*-dinitrobenzene has often been observed for $S_{RN}1$ reactions at aliphatic sites.[13] In the present case it is possible that **2b** reacts with *p*-dinitrobenzene to form the *p*-nitro derivative of **3b**[16] and that that product or something derived from it is the effective inhibitor. Such reaction would of course consume some **2b**, but the diminution in **2b** concentration would be negligible.

Di(*tert*-butyl) nitroxide is a familiar scavenger of reactive radicals.[17] The fact that, at the level of 10 mol % in respect to **2b**, it reduces the rate to about 5% of its normal value is consistent with a radical chain mechanism.

Inhibition by benzophenone is less familiar. Plausibly, it acts by taking an electron from the postulated ketyl intermediate of Scheme I, as sketched in eq 8. The benzophenone



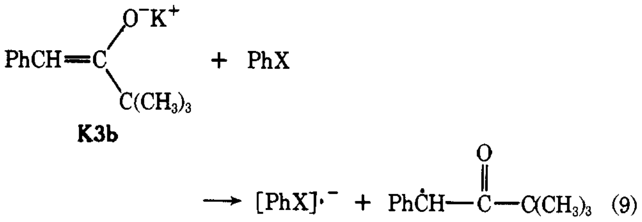
$$\mathrm{Ar{-}CH_2{-}\overset{O^-}{\underset{\cdot}{C}}{-}R + Ph_2CO \longrightarrow ArCH_2{-}\overset{O}{\overset{\|}{C}}{-}R + Ph_2\dot{C}{-}O^-} \quad (8)$$

ketyl thereby formed is undoubtedly a more stable species, less able to continue the propagating chain by furnishing an electron to an iodobenzene molecule in the manner of eq 4, more likely to accumulate and to act as a scavenger of reactive radicals.

Acceleration of the reaction of **1b** with **2b** by illumination is also compatible with a radical chain mechanism. Many radical chain mechanisms, including $S_{RN}1$ reactions at aromatic[4] and aliphatic[13] centers, are stimulated by photons, but photoacceleration is not by itself compelling evidence for a radical mechanism.

The fact that the iodobenzene/bromobenzene reactivity ratio is within experimental error identical, about 6, for the thermal and the photostimulated reactions is very important because it is strong evidence that the same mechanism prevails under both sets of conditions.

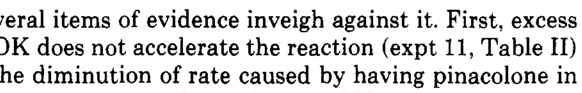
A plausible interpretation can be given for the fact that the potassium enolate of product **3b** accelerates the reaction of **1b** with **2b**. It is that **K3b** is especially effective in initiation of the radical chain. We have no direct evidence of the nature of the initiation process but we think it possible that it involves electron transfer from **2b** to **1b** so as to form the iodobenzene radical anion which enters the propagation sequence (Scheme I) at step 2. If so, **K3b** should be a better electron donor because of resonance stabilization of the resulting radical (eq 9).



$$\mathrm{\underset{\textbf{K3b}}{PhCH{=}C(O^-K^+)(C(CH_3)_3)} + PhX \longrightarrow [PhX]^{\cdot -} + Ph\dot{C}H{-}\overset{O}{\overset{\|}{C}}{-}C(CH_3)_3} \quad (9)$$

Thus numerous observations deny a nonchain mechanism but are consistent with a radical chain mechanism. The $S_{RN}1$ propagation sequence of Scheme I is compatible with the evidence.[18] Our ideas as to the probable nature of the initiation process are stated immediately above.

The present work provides no evidence as to what the termination steps are. Other work[6b] suggests that termination may involve the occasional reaction of phenyl radical with the enolate ion differently than in step 3, namely, by electron transfer as in step 10. The resulting β-keto alkyl radicals would then dimerize.



$$\mathrm{Ar\cdot + CH_2{=}C(O^-)(R) \longrightarrow Ar{:}^- + \cdot CH_2{-}\overset{O}{\overset{\|}{C}}{-}R} \quad (10)$$

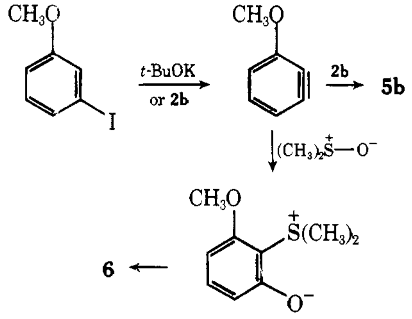
The Aryne Mechanism Possibility. Because solutions of enolate ions such as **2b** in Me_2SO are strongly basic and it is known that *t*-BuOK in Me_2SO at 25 °C can generate benzyne from bromobenzene (albeit slowly),[19a] the possibility of an aryne mechanism for reaction 1 needs to be seriously considered.

