

Hz, 2 H), 7.76 (td, $J = 7.50$, 1.67 Hz, 2 H), 7.59 (d, $J = 2.12$ Hz, 1 H), 6.48 (d, $J = 2.26$ Hz, 1 H), 1.34 (s, 9 H), 1.10 (s, 9 H); the OH signal was not seen.

Preparation of Authentic 19 and of Its Isomer 2-Acetamino-4-*tert*-butylphenol (20). Compound 19 is recorded as having mp 168–169 °C,¹³ differing from our mp 145–146 °C. Therefore, preparation of 19 was carried out as described in that patent. Sulfanilic acid (870 mg, 5.0 mmol) was dissolved in a hot solution of 270 mg (2.5 mmol) of Na₂CO₃ in 5 mL of water. To this solution, after it had cooled, was added a solution of 380 mg (5.0 mmol) of NaNO₂ in 1 mL of water. The resulting solution was poured into a mixture of 1.3 g (13 mmol) of concd HCl and 6 g of crushed ice. The suspension of the diazonium salt that had been formed was poured into a solution of 750 mg (5.0 mmol) of 2-*tert*-butylphenol (1h) and 1.1 g (28 mmol) of NaOH in 6 mL of water to which had been added 4 g of crushed ice. A dark red solution formed that was stirred at 5 °C for 30 min and then warmed to 75 °C. To the warm solution was added 2.8 g (16 mmol) of sodium hydrosulfite in small amounts. The temperature of the solution rose to 80 °C and the solution became pale yellow. A dark green oil settled out and solidified when cooled to 10 °C. The solid was removed, washed with a dilute sodium hydrosulfite solution, and dissolved in 3 mL of acetic acid containing 600 mg of acetic anhydride. This solution was warmed for 1 h on a steam bath and then poured into 20 mL of water. The precipitated solid was collected, dried under vacuum, and crystallized from aqueous methanol, giving 520 mg (2.5 mmol, 50%) of 19, mp 146–147 °C. ¹H NMR (CDCl₃/CD₃CN, 5:1): δ , 7.71 (br s, 1 H), 7.29 (dd, $J = 8.46$, 2.60 Hz, 1 H), 7.21 (d, $J = 2.52$ Hz, 1 H), 6.66 (d, $J = 8.42$ Hz, 1 H), 6.39 (s, 1 H), 2.09 (s, 3 H), 1.36 (s, 9 H).

Anal. Calcd for C₁₂H₁₇O₂N: C, 69.6; H, 8.21; N, 6.76. Found: C, 69.3; H, 8.49; N, 6.66.

20. A solution of 100 mg (0.61 mmol) of 2-amino-4-*tert*-butylphenol (Aldrich) in 2 mL of acetic acid containing 540 mg (5.3 mmol) of acetic anhydride was heated for 30 min under reflux. The solution was cooled and poured onto crushed ice. The precipitate was collected and dried under vacuum, giving 950 mg (0.46 mmol, 75%) of 2-acetamino-4-*tert*-butylphenol (20), mp 167–168 °C; lit.¹⁴ mp 170 °C. ¹H NMR (CDCl₃/CD₃CN, 5:1): δ , 8.91 (s, 1 H), 8.32 (br s, 1 H), 7.13 (dd, $J = 8.30$, 2.33 Hz, 1 H), 7.09 (d, $J = 2.02$ Hz, 1 H), 6.90 (d, $J = 8.28$ Hz, 1 H), 2.23 (s, 3 H), 1.28 (s, 9 H).

Reaction of Th⁺ClO₄⁻ with 4-*tert*-Butylphenol (14). (A) 2:1 Ratio. The amounts of reactants were 60 mg (0.40 mmol) of 14 and 250 mg (0.80 mmol) of Th⁺ClO₄⁻. Precipitation gave 160 mg (0.344 mmol, 86% based on 14) of 5-(5-*tert*-butyl-2-hydroxyphenyl)thianthreniumyl perchlorate (15), mp 214–215 °C,

having acceptable elemental analysis (Table IV). GC analysis of the filtrate on column A gave 82 mg (0.38 mmol, 47.5%) of Th and 2.1 mg (0.014 mmol, 3.5%) of unused 14.

15. ¹H NMR (CD₃CN): δ , 8.24 (dd, $J = 7.73$, 1.57 Hz, 2 H), 7.96 (dd, $J = 7.68$, 1.62 Hz, 2 H), 7.86 (td, $J = 7.61$, 1.55 Hz, 2 H), 7.76 (td, $J = 7.54$, 1.67 Hz, 2 H), 7.58 (dd, $J = 8.62$, 2.32 Hz, 1 H), 7.07 (d, $J = 8.62$ Hz, 1 H), 6.58 (d, $J = 2.20$ Hz, 1 H).

A solution of 100 mg (0.216 mmol) of 15 was treated with aqueous Na₂CO₃ to give 60 mg (0.17 mmol, 77%) of the quinonoid 5-(3-*tert*-butyl-6-oxo-2,4-cyclohexadien-1-ylidene)-5,5-dihydrothianthrene (26), mp 152–154 °C (from CH₃CN). ¹H NMR (CDCl₃): δ , 8.04 (m, 2 H), 7.67 (m, 6 H), 7.32 (dd, $J = 8.78$, 2.36 Hz, 1 H), 6.72 (d, $J = 8.84$ Hz, 1 H), 6.53 (d, $J = 2.34$ Hz, 1 H), 1.17 (s, 9 H).

(B) 4:1 Ratio. Reactants were 30 mg (0.20 mmol) of 14 and 250 mg (0.80 mmol) of Th⁺ClO₄⁻. Products by GC were Th (74 mg, 0.34 mmol, 43%) and ThO (9.2 mg, 0.040 mmol, 5.0%). Precipitation gave 120 mg (0.177 mmol, 89%) of the quinonoid monoperchlorate salt (16), mp 220–225 °C.

A solution of 20 mg (0.03 mmol) of 16 in 10 mL of dry CH₃CN was acidified with HClO₄. Addition of 50 mL of ether and overnight refrigeration of the mixture led to the precipitation of 18 mg (0.023 mmol, 77%) of the bis(thianthreniumyl) diperchlorate 22, mp 124–130 °C. ¹H NMR (CD₃CN): δ , 8.21 (dd, $J = 7.78$, 1.37 Hz, 4 H), 7.94 (dd, $J = 7.66$, 1.64 Hz, 4 H), 7.86 (td, $J = 7.53$, 1.51 Hz, 4 H), 7.75 (td, $J = 7.46$, 1.69 Hz, 4 H), 6.76 (s, 2 H), 0.90 (s, 9 H); the OH signal was not seen.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant No. D-028.

