Debromination *vs.* Dehydrobromination of *meso*- and *dl*-Stilbene Dibromides by Lithium Chloride, Potassium Fluoride, and Dimethylformamide in Dimethylformamide. A Halogen Nucleophilicity Scale[1]

W. K. KWOK AND SIDNEY I. MILLER*

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

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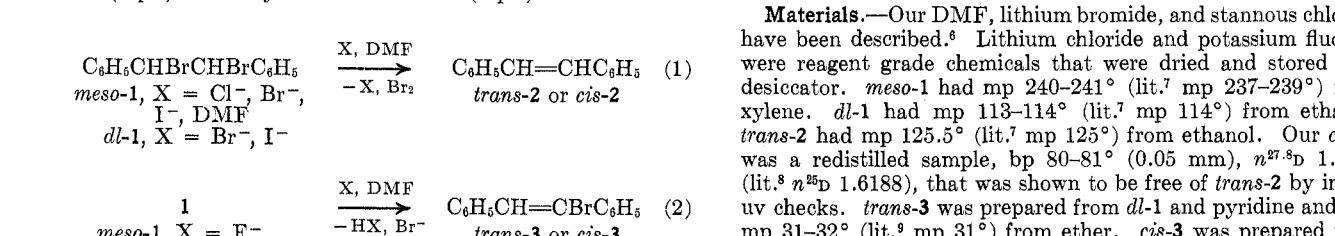
Rate data for the stereospecific reactions of the stilbene dibromides (1) with lithium chloride at 59.5° are: for *anti*-debromination of *meso*-1, $k = 4.45 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 21.6$ kcal/mol, and $\Delta S^{\ddagger} = -9.1$ eu; for *anti*-dehydrobromination of *dl*-1, $k = 1.42 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 24.8$ kcal/mol, and $\Delta S^{\ddagger} = -1.7$ eu. When dimethylformamide (DMF) is the attacking nucleophile, the processes are slower, but otherwise similar to those with chloride and 1. Both *meso*- and *dl*-1 undergo *anti*-dehydrobromination with potassium fluoride: $k(dl)/k(meso) \simeq 5$ at 59.5°. In DMF, nucleophilicities are much greater than in a protic solvent. The order is as follows: toward hydrogen of 1, $F^- > Cl^- >$ DMF; toward bromine of 1, $I^- > Br^- > Cl^- > Sn^{2+} >$ DMF. Our ambident electrophiles (1) point up a conformational factor that is implicit in our measures of nucleophilicity.

Previous work has established that the debrominations of the stilbene dibromides (1) by iodide and bromide ions are clean reactions in dimethylformamide (DMF).[2d,e] Since quantitative data on nucleophilicity toward a halogen site are almost unknown (eq 1),[3] we thought that it would be interesting to extend our kinetic studies to include chloride and fluoride ions. What we found, in fact, was the dichotomy, debromination (eq 1) *vs.* dehydrobromination (eq 2).



Dimethylformamide has been used more often as a medium and/or agent for dehydrohalogenation than for dehalogenation.[3-5] To complement the halide kinetics, we examined briefly the role of DMF and were able to add it to our list of nucleophiles in both eq 1 and 2. We were also interested in the speculation that DMF might be a syn eliminating agent.[5a] All of the eliminations of this paper turned out to be antistereospecific.

Experimental Section

The usual spectral checks, ir, nmr, and uv, were made on reactants and products.[1b] All of the kinetics that were followed spectrophotometrically were carried out in a Beckman DK2 spectrophotometer; certain products and their extinction coefficients were verified on a Cary Model 11 instrument (Table I). Melting points were determined on a Mel-Temp apparatus and are uncorrected. A Beckman pH meter (Model G) was used for potentiometric, and a Sargent Ampot was used for amperometric determinations of halides

Materials.—Our DMF, lithium bromide, and stannous chloride have been described.[6] Lithium chloride and potassium fluoride were reagent grade chemicals that were dried and stored in a desiccator. *meso*-1 had mp 240–241° (lit.[7] mp 237–239°) from xylene. *dl*-1 had mp 113–114° (lit.[7] mp 114°) from ethanol. *trans*-2 had mp 125.5° (lit.[7] mp 125°) from ethanol. Our *cis*-2, was a redistilled sample, bp 80–81° (0.05 mm), $n^{27.8}D$ 1.6162 (lit.[8] $n^{25}D$ 1.6188), that was shown to be free of *trans*-2 by ir and uv checks. *trans*-3 was prepared from *dl*-1 and pyridine and had mp 31–32° (lit.[9] mp 31°) from ether. *cis*-3 was prepared from *meso*-1 and potassium hydroxide and had bp 120° (0.1 mm), mp 18°, $n^{24.8}D$ 1.6445 (lit.[10] mp 19°). Compound 4 had mp 61–62° (lit.[11] mp 61°) from 95% ethanol.