Several items of evidence inveigh against it. First, excess *t*-BuOK does not accelerate the reaction (expt 11, Table II) and the diminution of rate caused by having pinacolone in excess (expt 14) is much less than would be expected if aryne formation were requisite to the reaction. Second, the reaction of *p*-iodotoluene with **2b** gives only the *p*-methyl derivative of **3b**. None of the *m*-methyl derivative, which was obtained separately by reaction of *m*-iodotoluene with **2b**, was detectable as a product from the reaction of *p*-iodotoluene with **2b**. Had the latter reaction gone via the aryne mechanism, addition of **2b** to the intermediate 4-methylbenzyne ought actually to have progressed to somewhat more of the *m*-methyl than of the *p*-methyl derivative of **3b**.[19b] Furthermore, 2-iodomesitylene, a substance incapable of being converted to a benzyne derivative, reacts with **2b** in the manner of eq 1.

However, a side reaction by the aryne mechanism was observed in the case of *m*-iodoanisole. The side reaction forms phenolic product **6** in yield about 13%. Earlier, phenol **6** had been obtained by Birch, Chamberlain, and Oloyede[20] by the action of dimsyl sodium on *o*-bromoanisole. It was explained to result from elimination of the elements of HBr from *o*-bromoanisole to generate 3-methoxybenzyne, addition of a dimethyl sulfoxide molecule with the negatively charged oxygen of the sulfoxide attaching to the arynic position meta to the methoxy group (the position favored for nucleophilic attack), and finally protonation at oxygen and demethylation from sulfur. Previously a similar reaction had been observed from the action of *t*-BuOK in Me_2SO on an aryl bromide, and it was similarly rationalized.[21]

We postulate the genesis of **6** in the reaction of *m*-iodoanisole with **2b** and/or *t*-BuOK to involve the same sort of process, as sketched in Scheme II. Besides adding dimethyl sulfoxide as mentioned, the postulated aryne intermediate conceivably may add the pinacolone enolate ion from **2b** and then a proton to form **5b**, the major product obtained. Rigorously, we should ask two questions: is *any* of the **5b** actually produced via the aryne route? Is perhaps *all* of the **5b** produced by that route? Our data show that the answers to these two questions are *yes* and *no*, respectively. The data indicate that some **5b** is produced by the aryne route but most by the $S_{RN}1$ mechanism.

Scheme II



The aryne mechanism (Scheme II) is a nonchain, ionic mechanism and should be insensitive to small amounts of the $S_{RN}1$ inhibitor, *p*-dinitrobenzene. Experimentally, the presence of 17 mol % of *p*-dinitrobenzene during the reaction of *m*-iodoanisole with **2b** strongly depressed the overall rate and strongly altered the product proportions so as to increase the **6**/**5b** product ratio (Table I, expt 6). In the presence of a greater amount of *p*-dinitrobenzene (expt 7), the **6**/**5b** product ratio was further elevated by a small amount.

Inasmuch as *p*-dinitrobenzene at the levels used in expt 6 and 7 absolutely stops the reaction of iodobenzene with **2b** (Table II, expt 21 and 22), the products formed from *m*-iodoanisole in the presence of *p*-dinitrobenzene must come totally or nearly so from the aryne route of Scheme II. The data indicate that under the conditions employed the aryne partitions almost equally between the pathways leading to **6** and to **5b**. It follows that in the absence of *p*-dinitrobenzene most of the **5b** is produced by the $S_{RN}1$ route and some by the aryne route; for example, in expt 1 or 3, Table I, about 20% of the **5b** was formed by the aryne route and about 80% by the $S_{RN}1$ route. This is a case of some pedagogical value: within a single reacting system two competing mechanisms, one ionic, the other a radical chain mechanism, lead from the same reactant to the same product.