Registry No. 1a, 128-39-2; 1b, 576-26-1; 1c, 2078-54-8; 1d, 87-65-0; 1e, 608-33-3; 1f, 28177-48-2; 1g, 108-95-2; 1h, 88-18-6; 1i, 1745-81-9; 2a, 134189-29-0; 2b, 134189-25-6; 2c, 134189-27-8; 2d, 139656-61-4; 2e, 139656-63-6; 2f, 139656-65-8; 2g, 51608-83-4; 2h, 51608-87-8; 2i, 139656-67-0; 3, 139656-78-3; 4a, 732-26-3; 4b, 489-01-0; 4c, 128-37-0; 5a, 64130-73-0; 5b, 139656-56-7; 5c, 139656-57-8; 5d, 139656-58-9; 5e, 139656-59-0; 6, 719-22-2; 7b, 2409-55-4; 8a, 762-84-5; 8b, 1118-32-7; 8c, 107-58-4; 9, 1879-09-0; 11, 139656-52-3; 13, 105-67-9; 14, 98-54-4; 15, 134189-31-4; 16, 139656-54-5; 17, 96-76-4; 18, 139656-55-6; 19, 4151-47-7; 20, 17791-62-7; 23, 134189-33-6; 24a, 139656-68-1; 24b, 139656-69-2; 24c, 139656-70-5; 24d, 139656-71-6; 24e, 139656-72-7; 24f, 139656-73-8; 24g, 139656-74-9; 24h, 139656-75-0; 24i, 139656-76-1; Th⁺ ClO₄⁻, 35787-71-4; Th, 92-85-3; ThO, 2362-50-7; *t*-BuOH, 71-36-3; Me₂C=CH₂, 115-11-7; MeCN, 75-05-8; EtCN, 107-12-0; CH₂=CHCN, 107-13-1.

Supplementary Material Available: Absorption spectroscopic data and melting points for compounds 2a–i and 24a–i in Table III and elemental analyses of compounds 2h,i, 5b,d,e, 11, 15, 16, and 24a–f in Table IV (2 pages). Ordering information is given on any current masthead page.

(13) Dutch Patent 6603932, September 28, 1966, to Aspro-Nicholas, Ltd., London, England.

(14) Burkhalter, J. H.; Tendick, F. H.; Jones, E. M.; Jones, P. A.; Holcomb, W. F.; Rawlins, A. L. *J. Am. Chem. Soc.* 1948, 70, 1363.

Kinetics and Mechanism of the Radical-Induced Deiodination of Aryl Iodides by Methoxide Ions¹

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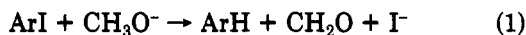
Kinetic study of the deiodination of *m*-chloriodobenzene (to chlorobenzene and iodide ion), as effected by sodium or potassium methoxide in methanol, with initiation by thermolysis of azobisisobutyronitrile (AIBN), reveals kinetic orders 1.0 in aryl iodide and 0.5 in AIBN. The reaction is 0.86 order in potassium methoxide, but the dependence of rate on sodium methoxide concentration is less easily stated. Nitrobenzene inhibits the reaction. At high inhibitor concentrations, the kinetic order in nitrobenzene approaches -1 and concomitantly the kinetic order in AIBN approaches unity. These and related features of kinetic behavior fail to disqualify the radical chain mechanism with electron-transfer steps that has been proposed for this reaction.

In recent years several types of radical chain mechanisms involving electron-transfer steps have been recognized.³

One general type involves abstraction of a hydrogen atom from an anion by a reactive radical, generating as a by-

product a radical anion that acts as an electron donor in a subsequent step of a propagation cycle. When the hydrogen-donor anion is an alkoxide ion derived from methanol or a primary or secondary alcohol, the byproduct is a ketyl, the radical anion of an aldehyde or ketone.

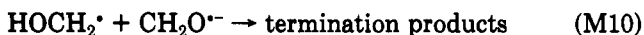
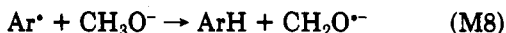
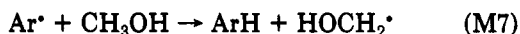
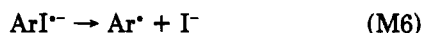
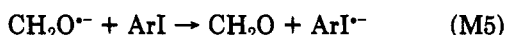
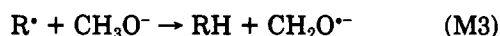
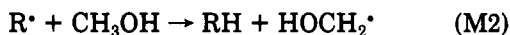
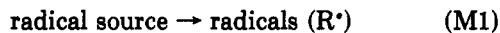
In 1967 Bunnett and Wamser⁴ reported that sodium methoxide in methanol, when provoked by a radical source, can efficiently bring about the deiodination of aryl iodides. That study revealed these cogent features of the process: it requires methoxide ion and a radical-furnishing initiator; at sufficient temperature and time it forms chlorobenzene and iodide ion quantitatively; and it is strongly retarded by nitrobenzene. The overall stoichiometry⁴ is as shown in eq 1, where "ArI" represents an aryl iodide. An elec-



trochemical investigation of this mechanism of reaction in ammonia solvent, by Savéant and co-workers,⁵ is noteworthy.

The mechanism proposed by Bunnett and Wamser is represented, with minor additional features, in Scheme I.

Scheme I



The sketched mechanism differs from that originally proposed⁴ in that it specifies what the termination steps may be and in its inclusion of hydrogen atom abstraction from methoxide ion (steps M3 and M8). The latter are included because of recognition that methoxide ion greatly exceeds methanol in hydrogen-donation reactivity toward aryl radicals.⁶ Also, the aryl iodide radical anion formed

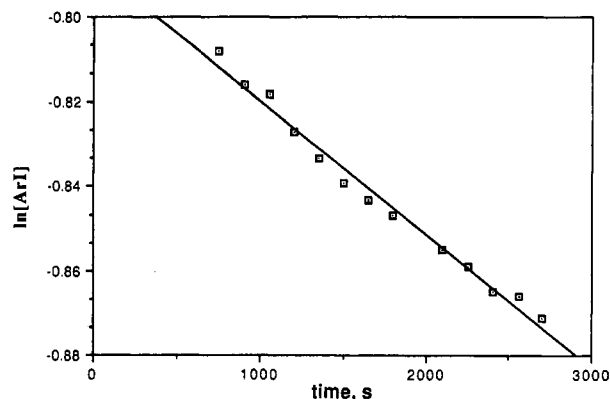


Figure 1. Somewhat representative first-order kinetic plot (for run Hs). This differs from most in comprising 13 data points (most were about 9) and in having correlation coefficient r (0.993) a little lower than most. The rate constant (negative of the slope of the linear regression line drawn) is $3.16 \times 10^{-6} \text{ s}^{-1}$.

in step M5 may not be a true intermediate; conceivably electron transfer (step M5) and C-I bond scission (step M6) are concerted.

