hydrogen-bonding effects are correctly unravelled, solvents exert parallel effects on many types of properties and reactivity parameters. That a solvent polarity–polarizability scale, based on electronic spectra, is successful in correlating such disparate properties as rates of a Menschutkin reaction, rates of a peroxyester decomposition, and free energies of transfer of a tetraalkylammonium halide between solvents seems an ultimate vindication of this concept.

**Acknowledgments.** The work by M.J.K., T.N.H., and J.B. was done under Naval Surface Weapons Center Foundational Research Task IR-201. The work by R.W.T. was supported in part by a grant from the Public Health Service.

**Registry No.** Acetic anhydride, 108-24-7; bis(2-methoxyethyl) ether, 111-96-6; butyronitrile, 109-74-0; cumene, 98-82-8; 1,2-dibromoethane, 106-93-4; *m*-dichlorobenzene, 541-73-1; *trans*-1,2-dichloroethylene, 156-60-5; diethyl malonate, 105-53-3; ethyl acetoacetate, 141-97-9; ethyl trichloroacetate, 515-84-4; fluorobenzene, 462-06-6; 3-heptanone, 106-35-4; 2,6-lutidine, 108-48-5; methyl acetate, 79-20-9; methyl formate, 107-31-3; methylal, 109-87-5; phenylacetone, 103-79-7; phenylacetonitrile, 140-29-4; pentachloroethane, 76-01-7; sulfolane, 126-33-0; trimethyl orthoacetate, 1445-45-0; trimethyl orthoformate, 149-73-5; *m*-xylene, 108-38-3; *N,N*-diethyl-3-nitroaniline, 2216-16-2; 4-methoxy-$\beta$-nitrostyrene, 3179-10-0; *N,N*-diethyl-4-nitroaniline, 2216-15-1; 4-nitroanisole, 100-17-4; *N,N*-diethyl-3-methyl-4-nitroaniline, 52177-26-1; *N,N*-dimethyl-4-nitroaniline, 100-23-2; *N,N*,3,5-tetramethyl-4-nitroaniline, 64325-04-8; 4-(dimethylamino)benzophenone, 530-44-9; 4,4′-bis(dimethylamino)benzophenone, 90-94-8; tripropylamine, 102-69-2; methyl iodide, 74-88-4; tetraethylammonium iodide, 68-05-3; pyridine, 110-86-1; *tert*-butyl peroxyformate, 819-50-1.

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# Substituent Effects on Reactivity in $S_{RN}1$ Reactions of Aryl Iodides with Pinacolone Enolate Ion[1]

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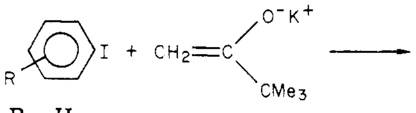
*Received January 16, 1979*

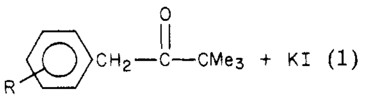
In the dark reactions of six aryl iodides with pinacolone enolate ion in dimethyl sulfoxide solution, which are believed to occur by the radical chain $S_{RN}1$ mechanism, relative reactivity varies enormously depending on the method of measurement. The maximum difference in reactivity among the six substrates *reacting separately* is nearly 400-fold, but the maximum difference *in competition* vs. bromobenzene is less than twofold. Such a huge difference is not unreasonable for radical chain reactions inasmuch as differences in initiation as well as propagation (and termination) reactivity are manifested in separate reactions whereas (if the chain is long) only differences in propagation reactivity are revealed by competition experiments. The two measures of reactivity correlate only roughly with $\sigma$ substituent parameters, but they correlate better with polarographic half-wave reduction potentials or with each other.

Iodo- and bromobenzene react spontaneously in the dark at room temperature with pinacolone enolate ion to form 3,3-dimethyl-1-phenyl-2-butanone (**3a**);[3] see eq 1. Reaction is believed on the basis of good evidence to occur by the radical chain $S_{RN}1$ mechanism. Most of the known aromatic $S_{RN}1$ reactions[4] require stimulation by photons or electrons in order for reaction to occur at a conveniently observable rate. Reactions such as that of eq 1 that occur spontaneously in the dark clearly involve some thermally activated initiation process, and that makes them particularly interesting.