At a very short reaction time (expt 4, Table I) the product mixture is much richer in ketone **5b** than at longer reaction times. This indicates that phenolic product **6** acts to inhibit the $S_{RN}1$ mechanism, allowing the aryne mechanism a greater share at later stages of the reaction.

Huisgen and Herbig[22] determined the rate of aryne generation from numerous substituted bromobenzenes through the action of lithium piperidide in diethyl ether solution. In the case of *m*-bromoanisole, only formation of 3-methoxybenzyne was detectable; it results from attack on the hydrogen between the bromine and methoxy substituents. The partial rate factor, relevant to attack on one ortho hydrogen in bromobenzene, was 600.

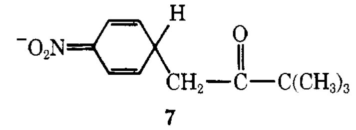
For purposes of discussion, let us assume that the same partial rate factor is applicable to reactions of **2b** with iodobenzene and with *m*-iodoanisole in Me_2SO. Taking account of the facts that about 40% of the reaction of *m*-iodoanisole is by the aryne mechanism, that *m*-iodoanisole reacts with **2b** by the $S_{RN}1$ mechanism about 39 times faster than iodobenzene,[10b] and that iodobenzene has two ortho hydrogens, we estimate that about 8% of the reaction of iodobenzene with **2b** would occur by the aryne mechanism. The estimate warrants low confidence because of uncertainty as to whether the partial rate factor can be transferred from one system to another of rather different character. For what it is worth, it does tend to confirm more direct evidence that the reaction of eq 1 does not occur by the aryne mechanism. It does suggest, however, that the aryne mechanism may have a minor role. Perhaps small amounts (1% or less) of *o*-(methylthio)phenol are produced by a process analogous to Scheme II. If so, inhibition of the $S_{RN}1$ reaction would occur. This may be the origin of the mysterious X in the denominator of eq 5.

Further evidence against the aryne mechanism is the fact that the reaction of bromobenzene with **2b** is slower than of iodobenzene, and that it is also halted by addition of *p*-dinitrobenzene. Bromobenzene is generally more reactive than iodobenzene by the aryne mechanism.[22,23]

New Questions. We report above some extraordinary kinetic effects of nitrobenzene, dioxygen, and ferric nitrate. We cannot explain them, but we wish to comment on their broad significance and their characteristics and to draw attention to them as topics for future attention.

The broad significance of the extraordinary accelerations caused by these additives, sometimes preceded by an induction period, is that they are incompatible with nonchain ionic mechanisms. On the other hand, the overall rates of radical chain reactions can in principle be greatly augmented by an added substance if it somehow causes an increased rate of initiation or ties up some substance which otherwise is active in termination. Therefore these extraordinary effects, even though unexplained, support the hypothesis that these reactions occur by a radical chain mechanism.

Nitrobenzene at first inhibited and then accelerated the reaction of **2b** with **1b**; see Figure 4. Observations associated with this spectacular behavior are that a good yield of **3b** was obtained, that most of the nitrobenzene was used up, and that no detectable amount of the *p*-nitro iderivative of **3b** was formed. One cannot be sure whether nitrobenzene itself or some species derived from it, or both, is responsible for the observed effects. Nitrobenzene is a good electron acceptor;[24] its inhibiting action may well involve accepting electrons from the postulated ketyl intermediate (Scheme I) in competition with propagation step 4. It is further possible that nitrobenzene adds the enolate ion to form a σ complex such as **7**. Two-electron oxidation of **7** plus deprotonation would form



7

the *p*-nitro derivative of **3b** which, though not obtained as such, may have been further converted to other substances. Presumably something derived from **7**, from the nitrobenzene radical anion, or from something else in the system acts as an initiator, but we do not know what it is.

Dioxygen in the first few minutes had little kinetic effect but later iodide ion release was faster than usual; see Figure 3. No **3b** was obtained, and it was shown that **3b** is destroyed under reaction conditions by an oxidation reaction which produces some benzoic acid. Hydroperoxides are believed to be intermediates in the oxidation.[14] Conceivably after they have accumulated to some extent they decompose to form radicals which effectively initiate the propagation sequence of Scheme I.