Making the usual steady-state assumption, one derives from this mechanistic model the kinetic expression of eq 2, where "In" represents an initiator that undergoes homolysis to form two reactive radicals. "ArI" is *m*-chloriodobenzene in the present work.

$$\frac{-d[\text{ArI}]}{dt} = \frac{k_5 K_4 (k_{1f})^{1/2} [\text{ArI}] [\text{MeO}^-] [\text{In}]^{1/2}}{[k_9 + k_{10} K_4 [\text{MeO}^-] + k_{11} K_4^2 [\text{MeO}^-]^2]^{1/2}} \quad (2)$$

In the study now reported, we conducted kinetic experiments to see whether the rate law dictated by experiment might require rejection of this model.

Experimental Section

Materials. Reagent-grade methanol (Mallinckrodt) was dried with use of magnesium metal. Sodium methoxide solutions were prepared by dissolving clean metallic sodium in methanol under nitrogen and then filtering through a fine sintered glass filter under nitrogen. Potassium methoxide solutions were made similarly, with external cooling by a bath of solid carbon dioxide in 2-propanol during the reaction of potassium metal with methanol. Stock solutions of these metal methoxides were standardized against standard hydrochloric acid solutions.

m-Chloriodobenzene (Eastman Kodak) and chlorobenzene and iodobenzene (Aldrich Chemical Co.) were shown to be pure by gas chromatography and by their infrared spectra. Azobisisobutyronitrile (AIBN) from Eastman Kodak and nitrobenzene from Matheson Coleman-Bell were used without further purification.

Equipment. Gas chromatography was performed on a Hewlett-Packard Model 5750 apparatus, temperature programmable, with a flame ionization detector. A 1.5-m column packed with 5% SE-30 on Chromosorb W (DMCS) was used. Infrared spectra were recorded on a Perkin-Elmer Model 237 instrument and mass spectra by means of a Finnigan Model 4000 GC/MS system. For potentiometric titrations, a Metrohm Model E 300 B pH meter was used.

Kinetics Procedure. The ampule technique⁷ was employed. For each run, a master solution of volume 25 or 50 mL was prepared, and nine equal aliquots were delivered into glass ampules that had been wrapped with aluminum foil. Each ampule was sealed with a torch. The nine ampules were placed in the thermostat bath (at 70.2 °C) at once. At recorded times, ampules were removed, plunged into ice-water for several minutes, and opened and their contents transferred quantitatively into a beaker containing distilled water. The aqueous mixture was extracted

(1) (a) Preliminary communication: *Chim. Ind. (Milan)* 1981, 63, 698. (b) Overview: Bunnett, J. F.; Wamser, C. C.; Tomaselli, G. A. *Atti Accad. Gioenia Catania (Italy)*, in press. (c) Review of general reaction type: Bunnett, J. F. *Acc. Chem. Res.*, in press.

(2) On leave from the Istituto Dipartimentale di Chimica e Chimica industriale dell'Università, Catania, Italy, 1979–80; grateful recipient of a fellowship from Consiglio Nazionale della Ricerche d'Italia.

(3) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 734. Bunnett, J. F. *Acc. Chem. Res.* 1978, 11, 413. Beletskaya, I. P.; Drozd, V. N. *Usp. Khim.* 1979, 48, 793 (Engl. transl. as *Russ. Chem. Rev.* 1979, 48, 431). Alder, R. W. *Chem. Commun.* 1980, 1184. Chanon, M. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 1. Hershberger, J. W.; Kingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* 1982, 104, 3034. Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; American Chemical Society: Washington, DC, 1983. Jönsson, L.; Wistrand, L.-G. *J. Org. Chem.* 1984, 49, 3340. Savéant, J.-M. *Proc. Robert A. Welch Found. Conf. Chem. Res.* 1986, 30, 289. Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: New York, 1987. Ashby, E. C. *Acc. Chem. Res.* 1988, 21, 414. Russell, G. A. *Acc. Chem. Res.* 1989, 22, 1.

(4) Bunnett, J. F.; Wamser, C. C. *J. Am. Chem. Soc.* 1967, 89, 6712.

(5) Amatore, C.; Badoz-Lambling, J.; Bonnel-Huyghes, C.; Pinson, J.; Savéant, J. M.; Thiébaud, A. *J. Am. Chem. Soc.* 1982, 104, 1979.

(6) Boyle, W. J., Jr.; Bunnett, J. F. *J. Am. Chem. Soc.* 1974, 96, 1418.

(7) Bunnett, J. F. *Investigation of Rates and Mechanisms of Reactions*, 4th ed.; Bernasconi, C. F., Ed.; John Wiley & Sons: New York, 1986; Part I, p 215.

twice with pentane, and the aqueous layer was diluted to known volume with water in a volumetric flask. Aliquots of this solution were titrated potentiometrically with standard silver nitrate (silver wire electrode vs glass electrode); the sharp end points revealed the amount of iodide ion released.

Plots of mmols of iodide ion formed vs time were constructed. These were often mildly S-shaped: an early period of increasing slope (an induction period), then a stretch nearly linear, and finally a portion of diminishing slope that we took to represent decline of rate as the concentration of ArI decreased. In such cases the data beyond the induction period were found to give good linear plots of $\ln [\text{ArI}]$ vs time, as for first-order kinetics, and the negatives of the slopes were taken as first-order rate constants. The first-order plot for a typical run (run Es) is presented as Figure 1.

The rate constants determined are presented in Table I. For a few runs, moles iodide ion vs time data from the linear stretch beyond the induction period afforded good linear correlations, the slopes of which approximate zero-order rate constants; division by the initial concentrations of ArI gave rate constants (k_{ψ}) in first-order units (s^{-1}). Sometimes there were substantial periods of both "zero-order" and first-order behavior, enabling the first-order rate constant to be estimated both directly and via the zero-order rate constant; in most cases the two estimates of the first-order rate constant fell within 15% of each other, and the greatest deviation was 22%. Four runs that gave plots of $[\text{I}^-]$ vs time that had constantly increasing slope were judged to represent induction period throughout; they are not reported, for from them no useful rate constant could be obtained.