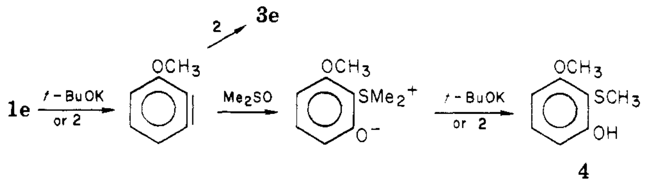
**1a**, R = H
**b**, R = $p$-$CH_3$
**c**, R = $m$-$CH_3$
**d**, R = $p$-$OCH_3$
**e**, R = $m$-$OCH_3$
**f**, R = $p$-F

**2**



**3a**, R = H
**b**, R = $p$-$CH_3$
**c**, R = $m$-$CH_3$
**d**, R = $p$-$OCH_3$
**e**, R = $m$-$OCH_3$
**f**, R = $p$-F

Scheme I



**4**

Heretofore little has been learned about reactivity in aromatic $S_{RN}1$ reactions as affected by substituents in the aromatic system. There have been a few qualitative observations that specific reactions occur satisfactorily when alkyl, alkoxy, aryl, fluoro, or carboxylate groups are present[5-7] but that they fail with substituents such as *m*-nitro and the ionized *p*-hydroxy group ($O^-$) as well as in the case of iodoferrocene. By competition experiments, Komin and Wolfe[8] have demonstrated the reactivity order

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(1) Research supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society. This work was presented in part at the 4th IUPAC Conference on Physical Organic Chemistry, York, England, September 1978.

(2) On sabbatical leave from Ripon College, 1975–1976.

(3) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1449.

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(6) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173.

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among aromatic systems, 2-haloquinoline > 2-halopyridine > halobenzene, for reactions with acetone enolate ion.

We now report a study of the effects of substituents in iodobenzenes on reactivity with pinacolone enolate ion (eq 1). We have studied reactivity in two ways: by direct measurement of reaction rate in experiments involving the various substituted iodobenzenes separately and by measuring the relative reactivity of each substituted iodobenzene vs. bromobenzene in a competition experiment. The two approaches give vastly different indications of relative reactivity, and that in itself is enlightening.

## Results

We have previously reported[3] that the reaction of *m*-iodoanisole, **1e**, with **2** in $Me_2SO$ gives, besides the expected **3e**, a significant amount (e.g., 13%) of phenol **4**. The latter has its genesis in an arynic reaction as sketched in Scheme I.

The products of reaction of substrates **1b**, **1c**, **1d**, and **1f** with **2** in $Me_2SO$ were therefore examined with care. In all these cases the only aromatic product found was the corresponding compound of type **3** representing ipso substitution of iodine by an acetonyl residue. In no other case was a phenolic product found.

In those experiments preliminary to rate measurements, an interesting qualitative observation was made, namely, that with the concentration of **2** nearly constant the extent of conversion of any substrate to products per unit time was much greater with the substrate at low concentration than at higher concentration. For example, when $[\mathbf{2}]_0$ = 0.29 M, $[t\text{-BuO}^-K^+]_0$ = 0.04 M, and $[\mathbf{1c}]_0$ = 0.0063 M, 59% of iodide ion was released in 62 min at 25 °C, but with the same initial concentrations of **2** and $t$-BuO$^-$K$^+$ but $[\mathbf{1c}]_0$ = 0.088 M only 25% of iodide ion was released in 200 min. At the higher substrate concentration, the percent of iodide ion released was less than half as great even in a reaction time more than three times as long. The conditions for these two experiments approach those in which pseudo-first-order kinetics should prevail if the reaction were second order, in which case the percent of iodide ion released per unit time should be the same for any initial substrate concentration. The import is that the kinetics are not simple second order.

In our previous report[3] of the kinetics of reaction of **1a** with **2**, we related that neither first- nor second-order kinetics were obeyed but that the data conformed to the differential equation of (2) in its integrated form (eq 3).

$$dx/dt = k_e[\mathbf{1}]/[\mathrm{X}] \qquad (2)$$

$$-x + a \ln [a/(a - x)] = k_e t \qquad (3)$$

In eq 2, X is an unidentified product and is taken to have concentration equal to that of iodide ion. However, it is not iodide ion, for we demonstrated that iodide ion does not retard the reaction. Likewise, we were unable to detect retardation by the potassium salt of product **3a**. In eq 3, $a$ is the initial concentration of substrate and $x$ is the concentration of X at any time.

In the present work we found our kinetic data also to conform rather well to eq 3. The plots for reactions of **1c**, **1d**, and **1f** showed minor deviations early in runs, suggestive of induction periods, but otherwise all plots were linear. As before, we are unsatisfied to use such a peculiar rate law, but again we do use it for the pragmatic purpose of expressing reactivity.

Rate determinations for reactions of six substrates with **2** in $Me_2SO$ in the dark are summarized in Table I. It will be noted that there was substantial variation in reactivity within this set of reactions.