Kinetic Procedures.—The ampoule technique was used. When stannous chloride was present, the ampoules were preflushed with nitrogen. After reaction, the ampoules were chilled and stored in a refrigerator. Volumetric determinations were made directly; spectrophotometric analyses were made on aliquots suitably diluted with DMF. All of the reactions were stoichiometrically simple, and second-order rate laws applied. Pseudo first-order rate constants (k_ψ) were obtained graphically and converted to k values taking into account corrections for the expansion of DMF.[4b] Arrhenius plots gave the activation energy (E_{act}) from which the other activation parameters were obtained.

$$\Delta H^{\ddagger} = E_{act} - RT \quad (3)$$

$$\Delta S^{\ddagger} = 2.303R\ (\log k - \log k\ T/h) + \Delta H^{\ddagger}/T$$

Stilbene Dibromides and Lithium Chloride.—The debromination of *meso*-1 in the presence of stannous chloride was followed spectrophotometrically at 310 mμ for the appearance of *trans*-2 to *ca.* 90% reaction. The concentrations of the reagents were

* Author to whom inquiries should be addressed.

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TABLE I

EXTINCTION COEFFICIENTS (ϵ) OF REACTANTS AND PRODUCTS IN DIMETHYLFORMAMIDE

Compd	Wavelength, mμ 310	299	297	295	290	287	281.5
meso-Stilbene dibromide	180		540				
dl-Stilbene dibromide	400		800				
trans-Stilbene	26,610		26,390				
cis-Stilbene	3,473		7,008				
Lithium bromide	0		0.2				
Lithium chloride	0		0.3				
Stannous chloride	25		81				
trans-Bromostilbene	12,250		17,800			19,060	
cis-Bromostilbene	4,790		7,558	7,866		8,687	
Diphenylacetylene		25,260			21,260		29,480

adjusted so that competition from the debromination of *meso*-1 by bromide ion, stannous chloride, and DMF was insignificant. The dehydrobromination of *dl*-1 was followed spectrophotometrically at 287 mμ for the appearance of *trans*-3 to *ca.* 90% reaction; the rate is the same with and without stannous chloride. The data are given in Tables II–IV.

TABLE II

DEBROMINATION OF *meso*-STILBENE DIBROMIDE BY LITHIUM CHLORIDE IN DIMETHYLFORMAMIDE

Temp, °C, ±0.05°	LiCl, *M*	*meso*-Dibromide $M \times 10^3$	$SnCl_2$, $M \times 10^3$	k, M^{-1} $sec^{-1} \times 10^4$
39.00	0.322	5.07	9.44	0.53
	0.233	1.15	2.58	0.49
			$k_{avg} = 0.51 \pm 0.02$	
50.10	0.183	2.70	5.49	1.73
	0.437	8.23	16.8	1.97
	0.133	0.631	3.12	1.68
	0.309	4.96	10.1	1.80
	0.128	1.50	4.16	1.78
	0.094	0.66	3.06	1.78
			$k_{avg} = 1.79 \pm 0.08$	
59.49	0.146	2.47	5.25	4.48
	0.094	0.64	3.21	4.65
	0.313	4.79	10.1	4.33
	0.125	1.49	4.09	4.32
			$k_{avg} = 4.45 \pm 0.12$[a]	
74.83	0.125	1.45	3.78	20.8
	0.124	2.95	4.74	20.5
	0.062	0.64	1.99	21.7
	0.063	1.44	3.93	22.0
	0.247	5.87	8.98	17.5
			$k_{avg} = 20.5 \pm 1.2$	
74.83	0	0.887	1.89	0.0014[b]

[a] Reference 3 reports 4.47×10^{-4} at 59.8° for *meso*-1 and tetrabutylammonium chloride. [b] $k_\psi = 1.03 \times 10^{-4}$ min^{-1}.