We have treated initiator concentration as constant and attribute the first-order kinetic behavior uniformly experienced to normal dependence on declining aryl iodide concentration. This treatment is based on three considerations: (1) The thermal decomposition of AIBN is relatively slow at 70 °C. Its half-life in toluene⁸ is 4.8 h and in propylene carbonate⁹ 4.6 h and varies little with change of solvent;¹⁰ most of our kinetic runs were of duration less than 2 h. (2) Although there is some chemical change in AIBN owing presumably to nucleophilic attack by methoxide ions, as shown by Cui,¹¹ the probable product of such attack, the bisimino ester corresponding to AIBN, probably has a thermolysis rate constant close to that of AIBN. (The bisimino ester is known,¹² but we have found no report of its thermolysis rate. The dimethyl ester of azobis(isobutyric acid) has a thermolysis rate constant at 80 °C a little less (by 19% or 29%) than that of AIBN;^{10,13} we presume that the structurally similar bisimino ester has a similar thermolysis rate.) (3) The fact that strictly first-order kinetics were observed indicates that the kinetic consequences of chemical change to AIBN during the short durations of our runs were negligible.

Results

Our first-order rate constant determinations are presented in summary of Table I.¹⁴

Reaction in the Absence of Inhibitors. Our interest was to assess the dependence of reaction rate on the con-

(8) Talât-Erben, M.; Bywater, S. *J. Am. Chem. Soc.* 1955, 77, 3710, 3712.

(9) Calculated from activation parameters of: Petersen, R. C.; Markgraf, J. H.; Ross, S. D. *J. Am. Chem. Soc.* 1961, 83, 3819.

(10) Ziegler, K.; Deprade, W.; Meye, W. *Liebigs Ann. Chem.* 1950, 567, 141.

(11) Cui, J.-j. Unpublished work at Santa Cruz. Cui first verified an earlier kinetic study⁹ of the reaction in toluene at 70 °C. He then studied thermolysis of AIBN in 0.8 M methanolic MeONa at reflux, where he found similarities and differences. Similar is a marked increase in absorption at 320 nm, by 78% in 1 h and 280% in 6 h. Different is that absorption increased slowly at 360 nm, by 19% in 6 h, whereas decrease at 360 nm is the basis of the kinetic determination of thermolysis rate in toluene.

(12) *Beilsteins Handbuch der Organischen Chemie*, 4th ed.; Prager, B., Jacobson, P., Eds.; Hauptwerk, Julius Springer: Berlin, 1922; Vol. 4, p 563.

(13) Lewis, F. M.; Matheson, M. S. *J. Am. Chem. Soc.* 1949, 71, 747.

(14) In Table I, runs are identified by capital letters followed by lower case letters that indicate critical constituents of the reaction solutions: s, MeONa, p, MeOK, n, nitrobenzene (with MeONa), and b, benzophenone (with MeONa).

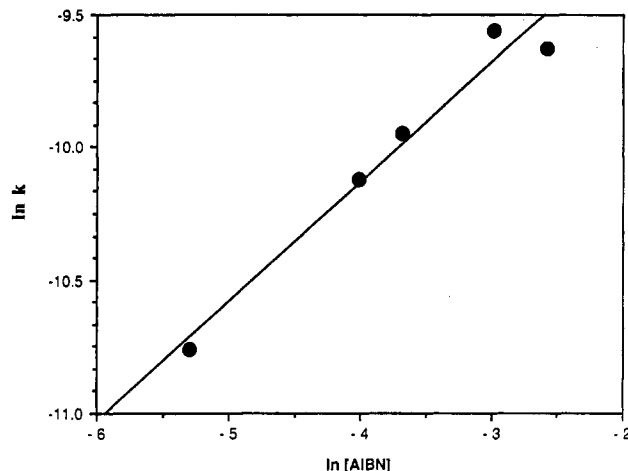


Figure 2. Kinetic order in AIBN; data of runs Ks-Os. The linear regression slope is 0.45; $r = 0.980$.

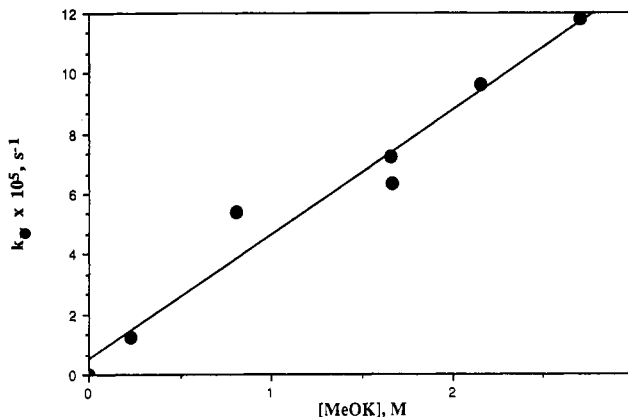


Figure 3. Dependence of rate on $[\text{MeOK}]$; data of runs Zo and Ap-Fp.

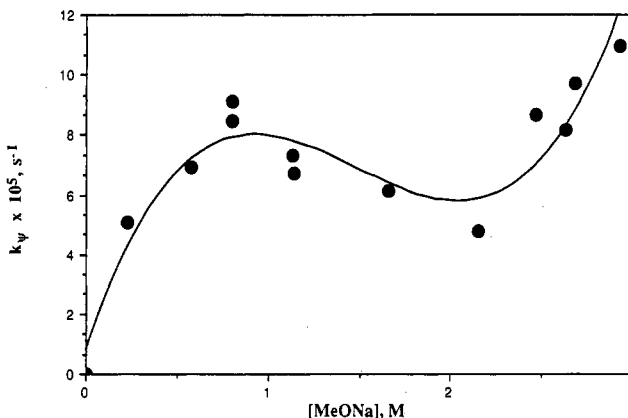


Figure 4. Dependence of rate on $[\text{MeONa}]$; data of runs As-Js, Ns, Ps-Us, and Zo. The curved line was drawn by a Cricket Graph polynomial (order 3) curve-fitting program; equation for the curve is $y = 0.774 + 18.37x - 14.38x^2 + 3.23x^3$.

centrations of *m*-chloriodobenzene (ArI), methoxide ion, and initiator azobisisobutyronitrile (AIBN).

As to dependence of rate on $[\text{ArI}]$, two kinds of evidence indicate strict first order. First, a plot of \ln (zero-order rate constant) vs $\ln [\text{ArI}]_0$ for six runs (Hs, Is, Js, Ns, Ps, and Qs) had slope 0.99, with r 0.967 and standard deviation of slope 0.13. Second, the first-order plots of $\ln [\text{ArI}]$ vs time for 37 of 45 runs were linear with correlation coefficients of 0.990 or greater, and for only 2 was r less than 0.980.