**Table I. Rate Constants for Reactions of Aryl Iodides with Potassium Pinacolone Enolate in Dimethyl Sulfoxide at 25 °C in the Dark**

| expt no. | substrate | substituent | $10^7 k_e$, M s$^{-1}$ | $k_{rel}$ |
|---|---|---|---|---|
| 1 | 1a | H | 7.0$^a$ | (1.0) |
| 2 | 1b | $p$-CH$_3$ | 0.65$^b$ | 0.093 |
| 3 | 1c | $m$-CH$_3$ | 0.67 | 0.096 |
| 4 | 1d | $p$-OCH$_3$ | 1.05$^b$ | 0.15 |
| 5 | 1e | $m$-OCH$_3$ | 260$^c$ | 37 |
| 6 | 1f | $p$-F | 23.6$^b$ | 3.4 |

$^a$ From ref 3. $^b$ Average of two determinations. $^c$ The measured constant of 2.95 × $10^{-5}$ M s$^{-1}$ was corrected for estimated 13% reaction to form **4**.

**Table II. Competition between Aryl Iodides and Bromobenzene in Reactions with Potassium Pinacolone Enolate in Dimethyl Sulfoxide in the Dark at 25 °C**

| expt no. | aryl iodide | substituent | $k_{ArI}/k_{PhBr}$ | $k_{ArI}$(rel) |
|---|---|---|---|---|
| 7 | 1a | H | 7.3$^a$ | (1.00) |
| 8 | 1b | $p$-CH$_3$ | 6.9$^b$ | 0.95 |
| 9 | 1c | $m$-CH$_3$ | 7.4$^c$ | 1.01 |
| 10 | 1d | $p$-OCH$_3$ | 6.4 | 0.88 |
| 11 | 1e | $m$-OCH$_3$ | 11.8$^d$ | 1.62 |
| 12 | 1f | $p$-F | 9.4$^e$ | 1.29 |

$^a$ From ref 3. $^b$ By GLC, estimated at 6.3. $^c$ By GLC, estimated as 7.2. $^d$ The apparent $k_{ArI}/k_{PhBr}$ during the initial 63 s, 12.4 (average of 2 runs), was multiplied by the yield ratio **3e**/(**3e** + **4**) for the initial 60 s, which was 0.95. $^e$ By GLC, estimated as 9.3.

Aryl radicals are intermediates in the $S_{RN}1$ mechanism believed to prevail in these reactions. One conceivable explanation of the slowness of reaction of **1b** and **1c** would be that the aryl radicals were in part abstracting hydrogen from toluene-type methyl groups of reactants and/or products, forming radicals of benzylic type which are rather unreactive. If so, the reactivity of iodobenzene (**1a**) should be reduced by having toluene present. However, toluene in amount equal to that of **1a** was found to have no effect on the reactivity of **1a**.

## Competition Experiments

In our previous study,[3] we conducted experiments in which **1a** and bromobenzene were placed in competition, reacting with **2** in $Me_2SO$. The reactivity ratio $k_{PhI}/k_{PhBr}$ was found to be 6.1.

We have now carried out experiments of that type with all the aryl iodides represented in Table I, in each case putting the aryl iodide in competition with a fourfold excess of bromobenzene. In each experiment, aliquots were withdrawn at intervals and titrated potentiometrically for bromide and iodide ion. The relative reactivities $k_{ArI}/k_{PhBr}$ thereby estimated varied only randomly and within a narrow range from aliquot to aliquot, except in the case of **1e** which is further discussed below. Details of representative experiments with **1b** and **1e** appear in the Experimental Section.

The ratio $k_{ArI}/k_{PhBr}$ was also determined in several cases from the relative yields of substituted phenylpinacolone (**3**) vs. unsubstituted phenylpinacolone (**3a**) as measured by GLC. Estimates by this technique were in good agreement with those by titration analysis.

Division of the values of $k_{ArI}/k_{PhBr}$ for the several substrates by that for iodobenzene gave the relative reactivity of each aryl iodide in the competition situation, symbolized $k_{ArI}$(rel). These reactivity indices as well as

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(8) Komin, A. P.; Wolfe, J. F. *J. Org. Chem.* 1977, 42, 2481.