Stilbene Dibromides and Potassium Fluoride.—Our attempt to determine the exact solubility of potassium fluoride in DMF was unsuccessful: after evaporation, the residue of 10 ml of a saturated solution kept at 59.4° had zero weight, within experimental error. Therefore, our kinetic runs were prepared by distributing aliquots of a stock solution of 1 into ampoules and adding solid potassium fluoride. The ampoules were capped and sealed. After reaction, the ampoules were opened and centrifuged to deposit the potassium fluoride, and an aliquot was taken for analysis.

The dehydrobromination of *meso*-1 by potassium fluoride was followed spectrophotometrically at 295 mμ for the appearance of *cis*-3. The dehydrobromination of *dl*-1 by potassium fluoride was followed spectrophotometrically at 287 mμ for the appearance of *trans*-3 and 299 mμ for the slower appearance of 4. The data are given in Table IV and one rate plot is shown (Figure 1).

Stilbene Dibromides and DMF.—The debromination of *meso*-1 in the presence of stannous chloride was followed spectrophotometrically for the appearance of *trans*-2 to *ca.* 95% reaction. The dehydrobromination of *dl*-1 to give *trans*-3 was followed to *ca.* 93% completion by bromide titration. The data are included in Tables II–IV.

TABLE III

DEHYDROBROMINATION OF *dl*-STILBENE DIBROMIDE BY LITHIUM CHLORIDE IN DIMETHYLFORMAMIDE

Temp, °C, ±0.05°	LiCl, *M*	*dl*-Dibromide $M \times 10^3$	$SnCl_2$, $M \times 10^3$	k, M^{-1} $sec^{-1} \times 10^4$
50.10	0.519	7.23	0	0.438
59.49	0.435	7.25	0	1.39
	0.215	3.25	0	1.45
			$k_{avg} = 1.42 \pm 0.03$	
74.83	0.218	3.61	4.86	7.92
	0.220	3.57	0	7.87
			$k_{avg} = 7.90 \pm 0.03$	
82.60	0.213	3.53	4.34	17.0
83.90	0.179	0.65	3.00	19.0
59.40	0	0.585	0	0.012[a]
74.83	0	0.681	0	0.017[b]
74.90	0	0.681	0	0.018[c]

[a] $k_\psi = 9.1 \times 10^{-4}$ min^{-1}. [b] $k_\psi = 1.28 \times 10^{-3}$ min^{-1}. [c] $k_\psi = 1.34 \times 10^{3}$ min^{-1}.

TABLE IV

ELIMINATION REACTIONS OF THE STILBENE DIBROMIDES IN DIMETHYLFORMAMIDE AT 59.4–59.5°

Stilbene dibromide	Reactants	% anti, process[a]	$k \times 10^6$ M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$-\Delta S^{\ddagger}$, eu	Ref[b]
meso	NaI	100, $-Br_2$	74200	16.3	15	2d
	LiBr		2360	20.6	9	2e
	LiCl		445	21.6	9.1	
	$SnCl_2$		373	15.5	28	2d
	DMF		<0.14[c]			
dl	NaI	83, $-Br_2$	481	22.3	7	2d
	LiBr	12, $-Br_2$	47	28.9	−8	2e
	$SnCl_2$	6, $-Br_2$	34	19.3	21	2b
meso	KF	100, −HBr	125/s[d]			
	KF		620/s[d]			
dl	LiCl		142	24.8	1.7	
	DMF		1.2			
dl	KF		9.2/s[d,e]			

[a] The selectivity of debromination or dehydrobromination is indicated. [b] This work, except as indicated. [c] Value at 75°. [d] The solubility of KF is $s < 4 \times 10^{-4}$ *M*. Initially, solutions were *ca.* 10^{-3} *M* in stilbene dibromide. Values are for duplicate runs. [e] Value for the dehydrobromination of *trans*-bromostilbene (eq 5).