The tremendous accelerating effect of ferric nitrate (expt 30, Table II) defies explanation. The accelerated reaction genuinely forms **3b**, but of the few ferric salts tried the nitrate was the only one with noteworthy effect. Apparently the nitrate ions are somehow involved.

Experimental Section

Materials. The Me_2SO was purified by the method of Steiner and Ritchie[25] except that distillation was from calcium hydride and sodium amide. It was stored under Ar in a foil-wrapped flask fitted with a three-way stopcock. Transfer was carried out by withdrawal through the stopcock using a long needle syringe with Ar flowing through the stopcock via the side arm. In one experiment using Me_2SO distilled only from calcium hydride (but not sodium amide), *m*-iodotoluene was observed to react only half as fast as had been observed several months earlier. When a new batch of Me_2SO was prepared, once again distilled from a mixture of calcium hydride and sodium amide, the rate was the same as observed earlier. The purity of the Me_2SO and care in transfer and handling are critical to good reproducibility of the kinetic data.

Potassium *tert*-butoxide was freshly sublimed just prior to use, quickly weighed, and transferred directly to the nitrogen flushed reaction flask.

Aryl halides were distilled until colorless and stored in foil-wrapped brown bottles.

Aldrich pinacolone was dried over molecular sieves for several days and distilled through a Vigreux column; a forerun of about 40% was discarded. The main fraction (bp 106 °C) was distilled again. A sizable forerun was again discarded and the main fraction, bp 106 °C, was stored over molecular sieves.

GLC Analysis. Gas chromatography was carried out on a Hewlett-Packard 5750 flame ionization instrument. A 3.2 mm × 0.91 m 4% Carbowax 20M on Chromosorb G column was used. Yields of products were determined by usual methods using internal standards. In all cases, the areas were corrected for molar response as determined from standard solutions of the products and the internal standard. Preparative GLC isolations were carried out on a Varian Aerograph A-90P instrument using either a 6.4 mm × 0.61 m 20% SE-30 on Chromosorb G or 6.4 mm × 0.91 m 14% Carbowax 20M on Chromosorb G column.

Dark Reaction of Halobenzene and Pinacolone Enolate in Me_2SO. Typical Procedure. A. Potassium *tert*-butoxide (freshly sublimed) was placed into a 100-ml one-neck flask with a gas inlet side arm and short condenser. The flask and fittings were completely wrapped with opaque tape and all reactions were carried out in a nitrogen atmosphere. Dimethyl sulfoxide (50 ml) was added with a syringe through the condenser and after several minutes of stirring the apparatus was placed in a 25 °C thermostat bath. After equilibration the appropriate amounts (Table I) of aryl halide and pinacolone were added and the flask was well swirled to mix the contents. At the desired time (Table I), the solution was acidified with dilute nitric acid, 150 ml of water was added, and the mixture was extracted with three portions of ether. The combined ether fractions were washed with water and dried. In preparative runs, the ether was removed and the resulting product was purified by preparative GLC and distillation. In analysis runs, an internal standard was added and the ether solution was analyzed by GLC. The aqueous extracts were usually titrated for halide ion.

B. Kinetic measurements were made as in A except that 5-ml aliquots were removed through the condenser at various intervals. In each case, care was taken not to introduce oxygen into the system by purging the pipet with Ar prior to insertion into the flask. The aliquots were delivered into an acidic quenching solution and titrated for free halide ion.

C. Competition experiments were carried out as in B except that bromobenzene was added with the iodobenzene. In one case, a portion of the solution was neutralized and worked up as described in A. Analysis of the ether revealed 0.127 mmol of **3b**. Total halide present was found to be 0.132 mmol, of which 0.042 mmol was bromide and 0.090 mmol iodide ion. This experiment shows that C_6H_5Br as well as C_6H_5I is converted to **3b**.

Detailed data on a representative competition experiment are given in Table IV.

D. Photochemical competition experiments were carried out in the same manner except that the Pyrex flask was not wrapped, and after dissolution of the *t*-BuOK the solution was placed in a Rayonet photochemical reactor which contained a water bath previously adjusted to ca. 25 °C. The reactor was turned on, halides and ketone were added, the flask was swirled, and aliquots quickly removed.