Scheme II

$$[\mathrm{ArI}]^{-\cdot} \rightarrow \mathrm{Ar}\cdot + \mathrm{I}^- \tag{M1}$$

$$\mathrm{Ar}\cdot + \underset{\mathbf{2}}{\mathrm{CH_2{=}C(O^-)CMe_3}} \rightarrow \underset{\mathbf{5}}{[\mathrm{ArCH_2C({=}O)CMe_3}]^{-\cdot}} \tag{M2}$$

$$\mathbf{5} + \mathrm{ArI} \rightarrow \underset{\mathbf{3}}{\mathrm{ArCH_2C({=}O)CMe_3}} + [\mathrm{ArI}]^{-\cdot} \tag{M3}$$

the $k_{\mathrm{ArI}}/k_{\mathrm{PhBr}}$ from which they derive are presented in Table II.

In the case of *p*-iodotoluene (**1b**), $k_{\mathrm{ArI}}$(rel) was also measured directly from the relative yields of **3b** and **3a** formed by reaction of a mixture of **1b** and **1a** with **2** in $\mathrm{Me_2SO}$. The value so obtained, 0.88, is in reasonable agreement with 0.95 as estimated indirectly through comparisons with bromobenzene.

In the case of *m*-iodoanisole (**1e**), the relative yield of iodide with respect to bromide ion increased steadily during each of two experiments performed. We understand this to be a consequence of suppression of the $\mathrm{S_{RN}1}$ reactions by **4**, which is the product of the aryne reaction, while the aryne reaction proceeds unrestrained. Accordingly we base our estimate of $k_{\mathrm{ArI}}/k_{\mathrm{PhBr}}$ for **1e** on halide ion release during the first minute of reaction during which inhibition by **4** was minimal, with correction for the small amount of **4** formed during that very early phase of the process. We noted that in competition between **1e** and PhBr, bromide ion release was very slow after the first 3 min owing to inhibition by **4**; see Experimental Section.

Curiously, the reaction of **2** with iodobenzene was somewhat retarded by the presence of bromobenzene. At similar concentrations ([**2**] = 0.3 M, [**1a**] ≈ 0.006 M, [*t*-BuOK] = 0.04 M) **1a** gave 83% of iodide ion in 5 min without PhBr but only 64% when 0.026 M PhBr was also present.

## Discussion

We have found an enormous difference in measures of the relative reactivity of substrates **1a–f**, depending on the method of measurement. When these substrates react separately with **2**, the spread in reactivity between the fastest and the slowest is nearly 400-fold (Table I), but when relative reactivity is measured by competition the spread is less than twofold (Table II).

This huge difference is rationally interpreted in terms of the $\mathrm{S_{RN}1}$ mechanism which was indicated for these reactions by our previous study.[3] That is a radical chain mechanism, and as such it comprises initiation, propagation, and termination steps. The propagation cycle is presented in Scheme II.

When two substrates react competitively, electron-transfer step M3 is probably the one in which relative reactivity is determined. Provided that the aryl iodide radical anion (as well as bromobenzene radical anion) react only by fragmentation (step M1), it is the relative rates of electron transfer to the two competing aryl halides in step M3 that governs the relative rates of consumption of the two substrates.

When two substrates react separately, overall reactivity is determined not only by events within the propagation cycle but also by the relative rates of initiation and termination. In principle, the sensitivity of initiation and termination rates to the effects of substituents may be very different from that of propagation rates. Thus, that there should be a great difference between our measures of relative reactivity by two approaches is intelligible.

Returning to the competition experiments, we note that the aryl halides probably are also involved in initiation steps and that there may be substantial differences in the rates of initiation steps involving different aryl halides, perhaps much greater than the differences in propagation rates. However, whichever substrate participates in initiation, reactive intermediates are generated which may then react with either substrate in propagation steps at rates determined only by substituent effects on those steps. This enables a substrate that is fast at initiation to entrain another that is slow at initiation, for example, in the observed acceleration of the reaction of bromobenzene with **2** caused by addition of iodobenzene.[3] Thus, if the propagation chain is long, the relative reactivities of substrates in competition will be unaffected by their relative reactivities in initiation.

Table III. Summary of Corrrelations

| ordinate | abscissa[a] | slope[b] | $\sigma_y$[c] | $r$[d] |
|---|---|---|---|---|
| log $k_e$ | $\sigma$ (Hammett) | 6.1 ± 1.9 | 0.61 | 0.850 |
| log $k_e$ | $\sigma$ (Wepster) | 9.1 ± 2.4 | 0.55 | 0.882 |
| log $k_e$ | $E_{1/2}$ ($\mathrm{LiClO_4}$) | 24 ± 6 | 0.50 | 0.902 |
| log $k_e$ | $E_{1/2}$ ($\mathrm{Me_4NCl}$) | 28 ± 6 | 0.43 | 0.929 |
| log $k_e$ | log $k_{\mathrm{ArI}}$(rel) | 9.7 ± 1.9 | 0.42 | 0.932 |
| log $k_{\mathrm{ArI}}$(rel) | $\sigma$ (Hammett) | 0.60 ± 0.16 | 0.053 | 0.878 |
| log $k_{\mathrm{ArI}}$(rel) | $\sigma$ (Wepster) | 0.87 ± 0.24 | 0.053 | 0.879 |
| log $k_{\mathrm{ArI}}$(rel) | $E_{1/2}$ ($\mathrm{LiClO_4}$) | 2.2 ± 0.6 | 0.052 | 0.884 |
| log $k_{\mathrm{ArI}}$(rel) | $E_{1/2}$ ($\mathrm{Me_4NCl}$) | 2.7 ± 0.6 | 0.045 | 0.915 |