Results and Discussion

The stoichiometries of the eliminations are well represented by eq 1 or 2. The products of the type $ClBr_2^-$ in eq 1 or $ClHBr^-$ in eq 2 do not appear to affect our rates. In each case, the kinetics are first order in 1

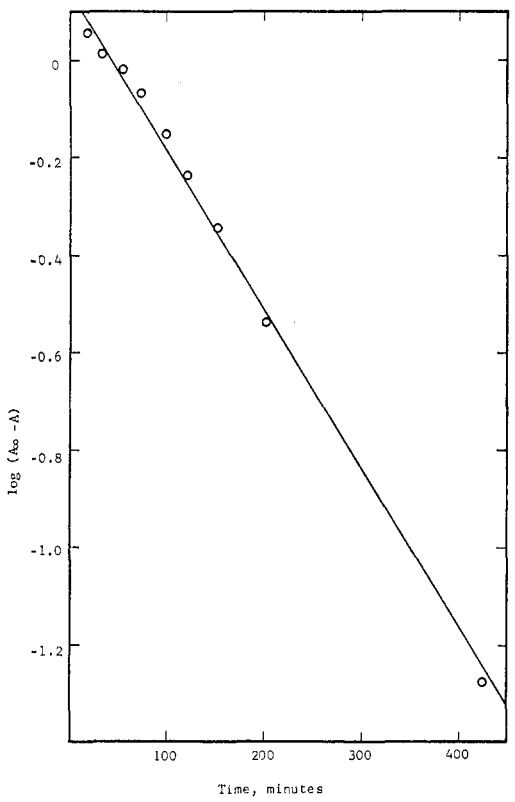

Figure 1.—Dehydrobromination of *meso*-stilbene dibromide by potassium fluoride in DMF at 59.4° (*meso*, 0.00162 mol/l.).

and first order in nucleophile. Wherever fluoride, chloride, and DMF are involved, the processes are anti stereospecific. In general, the debrominations of *meso*-**1** and the dehydrobrominations of both **1** are anti stereospecific; the debrominations of *dl*-**1** have variable stereoselectivity (Table IV).

The reactions of DMF with both **1** had been noted in earlier studies.[2c] Our brief kinetic studies here were particularly useful in establishing the level of the solvent reactions. Based on the configuration of the products, we are inclined to rule out syn eliminations by DMF; the possibility of two-pronged attack by nitrogen and oxygen of the DMF dipole, which once seemed attractive,[5a] did not materialize.

When we began this work, there was no indication that chloride ion had ever been used as a debrominating agent. Recently, Baciocchi and Schiroli reported debrominations of *meso*-**1** (and ring-substituted analogs) with tetrabutylammonium salts (I^-, Br^-, Cl^-) in DMF.[3] A bromine scavenger such as stannous chloride does not seem to be necessary for debromination studies of *meso*-**1** at 60°,[3] but it may be useful at higher temperatures, with weaker nucleophiles, and particularly with *dl*-**1**, since both *dl*-**1** and *cis*-**2** are readily isomerized by bromine.[2e]

With sodium iodide and lithium bromide, the debromination of **1** in DMF appeared to be subject to salt effects both in a general sense and because of ion pairing.[2d] Ion pair constants for lithium chloride in DMF are 0.0171 at 30° and 0.0142 *M* at 50°.[12] Nevertheless, no evidence of such effects were found with lithium chloride and *meso*-**1**, even when stannous chloride was present (Table II). As pointed out by Baciocchi and Schiroli, "It is noteworthy that the same value of the rate constant is obtained with either tetrabutylammonium chloride or lithium chloride...ion pairs or dissociated ions exhibit the same reactivity."[3]

In contrast to iodide and bromide in DMF, chloride dehydrobrominates *dl*-**1** (eq 2). This is reminiscent of the reactions of pyridine with **1**, namely, that *meso*-**1** follows eq 1 and *dl*-**1** follows eq 2. These observations provided early evidence for anti elimination;[9] later, they were used to illustrate the operation of the "cis" effect.[13] Since the equilibrium constant, $K = [trans\text{-}2]/[cis\text{-}2] > 300$ in our temperature range,[14] there is a substantial "steric" or conformational factor operating against the formation of *cis*-**2**.[15] With a strong hydrogen nucleophile, eq 2 is favored over eq 1.