E. Reactions in which added substance effects were studied were carried out as in A and B except that the appropriate inhibitor was added with or just prior to halobenzene and pinacolone addition.

3,3-Dimethyl-1-(*p*-methylphenyl)-2-butanone (4) was prepared from *p*-iodotoluene as described in A above and had mp 35–36 °C; NMR (CCl_4) δ 1.15 (s, 9 H), 2.33 (s, 3 H), 3.67 (s, 2 H), and 7.07 (s, 4 H); IR (film) 1715, 1515, 1475, 1365, 1060, and 770 cm^{-1}; MS *m/e* 190 (molecular ion) and 105 (base peak).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.29; H, 9.57.

3,3-Dimethyl-1-(*m*-methylphenyl)-2-butanone (5a) was prepared from *m*-iodotoluene as described in A above and isolated as a colorless liquid: NMR (CCl_4) δ 1.10 (s, 9 H), 2.27 (s, 3 H), 3.58 (s, 2 H), and 6.7–7.1 (m, 4 H); IR (film) 1715, 1615, 1480, 1370, 1060, 760, and 690 cm^{-1}; MS *m/e* 190 (molecular ion) and 105 (base peak).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.63, 81.54; H, 9.67, 9.61.

Reaction of *m*-Iodoanisole and Pinacolone Enolate in Me_2SO. The reaction of 1.00 g (4.27 mmol) of *m*-iodoanisole, 1.50 g (15 mmol) of pinacolone, and 1.90 g (17.0 mmol) of *t*-BuOK was carried out for 3 h as described in A above. GLC analysis revealed an unknown product with retention time slightly less than that of the substitution product **5b**. Preparative GLC (SE-30 column) afforded pure **5b** (formed in 58% yield): mp 57.5–58 °C; NMR (CCl_4) δ 1.18 (s, 9 H), 3.67 (s, 2 H), 3.77 (s, 3 H), 6.42–7.33 (m, 4 H); IR (film) 1715, 1585, 1490, 1265, 1055, 765, and 690 cm^{-1}; MS *m/e* 206 (molecular ion) and 121 (base).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.90; H, 8.71.

The other product, collected at 162 °C, was 3-methoxy-2-(methylthio)phenol (**6**) (formed in 11% yield) and had NMR (CCl_4) δ 2.22 (s, 3 H, CH_3S), 3.87 (s, 3 H, CH_3O), and 6.23–7.27 (m, 4 H); IR (film) 3380, 2930, 2840, 1600, 1470, 1450, 1320, 1265, 1220, 1080, and 775 cm^{-1}; MS *m/e* 170 (molecular ion and base peak) and 155.

The 3,5-dinitrobenzoate derivative had mp 146–147.5 °C (three recrystallizations from aqueous ethanol) (lit. 146–148 °C).[20]

Preparation of 3,3-Dimethyl-1-mesityl-2-butanone. Ammonia (250 ml) was distilled from K into a three-neck flask flushed with N_2. Potassium *tert*-butoxide (3.36 g, 0.03 mol), pinacolone (2.00 g, 0.02 mol), and iodomesitylene (2.46 g, 0.01 mol) were added. The flask was irradiated in a Rayonet photochemical reactor for 2 h; then 2.4 g of ammonium nitrate was added. The ammonia was evaporated and the residue was taken up in ether and water. The ether layer was washed with water, dried, and concentrated. Addition of 20 ml of petroleum ether and cooling on dry ice gave crystalline product, mp 79–80 °C (lit.[26] 80–81 °C); the yield in two crops was 1.15 g (53%); NMR (CCl_4) δ 1.23 (s, 9 H), 2.06 (s, 6 H), 2.23 (s, 3 H), 3.72 (s, 2 H), 6.76 (s, 2 H).

This product was identical with that obtained in the reaction of iodomesitylene and **2b** carried out as in A and B above.

Registry No.—**1a**, 108-86-1; **1b**, 591-50-4; **2b**, 51742-96-2; **3b**, 6721-67-1; **4**, 61394-79-4; **5a**, 61394-80-7; **5b**, 61394-81-8; **6**, 33617-66-2; potassium *tert*-butoxide, 865-47-4; *p*-iodotoluene, 624-31-7; *m*-iodotoluene, 625-95-6; *m*-iodoanisole, 766-85-8; 3,3-dimethyl-1-mesityl-2-butanone, 61394-82-9; iodomesitylene, 4028-63-1.