[a] $\sigma$ (Hammett) from: Bunnett, J. F. In "Investigation of Rates and Mechanisms of Reactions"; Lewis, E. S., Weissberger, A., Eds.; Interscience Publishers: New York, 1961, p 215. $\sigma$ (Wepster) from ref 9, with choice of −0.175 for *p*-$\mathrm{OCH_3}$. $E_{1/2}$ from ref 10. [b] The standard deviation of the slope is shown. [c] Standard deviation of points from the linear regression line in the *y* direction. [d] Correlation coefficient.

We have sought to correlate our rate data with substituent ($\sigma$) parameters, and the results are displayed in Table III. Neither log $k_e$ (for substrates reacting separately) nor log $k_{\mathrm{ArI}}$(rel) (from competition experiments) correlates very well with either the original Hammett $\sigma$ parameters or with the $\sigma$ parameters of van Bekkum, Verkade, and Wepster[9] (which are free of the contribution of mesomeric interaction between para substituents and the carboxyl group of benzoic acids). Correlation is somewhat better with the Wepster $\sigma$ parameters. (It is worse with $\sigma^+$.) The slope parameter for log $k_e$ is in either case about 10 times greater than for log $k_{\mathrm{ArI}}$(rel).

Because the step or steps in which reaction rate is determined probably involve electron transfer, we also explored correlation of our rate data with polarographic half-wave reduction potentials. Such are available for our substrates, both for 1 M $\mathrm{LiClO_4}$ and for 0.1 M $\mathrm{Me_4NCl}$ as supporting electrolyte, in a report by Hussey and Diefenderfer.[10] In interpreting $E_{1/2}$ values for the irreversible cathodic reduction of aryl iodides, one must bear in mind that they are not pure thermodynamic values but also reflect kinetic parameters[11] which for the present system are poorly understood.

As evident in Table III, both log $k_e$ and log $k_{\mathrm{ArI}}$(rel) correlate better with $E_{1/2}$ values than with $\sigma$ values, as judged either by the lower standard deviation of points from the linear regression line ($\sigma_y$) or by the higher correlation coefficient ($r$).

It is perhaps significant that the best correlation is of log $k_e$ with log $k_{\mathrm{ArI}}$(rel), as judged either by the $\sigma_y$ or the $r$ statistical parameters, although it is only slightly better

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(9) van Bekkum, H.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 815.

(10) Hussey, W. W.; Diefenderfer, A. J. *J. Am. Chem. Soc.* **1967**, *89*, 5359.

(11) Perrin, C. L. *Prog. Phys. Org. Chem.* **1965**, *3*, 165.

than the correlation of either with $E_{1/2}(Me_4NCl)$. This suggests that similar factors influence relative reactivity separately, as in competition experiments, despite the great difference in sensitivity to those factors.

In step M3 of the propagation cycle (Scheme II), the transferred electron is probably received into a $\pi^*$ MO of the aromatic $\pi$ system, and the effects of substituents probably are in large part concerned with their effects on the energy level of that MO and on the energy barrier to electron transfer. This is an area which has not been illuminated very well either by theoretical studies[12] or by experiment. One consideration is that the two lowest unoccupied MO's of a benzenoid $\pi$ system, corresponding to wave functions $\psi_4$ and $\psi_5$, which are degenerate in benzene itself, may differ in energy level in a substituted benzene. It is conceivable that some substituents and/or orientations may favor one $\pi^*$ orbital, and others the other. The substituent effects that are exerted in this system are of a different sort than those which govern reactivity in molecules without occupation of $\pi^*$ orbitals.[13] Indeed, it is perhaps more remarkable that we observed any correlation with Hammett or Wepster $\sigma$ values than that the correlations are poor. It is noteworthy that polarographic $E_{1/2}$ values for aryl iodides correlate only roughly with Hammett $\sigma$ values.[10]

Possibly the substituents also affect the energy levels and electron-transfer reactivity of radical anions of type **5** in step M3. With the trivial exception of the iodobenzene case, in every competition experiment from a third to a half of those type **5** species had no substituent, being derived from bromobenzene. For those that bore a substituent, it is possible that the extra electron was carried in the $\pi^*$ MO of the carbonyl group, rather far from the substituent and probably little affected by it. Thus it seems likely that substituent effects on step M3 have more to do with the receiving than with the donating aspect of the process.