Five runs (Ks-Os) that had virtually identical $[\text{ArI}]_0$ and $[\text{MeONa}]$ but variable $[\text{AIBN}]$ were appropriate to indi-

Table I. Kinetics of Deiodination of *m*-Chloriodobenzene with Alkali Metal Methoxides in Methanol at 70.2 °C

run ^a	[ArI] ₀ M	[AIBN], M	[MeONa], M	[MeOK], M	[PhNO ₂], M	10 ⁵ <i>k_p</i> , s ⁻¹
As	0.0501	0.0251	0.229			5.07
Bs	0.0501	0.0251	0.572			6.93
Cs	0.0501	0.0251	0.801			8.44
Ds	0.0501	0.0251	0.801			9.13
Es	0.0501	0.0251	1.129			7.33
Fs	0.0501	0.0250	1.144			6.72
Gs	0.0502	0.0251	1.659			6.10
Hs	0.4512	0.0251	2.030			3.16
Is	0.3103	0.0251	2.064			3.73
Js	0.1477	0.0246	2.108			4.67
Ks	0.0502	0.0758	2.129			6.56
Ls	0.0501	0.005 02	2.151			2.12
Ms	0.0501	0.0180	2.151			4.02
Ns	0.0501	0.0250	2.150			4.77
Os	0.0501	0.0505	2.151			7.05
Ps	0.2305	0.0251	2.151			8.07
Qs	0.6094	0.0251	2.151			3.25
Rs	0.0501	0.0250	2.465			8.67
Ss	0.0501	0.0250	2.631			8.17
Ts	0.0501	0.0251	2.673			9.71
Us	0.0501	0.0251	2.920			10.96
Xs	0.0501	0	2.920			0.061
Zo	0.0501	0.0251	0	0		0
Ap	0.0501	0.0251		0.223		1.22
Bp	0.0501	0.0250		0.801		5.39
Cp	0.0501	0.0251		1.658		7.23
Dp	0.0501	0.0250		1.660		6.33
Ep	0.0501	0.0250		2.150		9.62
Fp	0.0501	0.0250		2.700		11.80
An	0.0501	0.0251	0.801		0.000 081	5.84
Bn	0.0501	0.0250	0.801		0.000 163	4.75
Cn	0.0501	0.0251	0.801		0.000 569	2.49
Dn	0.0501	0.0250	0.801		0.001 251	1.50
En	0.0501	0.004 28	0.801		0.002 648	0.119
Fn	0.0501	0.009 55	0.801		0.002 648	0.306
Gn	0.0501	0.0158	0.801		0.002 648	0.642
Hn	0.0501	0.0250	0.801		0.002 648	0.806
In	0.0501	0.0502	0.801		0.002 648	1.01
Jn	0.0501	0.1031	0.801		0.002 648	1.37
Kn	0.0501	0.009 58	0.801		0.008 058	0.128
Ln	0.0501	0.0258	0.801		0.008 025	0.328
Mn	0.0501	0.0506	0.801		0.008 058	0.536
Nn	0.0502	0.0747	0.801		0.008 09	0.675
On	0.0501	0.0250	0.801		0.014 07	0.182
Ab	0.0501	0.025	0.801			5.45

^aThe cardinal designation of runs is a capital letter. The trailing lower case letter indicates a prominent constituent of the reaction system: s, sodium methoxide; o, no base; p, potassium methoxide; n, nitrobenzene; and b, benzophenone.

cate the kinetic order in initiator. For them, a plot of $\ln k_p$ vs \ln [AIBN], displayed as Figure 2, was approximately linear ($r = 0.980$), with slope 0.45 ± 0.21 . A partially different set of six runs (Ls–Qs), chosen for strictly identical [MeONa] but with some variation in [ArI]₀, afforded a similar plot of slope 0.53. The reaction is thus half-order in AIBN, within experimental error.

Six runs (Ap–Fp) with potassium methoxide afforded a linear plot of k_p vs [MeOK], presented as Figure 3. The plot of $\log k_p$ vs \log [MeOK] had slope 0.86, which we take as the kinetic order in potassium methoxide.

The dependence of rate on sodium methoxide concentration, shown in Figure 4, was less uniform. The plot looks something like the great Santa Cruz roller coaster. Despite its curious shape, the plot of Figure 4 affirms previous evidence⁴ that the reaction fails in the absence of methoxide ion and is fastest at high concentration of it.

Noteworthy is inversion of the relative reactivity of MeONa vs MeOK as metal methoxide concentration augments. At moderate metal methoxide concentrations,

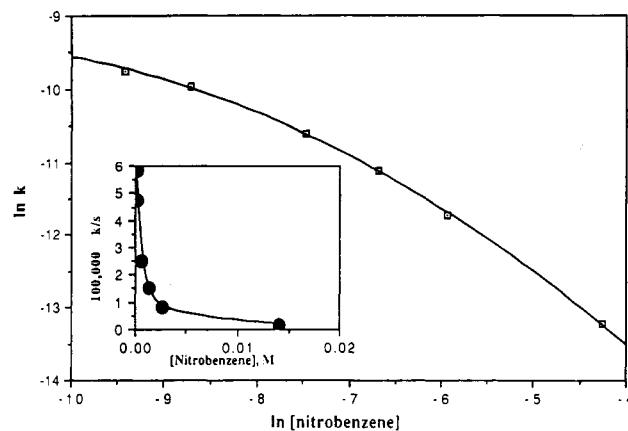


Figure 5. Dependence of rate constant on [PhNO₂]; data of runs An–Dn, Hn, and On. Inset: k vs [PhNO₂]; main figure: $\ln k$ vs \ln [PhNO₂].

reaction with MeONa is faster than with MeOK. At [MeOM] ca. 0.23 M, the observed k_p value for MeONa (run As) is more than four times that for MeOK (run Ap). At [MeOM] ca. 0.8 M, the k_p for MeONa (runs Cs and Ds) is about 60% higher than for MeOK (run Bp). In contrast, rates with the two metal methoxides are similar at [MeOM] ca. 1.66 M (run Gs vs Cp or Dp). Reactivity with MeOK at 2.15 M (run Ep) is about double that with MeONa at the same concentration (run Ns). At [MeOM] ca. 2.7 M, MeOK is also conducive to higher reaction rate (run Fp) than is MeONa (run Ts).