References and Notes

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(18) The radical anion structure presented in steps 3 and 4, Scheme I, shows the extra electron to be located, in effect, in a carbonyl group π^* orbital. Another possible location for it is a benzene ring antibonding π orbital. Transfer of the electron between the two π systems is doubtless rapid; cf. M. Szwarc and J. Jagur-Grodzinski in M. Szwarc, "Ions and Ion Pairs in Organic Reactions", Vol. 2, Wiley, New York, N.Y., 1974, pp 71–85.

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Notes

Photostimulated $S_{RN}1$ Reactions of Halobenzenes with Ketone Enolate Ions in Dimethyl Sulfoxide Solution[1a]

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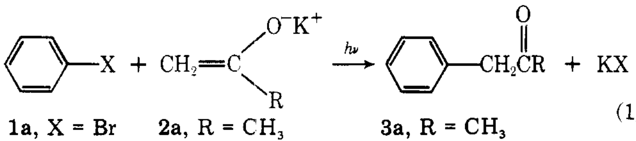
Many ketone enolate ions react with halobenzenes in liquid ammonia, under Pyrex-filtered irradiation, to form α-phenyl derivatives of the ketones.[2–5] Reactions occur, for example, as shown in eq 1. These reactions may be viewed as aromatic nucleophilic substitutions, and they are believed to occur by the $S_{RN}1$ mechanism.[6–9]



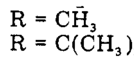
(1)

1a, X = Br 2a, R = CH_3 3a, R = CH_3

b, X = I b, R = $C(CH_3)_3$ b, R = $C(CH_3)_3$

It has also been observed that reactions according to eq 1 occur in dimethyl sulfoxide (Me_2SO) solution.[4,10] We now describe further observations of the reaction in Me_2SO.

Several experiments of descriptive character are summarized in Table I. The reactions of bromo- and iodobenzene with the enolate ions of both acetone and pinacolone occur readily to give high yields of monophenylation products of type **3** often accompanied by small yields of diphenylation products of type **4**.



$$\mathrm{Ph_2CH\overset{\overset{\displaystyle O}{\|}}{C}R}$$

4a, R = CH_3

b, R = $C(CH_3)_3$

Some preliminary measurements of the rate of reaction of bromobenzene with **2b** are presented in Table II. In most of these experiments, samples withdrawn at various times were analyzed by titration for bromide ion. Results of a typical experiment are displayed in Figure 1. During about the first 40% of the reaction the absolute rate, in M s^{-1}, was nearly constant; later it diminished. We were unable to fit the data for entire experiments to simple rate expressions, such as those for first- and second-order kinetics, and therefore tabulate initial zero-order rate coefficients in Table II.

In Table II, one can see that there was considerable variation in rate among experiments conducted identically or nearly so. For example, compare expt 11, 14, 15, and 16. Changing the concentration of bromobenzene or the enolate ion by a factor of 2 affected the rate very little; compare expt 16 with 17, or 12 and 13 with 11, 14, 15, and 16, or 18 with 19. Experiments 18 and 19 were carried out with a lower intensity of irradiation than the rest; they are based on the same batch of solution of **2b** in Me_2SO, and were performed the same day.

In early work efforts were made to determine the rate of photostimulated reaction of iodobenzene with **2a** and **2b**. We found that a substantial fraction of the reaction occurred before irradiation was started. Study of the photostimulated reaction with bromobenzene was more attractive because the dark reaction is much slower. We report elsewhere[11] a study of the kinetics of the dark reaction of **2b** with iodobenzene.

Spectrophotometric studies between 300 and 400 nm showed weak absorption by bromobenzene, strong absorption by **2b**, and very strong absorption ($A > 3$) by the enolate ions of **3a** and **3b** and by the reaction solution from expt 16, Table II, after 27 min irradiation (60% reaction). The very strong absorption by product enolate ions is perhaps a reason for the diminution in zero-order rate at later stages of reaction; see Figure 1.

Also noteworthy is that typical reaction mixtures, although initially colorless to the eye, became yellow on exposure to the atmosphere. This complicates transfer of solution aliquots, as in the dispensing of portions of a master reaction solution into tubes intended to be removed for analysis at different