For initiation, a probable mechanism is thermally activated electron transfer from enolate ion **2** to substrate; see eq M4. If so, substituent effects may be similar to

$$ArI + \mathbf{2} \rightarrow [ArI]^{-\cdot} + \cdot CH_2C(=O)CMe_3 \qquad (M4)$$

those in step M3. It is conceivable that reactivity in separate reactions is largely determined by rates of initiation. It would then follow that relative reactivity in separate reactions should correlate with relative reactivity in competition, which is somewhat the case (Table III).

## Experimental Section

Materials, experimental procedures, and methods of analysis were as previously described.[3]

Several early experiments were conducted so as to provide qualitative indications of (separate) reactivity and for the purpose of preparing samples of the several products of type **3** for use in standardizing GLC analyses. After reaction of each substrate with **2** in the dark for a period of 60–202 min, an aliquot was removed for analysis by titration for iodide ion, and then the reaction was allowed to proceed nearly to completion either in the dark or with irradiation in the Rayonet Model RPR-100 photochemical reactor for periods varying from 60 to 132 min. Properties of most of the arylpinacolones were described earlier.[3]

**3,3-Dimethyl-1-(*p*-methoxyphenyl)-2-butanone (3d)** was prepared from *p*-iodoanisole in 81% yield and isolated by liquid chromatography on silica gel with elution first with petroleum ether (which eluted unreacted **1d**) and then with a mixture of 10% diethyl ether and 90% petroleum ether which eluted **3d**. **3d** was obtained as an oil: NMR ($CCl_4$) $\delta$ 1.12 (s, 9 H), 3.58 (s, 2 H), 3.67 (s, 3 H), 6.83 (q, 4 H); IR (film) 1720, 1615, 1515, 1465, 1365, 1245, 1175, 1060, 1030, 815, 780 cm$^{-1}$; MS *m/e* 206 (molecular ion), 121 (base peak).

Table IV. A Representative Competition Experiment: *p*-Iodotoluene (**1b**) vs. Bromobenzene in Reaction with **2**[a]

| time, min | vol of $AgNO_3$ for $I^-$, mL | vol of $AgNO_3$ for $Br^-$, mL | $k_{ArI}/k_{PhBr}$ |
|---|---|---|---|
| 10 | 0.51 | 0.30 | 6.90 |
| 20 | 0.58 | 0.33 | 6.69 |
| 30 | 0.66 | 0.39 | 7.20 |
| 45 | 0.75 | 0.47 | 7.00 |
| 60 | 0.79 | 0.52 | 6.75 |
| ∞ | (1.84)[b] | (6.52)[b] | 6.91[c] |

[a] Initial concentrations: PhBr, 0.0263 M; **1b**, 0.00742 M; **2**, 0.288 M; *t*-BuOK, 0.038 M. Aliquots (5 mL) were withdrawn and titrated with 0.0202 M $AgNO_3$. [b] Theoretical values. [c] Average of five determinations, tabulated in Table II.

Table V. Competition between *m*-Iodoanisole (**1e**) and Bromobenzene in Reaction with **2**[a]

| time, min | vol of $AgNO_3$ for $I^-$, mL | vol of $AgNO_3$ for $Br^-$, mL | $k_{ArI}/k_{PhBr}$ |
|---|---|---|---|
| 1.05 | 0.38 | 0.14 | 11.4 |
| 3.00 | 0.58 | 0.22 | 11.9 |
| 5.15 | 0.69 | 0.25 | 13.1 |
| 7.10 | 0.77 | 0.26 | 14.5 |
| 10.00 | 0.85 | 0.28 | 15.5 |
| ∞ | (1.70)[b] | (6.41)[b] | |

[a] Initial concentrations: PhBr, 0.0259 M; **1e**, 0.00688 M; **2**, 0.288 M; *t*-BuOK, 0.038 M. Aliquots (5 mL) were withdrawn and titrated with 0.0202 M $AgNO_3$. [b] Theoretical values.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.60; H, 8.79.