Despite its "insolubility" in DMF, potassium fluoride has found increasing use as a base or as a nucleophile.[16] (We estimate that its solubility is $<4 \times 10^{-4}$ *M* at 60°.) Ours is probably the first kinetic study of this suspension of dry potassium fluoride in DMF (Figure 1). We assume here that the concentration of fluoride remained constant and that anti dehydrobromination reactions with both **1** were typically second order overall. In a second step, potassium fluoride dehydrobrominates *trans*-**3** in the anti sense and fails to dehydrobrominate *cis*-**3**, presumably because of the

$$meso\text{-}1 \xrightarrow[\text{DMF}]{\text{KF}} cis\text{-}3 \qquad (4)$$

$$dl\text{-}1 \xrightarrow[\text{DMF}]{\text{KF}} trans\text{-}3 \xrightarrow[\text{DMF}]{\text{KF}} \underset{\mathbf{4}}{C_6H_5C{\equiv}CC_6H_5} \qquad (5)$$

reluctance of groups to depart in the syn sense. In view of its extraordinary nucleophilicity (Table IV), detailed studies of this reagent would be of great interest.

In contrast to the other systems of this series,[2] potassium fluoride reacts more readily with *dl*-**1**, that is $k(dl)/k(meso) = 4.9$ or $(\Delta G^{\ddagger}_{dl} - \Delta G^{\ddagger}_{meso}) = 1.0$ kcal/mol at 59.4°. Since $(G_{dl} - G_{meso}) \simeq 0.78$ kcal/mol at 80°,[2e] it appears that the transition state energy difference is small, or $(G^{\ddagger}_{dl} - G^{\ddagger}_{meso}) \simeq 0$.[15] Note that stereospecific anti eliminations are being compared here and that the transition states have begun to incorporate some of the product properties in which $(G_{cis} - G_{trans})$ is presumably positive.[17] An analogous result was found by Cristol and Bly for the diastereoisomeric stilbene dichlorides reacting with potassium hydroxide in 92% ethanol in which $k(dl)/k(meso) = 8$ at 43°.[19]

In Table IV, we have collected all of our rate data concerned with eq 1 and 2 in DMF. There is sufficient variation in the activation parameters, which is not apparent in the trend of the *k*'s, such that evaluations of mechanism,[2] substituent effects,[3] solvent effects, and nucleophilicity should be based on all of these quantities.

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Halogen *vs.* Hydrogen Nucleophilicity.—The data in Table IV comprise the first experimental scale of nucleophilicity toward bromine. There have been many ratings, of nucleophilicity at other sites, *e.g.*, carbon, carbonyl, phosphorus, silicon, platinum, peroxide, etc.[20-24] Apart from the Brønsted equation, the relation of these scales to one another, to a single equilibrium constant, or to another physical property involving the nucleophile is not usually linear; hence the Edwards equations[22] and the recent elaborations of the hard-soft acid-base (HSAB) theme.[23,24] In this section, we examine the factors that contribute to the choice, eq 1 *vs.* eq 2, and to the level of reactivity for each process.

The base strengths of the halides, leveled in water, are differentiated in DMF; in both solvents, the trend is the same, $F^- > Cl^- > Br^- > I^-$; nucleophilicity toward sp^3 carbon differentiated in protic solvents with $I^- > Br^- > Cl^-$ is leveled in aprotic solvents with $Cl^- > Br^- > I^-$.[20,21] Comparable data on reactivity toward halogen are scarce. For our purposes, the formation constants (K) for the series XBr_2^- might seem appropriate, *i.e.*, 370 (IBr_2^-), 17.8 (Br_3^-), and 1.1 M^{-1} ($ClBr_2^-$), but these values are for the solvent water and the corresponding values in DMF are all likely to cluster at *ca.* 10^7 M^{-1}.[25] The K values of the trihalide ions (X_3^-) increase by a factor of at least 10^4 in going from water to aprotic solvents, and there is also a reversal from the order of stability in water, $I_3^- > Br_3^- > Cl_3^-$.[25] This then is some of background of fact on halogen *vs.* hydrogen nucleophilicity.