Reaction in the Presence of Nitrobenzene or Benzophenone. Nitrobenzene strongly inhibits deiodination, as shown by the inset in Figure 5, which is reminiscent of the nitrobenzene effect on yields under uniform conditions observed in the earlier study.⁴ The same data, except for the datum for nitrobenzene absent, are presented in Figure 5 (main plot) as a log/log plot. The slope between the two points in the main plot for lowest [PhNO₂] is -0.30 , while it is -0.87 between the two for highest [PhNO₂]. The kinetic order in nitrobenzene is thus negative and variable, depending on the concentration of this inhibitor.

A single run (Ab, in Table I) with benzophenone present in low concentration (1.14×10^{-3} M) showed reactivity about 38% less than under the same conditions without inhibitor (runs Cs and Ds). In contrast, nitrobenzene at about the same concentration (run Bn) causes an approximate 83% reduction in rate.

Several runs provide information about rate dependence on AIBN concentration when nitrobenzene is present. Data from six runs (En–Jn) at [PhNO₂] 0.002 65 M provide a curved plot, concave downward, of $\ln k$ vs \ln [AIBN]; the linear regression slope is 0.75. Four runs (Kn–Nn) at 0.008 M nitrobenzene afford a less curved plot of similar character, with linear regression slope 0.82. These plots are not shown.

Discussion

Reaction in the Absence of Inhibitors. We find that the radical-induced deiodination of *m*-chloriodobenzene by methoxide ion is first order in ArI and one-half order in AIBN and that it approaches negative first order in nitrobenzene at higher nitrobenzene concentrations. The rate dependence on metal methoxide concentration is complex, as shown in Figures 3 and 4. How well do these experimental findings match expectations, as expressed in eq 2, from the mechanism model of Scheme I?

The Aryl Iodide. The observed kinetic order of unity in *m*-chloriodobenzene is as expected (eq 2). Rate laws

first order in substrate are however commonplace, by no means unique to this mechanism. Within the context of Scheme I, the observation of first order in ArI is nevertheless significant, for it indicates that ArI is involved in a crucial propagation step.^{15,16} A further implication is that the species that react(s) with ArI that step is/are involved in the effective termination step(s).¹⁶

Termination Steps. The postulated effective termination steps (M9, M10, M11) involve interaction between hydroxymethyl radicals and/or formaldehyde radical anions. Plausible products from those steps, after product workup, are ethane-1,2-diol (from colligation) and disproportionation products methanol and formaldehyde. We sought to isolate and identify ethanediol as a product, but were not able to find it. Our efforts would not have revealed formation of products from disproportionation steps, for both were present in the system in substantial amounts, one as the solvent and the other as a product of a major propagation step.

The Initiator. For radical chain mechanisms initiated by a substance that undergoes homolysis into two reactive radicals, the observation of kinetic order one-half in initiator is a common one. It is a consequence of the crucial termination steps involving interaction of two radicals capable of chain propagation.¹⁶ Our observed kinetic order of 0.5 in AIBN is therefore strong evidence for a radical chain mechanism and is consistent with the expectation from Scheme I, as expressed in eq 2.

Sodium and Potassium Methoxides. The kinetic order in methoxide ion to be expected on the basis of eq 2 depends on the relative magnitudes of the three terms in the denominator. If k_9 , k_{10} , and k_{11} are invariant as metal methoxide concentration changes, those magnitudes depend on the value of K_4 and on methoxide ion concentration. At very low K_4 and $[\text{MeO}^-]$, the first term (k_9) is much larger than the other two, and the reaction should be first order in methoxide ion. If both K_4 and $[\text{MeO}^-]$ are high, and k_{11} sufficient, the third term overwhelms the other two, and the reaction should be zero order in methoxide ion. Thus, at appropriate values of K_4 , k_9 , k_{10} , and k_{11} , the plot of k_p vs $[\text{MeO}^-]$ could be curved: zero rate in the absence of $[\text{MeO}^-]$ and kinetic order in methoxide ion varying from unity at low $[\text{MeO}^-]$ through ever-diminishing fractional orders, as $[\text{MeO}^-]$ increases, to zero order at high $[\text{MeO}^-]$.

Our kinetic data for reactions with sodium methoxide, plotted in Figure 4, approximate the conceivable curved plot, albeit with some scatter, up to about 1 M MeONa. There are, however, reasons to doubt the suggested interpretation. First, our data for reactions with potassium methoxide (Figure 3) afford a linear plot; that would mean in terms of eq 2 that K_4 was rather small. Second, reactivity with MeOK is lower than with MeONa at low base concentrations but higher at high base concentrations, as mentioned above. Third, the remarkable augmentation of rate at $[\text{MeONa}] > 2.2$ M (Figure 4) is not illuminated by eq 2.

The differences between MeONa and MeOK reactions indicate ion pairing to affect reactivity. Ion pairing of alkali metal cations with methoxide ion in methanol is significant. Conductance measurements show that sodium ion is more tightly associated with methoxide ion than is

potassium.^{17,18} Ion pairing could in principle affect the equilibrium constant for step M4p, the ion-paired analogue of free-ion step M4,¹⁹ as well as rate constants for steps involving ionic reagents.



Formaldehyde radical anion is doubtless also ion paired. Ion pairing with methoxide ion, with its negative charge localized in rather closely held atomic p-orbitals, is probably the tighter, making CH_3O^- in effect a small anion with an uncharged methyl appendage, whereas the extra electron of formaldehyde radical anion that confers its negative charge is in a diffuse molecular π^* -orbital.²⁰ Ion pairing tends to be stronger when ionic radius is smaller.²¹ Accordingly, ion pairing should reduce K_{4p} below K_4 . Moreover, since both theory²¹ and empirical evidence^{17,18} indicate Na^+ to pair more tightly than K^+ with oxy anions, K_{4p} should be lower for sodium than for potassium.²² In terms of eq 2, that should cause a plot such as in Figure 3 or 4 to be more linear for sodium than for potassium, the opposite of what we observed.

Ion pairing could affect the phenomenological rate "constants",²³ k_5 , k_{10} , and k_{11} , for steps M5, M10, and M11. k_5 is a factor in the numerator of the derived kinetic expression (eq 2), regardless of metal methoxide concentration. Step M5 involves electron transfer from formaldehyde radical anion to the aryl iodide. Prediction of whether ion pairing of this electron donor would raise or lower electron-transfer rate is difficult. Ion pairing retards electron transfer in numerous instances²⁴ but ketyl \rightarrow ketone electron transfer²⁵ is accelerated by ion pairing. In the latter system, electron transfer is coordinated with cation transfer. That might also occur if steps M5 and M6 are merged, in which case the metal ion might assist detachment of iodide ion from carbon.