**3,3-Dimethyl-1-(*p*-fluorophenyl)-2-butanone (3f)** was prepared from **1f** in 71% yield, accompanied by a substance, mp 147–148 °C (from methanol), whose NMR and mass (*m/e* 203, 201, 183, 85, 57) spectra and elemental analysis suggested but did not confirm the structure 3,3-dimethyl-1,1-bis(*p*-fluorophenyl)-2-butanone. **3f** was isolated by liquid chromatography as described above except that elution of **3f** was by means of petroleum ether containing 2% of diethyl ether. **3f** was obtained as an oil: NMR ($CCl_4$) $\delta$ 1.07 (s, 9 H), 3.60 (s, 2 H), 6.5–7.17 (m, 4 H); IR (film) 1715, 1515, 1225, 1060, 785 cm$^{-1}$; MS *m/e* 194 (molecular ion), 109 (base peak).

Anal. Calcd for $C_{12}H_{15}FO$: C, 74.20; H, 7.78. Found: C, 74.05; H, 7.84.

**Rate Measurements.** The procedures previously described[3] were employed. Initial concentrations were approximately 0.025 M for the aryl iodide, 0.10 M for **2**, and 0.06 M for free potassium *tert*-butoxide (beyond that used to convert pinacolone to **2**). Plots of data according to eq 3 for **1c**, **1d**, and **1f** showed lower slopes early in runs, suggestive of induction periods, but were otherwise linear. We note particularly that the plot for **1e** was linear to 82% completion of reaction, with downward slope after that.

***Competition Experiments.*** *Initial concentrations* were approximately 0.026 M for bromobenzene, 0.007 M for the aryl iodide, 0.288 M for **2**, and 0.038 M for free potassium *tert*-butoxide, in purified dimethyl sulfoxide as solvent. Aliquots (5 mL) were withdrawn at recorded times, diluted with water, acidified with nitric acid, and titrated potentiometrically with $AgNO_3$. Data for a representative experiment, involving **1b**, are presented in Table IV. Relative reactivity ($k_{ArI}/k_{PhBr}$) was calculated by eq 4, where $[ArI]_0$ and $[ArI]_t$ represent concentrations at time zero and at time *t*, respectively.[14]

$$k_{ArI}/k_{PhBr} = \ln([ArI]_0/[ArI]_t)/\ln([PhBr]_0/[PhBr]_t) \quad (4)$$

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[12] Hinde, A. L.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 4681.

[13] Considerations of a similar sort, but involving $\psi_2$ and $\psi_3$, were discussed by: Hanstein, W.; Berwin, H. J.; Traylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 829.

Whereas in experiments with all substrates but **1e** the value of $k_{\mathrm{ArI}}/k_{\mathrm{PhBr}}$ reckoned from each aliquot varied randomly within a run, as illustrated in Table IV, a different pattern of behavior was encountered with **1e**. One of two nearly identical experiments is detailed in Table V. It should be noted that bromide ion release nearly ceased after 3 min. In the other experiment, the value of $k_{\mathrm{ArI}}/k_{\mathrm{PhBr}}$ for the initial aliquot was 13.4. The average of 11.4 (Table V) and 13.4 is 12.4, and this was multiplied by the fraction of **3e** in the product mixture of **3e** and **4** to get the value of $k_{\mathrm{ArI}}/k_{\mathrm{PhBr}}$ for the $S_{RN}1$ reaction of **1e** listed in Table II.

**Registry No. 1a**, 591-50-4; **1b**, 624-31-7; **1c**, 625-95-6; **1d**, 696-62-8; **1e**, 766-85-8; **1f**, 352-34-1; **2**, 51742-96-2; **3a**, 6721-67-1; **3b**, 61394-79-4; **3c**, 61394-80-7; **3d**, 65853-51-2; **3e**, 61394-81-8; **3f**, 70445-94-2; **4**, 33617-66-2; bromobenzene, 108-86-1.

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[14] Bunnett, J. F. In "Investigation of Rates and Mechanisms of Reactions", 3rd ed.; Lewis, E. S., Ed.; Wiley: New York, 1974; p 159.