In considering the site of attack on our ambident electrophiles (**1**), we shall look at substrate, solvent, and nucleophile. We have seen that *dl*-**1** is more susceptible than *meso*-**1** to attack on its hydrogen (eq 2). It is reasonable that debromination of *meso*-**1** would lead to *trans*-**2** and that would of *dl*-**1** lead to *trans*-**3**, since the stereoelectronic factor inherent in the anti process and the steric factor that avoids syn (or near syn) phenyl groups in the transition state are aligned.[2,15] If these factors are opposed, rate retardations, such as $k(dl) < k(meso)$ in debromination with iodide[2a,d] or $k(meso) < k(dl)$ in dehydrobromination with fluoride are observed. This opposition may also lead to mechanistic complexity: the reaction of *dl*-**1** with iodide in methanol leads to both **2** as well as solvolytic products;[2a] the reaction of *dl*-methyl 1,2-dibromosuccinate with lithium bromide in DMF involves both debromination (*ca.* 90%) and dehydrobromination (*ca.* 10%).[5c] For this reason, one should obviously identify the process, *i.e.*, eq 1, eq 2, or both. Likewise, one should be aware of mechanistic variation within a given process, *e.g.*, in dehalogenation.[2,26] With respect to our dibromides, we believe that the rate-determining step is attack by the nucleophile on bromine in eq 1 or on hydrogen in eq 2. Variations in the overall mechanism of eq 1 with change in nucleophile are probable and have been discussed both with respect to the nature of the intermediates and in the fast succeeding steps.[2]

Among the halide ions, iodide is a debrominating agent (eq 1) and none appear to be dehydrobrominating agents (eq 2) of **1** in methanol.[2a,3] Yet, the reactivity both toward bromine and hydrogen of **1** are enhanced in transferring a nucleophile from methanol to DMF. Although precise dissection of the origins of this effect is not possible, except for iodide,[2d] the major reason for the enhancement can be given. Parker has listed solvent activity coefficients for species in DMF (D), relative to methanol (M):[20] $\log {}^{M}\gamma_{X^-}{}^{D}$ 2.6 for I^-, 4.9 for Br^-, 6.5 for Cl^-; by analogy with the figure of 9.2 given for OAc^-, we estimate $\log {}^{M}\gamma_{X^-}{}^{D} \simeq 10$ for F^-. Since the activity coefficients of **1** and the transition states of eq 1 and 2 are probably small by comparison, that is $|\Sigma_i \log {}^{M}\gamma_i{}^{D}| < 2$,[20] the transfer activity coefficient of bromide, chloride, and fluoride leads to factors in $k_{X^-}{}^{DMF}/k_{X^-}{}^{CH_3OH}$ of *ca.* 10^3, $10^{4.5}$, and 10^8, respectively.

We come now to the role of the nucleophile. On the basis of the results with *dl*-**1** we can construct the following *preliminary* picture. The stronger the base, *e.g.*, $F^- > Cl^-$, the more probable will be process 2; the more powerful the reductant, *e.g.*, $I^- > Br^- > Cl^-$, the more probable will be process 1.[27] Unfortunately, the preceding view is too limited: DMF, as a hydrogen nucleophile, and stannous chloride, as a bromine nucleophile, are anomalous. Indeed, none of the quantities which have been considered as measures of nucleophilicity, pK, standard electrode potential, polarizability, nucleophilicity toward carbon, etc.,[20,22] are adequate by themselves to correlate the rate data. A double nucleophilicity scale is the least complex that might correlate the rate data, but more information on nucleophiles as different as DMF and tin (II) is required before Edwards' equations or Klopman's theoretical treatment can be tested.[22,24]

In summary, increased hydrogen and halogen nucleophilicity in DMF has uncovered new elimination systems, and a start on a practical halogen nucleophilicity scale has been made. The factors that favor one reaction site over another in an ambident electrophile have not yet been evaluated, but one of these certainly must be stereochemical.

Registry No.—*meso*-**1**, 13440-24-9; *dl*-**1**, 13027-48-0; KF, 7789-23-3; LiCl, 7447-41-8; DMF, 68-12-2.

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(27) Our scale is appropriate for the reagents and concentrations actually used. The question of ion pairing in DMF is certainly relevant, for an ideal scale represents all nucleophiles in their standard states. It has been shown, however, that the rates of reaction of *meso*-**1** with several bromide and chloride salts are essentially constant, while the rates with several iodides vary somewhat (Table II).[2d,e,3]