If indeed ion pairing accelerates step M5 or merged M5-M6, and sodium associates more strongly than potassium ion with formaldehyde radical anion, although not so strongly as with methoxide ion, reaction with MeONa should be faster than with MeOK at low base concentrations whether the denominator is substantially independent of ion pairing because its k_9 term is predominant. In

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(18) In other systems tighter association of sodium than of potassium ion with oxyanions has been observed; thus, for $t\text{-BuO}^-\text{M}^+$ and MeO^-M^+ in dimethyl sulfoxide, see: Exner, J. H.; Steiner, E. C. *J. Am. Chem. Soc.* 1974, **96**, 1782. For OH^-M^+ , RCO_2^-M^+ , and $\text{P}_2\text{O}_7^{4-}\text{M}^+$ in water, see: Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions*; John Wiley & Sons: New York, 1975; p 397. See also: Castilho, P. C. M. F.; Crampton, M. R.; Yarwood, J. *J. Chem. Soc., Perkin Trans. 2* 1991, 639.

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(22) Dispersion forces can make some contribution to ion pairing. This factor is greater as the participating entities have higher polarizability, which is somewhat related to volume. Since K^+ exceeds Na^+ and formaldehyde radical anion exceeds methoxide ion in polarizability, dispersion forces should supplement making K_{4p} for K^+ greater than for Na^+ .

(23) Alternatively, one might think in terms of invariant rate constants and appropriate activity coefficients; thus, for step M5:

$$k_5 \text{ (phenomenological)} = k_5 \text{ (invariant)} \gamma_{\text{CHO}} \cdot \gamma_{\text{ArI}} / \gamma_{\mu}$$

(24) Szwarc, M.; Jagur-Grodzinski, J. In *Ions and Ion Pairs in Organic Reactions*, Szwarc, M., Ed.; John Wiley & Sons: New York, 1974; Vol. 2, p 72.

(25) Wong, B. F.; Hirota, N. *J. Am. Chem. Soc.* 1972, **94**, 4419.

(15) For a radical chain mechanism, the concept of "rate-limiting step" is inappropriate, for reactivity is governed by the product/quotient of rate coefficients for initiation, propagation, and termination steps. Those steps whose rate coefficients appear in the derived kinetic expression are "crucial".

(16) Huyser, E. S. *Free-Radical Chain Reactions*; John Wiley & Sons: New York, 1970; p 47. Reference 7, p 266.

fact, that very difference is manifested when metal methoxide are ca. 0.23 M, as mentioned above.

At high metal methoxide concentrations, the k_{11} term is believed to be substantial in the denominator of eq 2, as discussed. Step M11 involves interaction between two formaldehyde radical anions. k_{11} is lower than k_9 or k_{10} ,²⁶ no doubt because it involves reaction between two negatively charged entities. k_{11} for ion-paired CH_2O^- should be higher than for free ions because the ion pairs are overall electrically neutral. Inasmuch as Na^+ associates with oxanions more strongly than does K^+ , there should be more augmentation of phenomenological k_{11} for sodium than for potassium.²⁷ By increasing the denominator, ion pairing decreases overall reactivity, more for sodium than for potassium, possibly enough to overcome a higher k_5 with sodium, and thus make the overall reaction faster with potassium methoxide at high concentrations. That is the relationship observed.

This rationalization thus tends to attribute the dip in Figure 3 around 2 M MeONa to depression of reactivity owing to ion pairing rather than to a shift in the state of equilibrium M4 as $[\text{MeO}^-]$ increases. It does not, however, interpret the remarkable rise in reactivity at $[\text{MeONa}] > 2.2$ M. Some other interpretation that doesn't come currently to mind perhaps can give a superior account of our observations.

If our rationalization is valid in its main features, it follows either that the ion-pairing effect to depress K_4 below K_4 is huge or that previous estimates of K_4 must be revised downward.²⁸ Johnson and Salmon²⁶ estimated K_4 , expressed as $[\text{CH}_2\text{O}^-]/([\text{HOCH}_2\cdot][\text{MeO}^-])$, to be 86 M^{-1} . Boyle and Bunnett⁶ estimated from $\text{p}K_a$ information a K_4 defined the same way²⁹ as about 25 M^{-1} . If for purposes of a rough estimate K_4 were taken to be the average of these two evaluations, 55 M^{-1} , at 1 M methoxide ion the hydroxymethyl radical should exist 98% as formaldehyde radical anion. The relative magnitudes of the three terms in the denominator when $[\text{MeO}^-]$ is 1 M would then be k_9 term: k_{10} term: k_{11} term = 1:57:448. If the k_{11} term so dominated the denominator, the reaction should be zero order in metal methoxide, a situation certainly not observed (Figure 3) for MeOK and questionable (Figure 4) for MeONa.

Reaction in the Presence of Nitrobenzene of Benzophenone. The Effect of Nitrobenzene. No doubt nitrobenzene inhibits the deiodination chiefly by "stealing" from the formaldehyde radical anion, via step M12, the electron that otherwise would be transferred to ArI (step M5) to continue the propagation cycle. If step M12 is effectively irreversible, as we judge it would be, and termination were occurring *entirely* via step M12, the reaction order in nitrobenzene should be -1 . (The equilibrium constant for the addition of methanol to formaldehyde³⁰ to form $\text{CH}_3\text{OCH}_2\text{OH}$ is 1300; the formaldehyde formed in M12 would thus be essentially fully converted to the hemiacetal or its conjugate base.)



As mentioned above, the slope of the plot in Figure 5 for the two points at highest $[\text{PhNO}_2]$ is -0.87 , and thus agreement between experiment and the model is pretty good insofar as this feature is concerned.

The nitrobenzene radical anion formed in step M12 could itself act as a termination reagent. Nitrobenzene radical anion is known to persist for some while in alcoholic solvents;^{31,32} if it were fully effective in destroying $\text{HOCH}_2\cdot$ or CH_2O^- radicals, the kinetic order in nitrobenzene would nevertheless be -1 . This further termination activity would increase the apparent termination rate constant, but not affect the kinetic order in nitrobenzene.