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# Considerations on the Effect of a Carbonyl Group on the Ring Opening of a Neighboring Bromonium Ion

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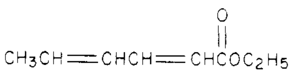
*Received January 23, 1979*

Studies on the addition of bromine chloride (BrCl) to methyl acrylate (**3a**), methyl isocrotonate (**3b**), and methyl crotonate (**3c**) under ionic and radical conditions are reported. Under ionic conditions, the following percentages of $\alpha$ attack (adjacent to carbonyl group) of the chloride ion on the intermediate bromonium ions to give bromo chlorides occurred respectively: **3a** (17%), **3b** (7%), and **3c** (8%). On the basis of these results, we conclude that the carbonyl group in the bromonium ions for **3a–c** does not accelerate ring opening at the $\alpha$ position as might be anticipated if the ring openings occurred by an $S_N2$ process. On the other hand, an $S_N1$ mechanism in these ring openings is not supported by the results from **3c**. More $\beta$ attack should occur with **3c** than **3a** if the mechanism is $S_N1$ since the methyl group should stabilize development of a positive charge at the $\beta$ carbon. Perhaps the ring openings occur by an $S_N2$ process, but the carbonyl group fails to accelerate $\alpha$ attack because the essential orbitals do not align properly with the $\pi$ bond of the carbonyl group. Radical addition of BrCl to **3a** produced exclusively methyl 3-bromo-2-chloropropionate. Apparently, the bromine atom attacks the $\beta$ carbon to give a resonance-stabilized intermediate which abstracts a chlorine atom from BrCl. The ionic reactions of BrCl with **3b,c** are so rapid that there appears to be little radical addition in these cases.

During recent investigations of ours[1,2] on the halogenation of ethyl sorbate (**1**), we became interested in the effect that the carbonyl group exerts on the direction of ring opening of a neighboring bromonium ion (**2**). The literature contains numerous references to studies on the first step in halogenation reactions (halonium ion formation), but there have been few investigations of factors which influence the direction of halonium ion ring openings (the second step).

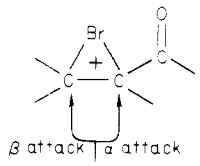
When we began our study, the only previous investigation in this area was done by de la Mare and coworkers[3a–c] on the addition of hypochlorous acid and chlorine acetate to cinnamic acid and methyl cinnamates. In these reactions, the chloronium ion was opened exclusively at the carbon adjacent to the phenyl ring. These investigators also determined the kinetics of the addition of chlorine acetate to acrylic acid but did not establish the composition of the product. They did state, however, that, "It is interesting to note, however, that the reaction does not appear to be completely regiospecific...".[3c] Recently, Dubois and Chretien discussed the ring openings of bromonium ions from the standpoints of charge distribution in the bromonium ion and hard–soft acid–base theory.[4]

We choose to study the addition of bromine chloride, BrCl, in methylene chloride to the following carbonyl conjugated olefins: methyl acrylate (**3a**), methyl isocrotonate (**3b**), and methyl crotonate (**3c**). To the best of our knowledge, BrCl or other unsymmetrical electrophiles have not been added to **3a–c** or closely related alkenes under the conditions described in this paper.[5]

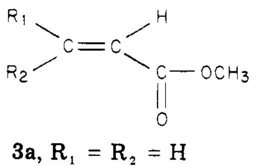


$CH_3CH{=}CHCH{=}CH\overset{O}{\overset{\|}{C}}OC_2H_5$

**1**



**2**



**3a**, $R_1 = R_2 = H$
**b**, $R_1 = H$; $R_2 = CH_3$
**c**, $R_1 = CH_3$; $R_2 = H$

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[1] D. F. Shellhamer, V. L. Heasley, J. E. Foster, J. K. Luttrull, and G. E. Heasley, *J. Org. Chem.*, **42**, 2141 (1977).

[2] D. F. Shellhamer, V. L. Heasley, J. E. Foster, J. K. Luttrull, and G. E. Heasley, *J. Org. Chem.*, **43**, 2652 (1978).

[3] (a) P. B. D. de la Mare and M. A. Wilson, *J. Chem. Soc., Perkin Trans. 2*, 653 (1973); (b) P. B. D. de la Mare, M. A. Wilson, and M. J. Rosser, *ibid.*, 1480 (1973); (c) P. B. D. de la Mare, C. J. O'Connor, and M. A. Wilson, *ibid.*, 1150 (1975).

[4] J. E. Dubois and J. R. Chretien, *J. Am. Chem. Soc.*, **100**, 3506 (1978).

[5] Bromine chloride in aqueous solution, prepared in situ from $KBrO_3$, KBr, and 25% HCl, was added to acrylic acid and *n*-butyl methacrylate. Only anti-Markownikov addition ($\beta$ attack) was reported: S. Groszkowski and J. Sienkiewicz, *Rocz. Chem.*, **45** (10) 1779 (1971). P. Melikoff (*Ber.*, **12**, 2227 (1879); **13**, 2153 (1880)) reported that 2-chloro-3-hydroxypropanoic acid and 3-chloro-2-hydroxypropanoic acid are formed in the addition of HOCl to acrylic acid.

0022-3263/79/1944-2608$01.00/0