Reaction Order in AIBN, in the Presence of Nitrobenzene. If termination occurs exclusively through reactions of radicals with nitrobenzene, as in step M12 and related processes, the kinetic order in initiator should be unity.³³ Four runs with $[\text{PhNO}_2]$ 0.008 M (runs Kn–Nn) provide a somewhat curved plot of $\ln k$ vs $\ln [\text{AIBN}]$ with linear regression slope (apparent kinetic order in AIBN) 0.82. The slope between the two points at lower $[\text{AIBN}]$ is 0.95 and between the two others 0.59. These approach, respectively, kinetic order unity when CH_2O^- and $\text{HOCH}_2\cdot$ are terminated by nitrobenzene, with no chance to terminate by interaction between themselves, and the order of 0.5 called for by eq 2, which assumes no involvement of nitrobenzene in termination. Such an outcome seems reasonable inasmuch as low steady-state concentrations of those radicals are expected at low initiator concentrations. We conclude that at these low nitrobenzene concentrations termination occurs partly according to steps M9–M11 of Scheme I and partly by electron transfer to nitrobenzene (step M12).

The six runs (En–Jn) with $[\text{PhNO}_2]$ 0.00265 M afford a more obviously curved plot of $\log k$ versus $\log [\text{AIBN}]$. While the linear regression slope is 0.75, the three points at lower $[\text{AIBN}]$ define a pretty good line of slope 1.27, and the three at higher $[\text{AIBN}]$ define a line of slope 0.38. These values overstep the bounds of 1.00 and 0.50 mentioned above. Although qualitatively the change in slope is in a reasonable direction, it is difficult to account for the slopes being outside the pale. Perhaps the situation is complicated by some artifact. If so, the problem is not lack of precision in the kinetic determinations; for all six runs, the first-order plots comprised nine points with correlation coefficients (r) of 0.996, except for one that had r 0.990.

The Effect of Benzophenone. Our single run (Ab) with this substance present shows it to be an inhibitor, but weaker than nitrobenzene at about the same concentration (run Dn). Benzophenone is a good electron acceptor. We believe that its inhibitory effect is due to taking electrons from formaldehyde radical anion, in fashion analogous to the behavior of nitrobenzene (step M12). That it is a weaker inhibitor than nitrobenzene is no doubt related to the fact that benzophenone has a more negative redox potential.³⁴

Concluding Remarks

This kinetic study provides numerous observations that are consistent with the mechanism outlined in Scheme I, and none that disqualify it. Although the mechanism cannot be considered to have been proven, we do consider

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(27) Bethell and Parker (Bethell, D.; Parker, V. D. *Acc. Chem. Res.* 1988, 21, 400) have independently seen evidence that dimerization of radical anions is accelerated when the gegenion is smaller.

(28) A reviewer has suggested, alternatively, that the literature value of k_{11} may be too high.

(29) The constant estimated by Boyle and Bunnett as 630 would, according to the definition of Johnson and Salmon, be $K_4[\text{MeOH}]$. Division by $[\text{MeOH}]$ in methanol gives the estimate quoted in the text.

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it to be a suitable basis for consideration of our further studies of structural effects on reactivity in alkoxide dehalogenations, soon to be reported.

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Registry No. *m*-Chloriodobenzene, 625-99-0; sodium methoxide, 124-41-4; potassium methoxide, 865-33-8; azobisisobutyronitrile, 78-67-1; nitrobenzene, 98-95-3.

Enolboration. 2. Dicyclohexylchloroborane/Triethylamine as a Convenient Reagent for Regio- and Stereoselective Enolboration of Representative Classes of Ketones

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A smooth, rapid, regio- and stereoselective enolboration of representative classes of ketones is achieved with dicyclohexylchloroborane in the presence of triethylamine in simple solvents such as methylene chloride, diethyl ether, carbon tetrachloride, and hexane. All classes of ketones, methyl, ethyl, α,β -unsaturated, cyclic, bicyclic, heterocyclic, and aromatic, except the sterically hindered isopropyl ketones and related ketones containing two sec-alkyl groups attached to the carbonyl group, undergo enolboration successfully. The enol borinates, generated instantaneously with concurrent formation and precipitation of triethylammonium chloride, react readily with aldehydes at temperatures as low as -78°C , comparable to the behavior of the organoboron triflates previously utilized for such enolboration. The remarkable reactivity, regioselectivity, stereoselectivity, ease of preparation and handling, and the greater stability of dicyclohexylchloroborane all make it a preferred reagent for enolboration.

Enol borinates are highly reactive and are used as important intermediates in organic synthesis.³⁻⁷ Developing simple methodologies for generating enol borinates has been a challenge to organic chemists. One of the methodologies involves the reaction of ketone with a suitable organoboron derivative, R_2BX , having a good leaving group, in the presence of a suitable tertiary amine. Various reagents employed previously are R_2BOTf ,⁷ ethylene chloroboronate,⁸ ROBCl_2 ,⁹ BCl_3 ,⁹ and PhBCl_2 .¹⁰ However, these reagents are either difficult to prepare in the pure form or give only a moderate yield of the desired enolates. These limitations of the available reagents together with the lack of availability of boron reagents to achieve selective formation of *E* enol borinates suggested a search for new boron reagents possessing better selectivity and reactivity while being easily accessible.

Dialkylboron triflates have been widely used for enolboration. However, these reagents must be freshly prepared each time prior to their use. On standing for 3-4 weeks, the original colorless reagent becomes colored and

the ^{11}B NMR shows many peaks. On the other hand, the R_2BCl reagents show the same single ^{11}B NMR peak even after 1 year. The preparation of R_2BCl reagents is also easy.¹¹ We have prepared and used various R_2BX reagents in our laboratory for asymmetric reduction,¹² asymmetric opening of *meso*-epoxides,¹³ and synthesis of secondary amines.¹⁴ Our examination of various R_2BCl reagents for the enolboration of representative classes of carbonyl compounds suggested dicyclohexylchloroborane, Chx_2BCl , as the preferred reagent in the presence of triethylamine.¹⁵ A pleasant bonus from this exploration was the unexpected achievement of a considerable control of enolate geometry.¹⁶ Therefore, it appeared appropriate to explore the applicability of $\text{Chx}_2\text{BCl}/\text{Et}_3\text{N}$ for the enolboration of various classes of ketones. This paper reports the successful regio- and stereoselective enolboration of a wide variety of ketones with $\text{Chx}_2\text{BCl}/\text{Et}_3\text{N}$.

Results and Discussion

The present study explores the following classes of ketones for the enolboration using Chx_2BCl and Et_3N : (i) methyl ketones; (ii) ethyl ketones; (iii) isopropyl ketones; (iv) α,β -unsaturated ketones; (v) cyclic ketones; (vi) bicyclic ketones; (vii) heterocyclic ketones, and (viii) aromatic ketones. The detailed study which led to the selection of

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